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Sc,Y,La-Lu

A6b

GEOCHEMISTRY

1988

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Sc, Y, La−Lu

RARE EARTH ELEMENTS

A6b

Y, La, and the Lanthanoids

Geochemistry: Hydrosphere. Atmosphere.
Cosmo− and Geochemical Cycles. Balance

With 2 illustrations

AUTHORS   Bärbel Sarbas, Wolfgang Töpper

EDITORS   Wolfgang Töpper

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Preface

The present volume "Rare Earth Elements" A 6b describes in its first part the origin, mode of occurrence, and behavior of Y and/or RE elements in the hydrosphere and atmosphere. Separately for marine and non-marine environments (surface, subsurface, mineral, and thermal waters), the behavior of RE (including Y) in the hydrosphere comprises especially the relationship between content/composition and the chemistry of water, and the processes acting during migration, removal, and precipitation are outlined; the influence of biological material is mentioned. Behavior of RE in the atmosphere involves mainly transport, regional differences, and temporal variations as well as removal by precipitation; the anthropogenic influence is only outlined.

The second part of this volume treats, partly in a more summary manner, the cosmo- and geochemical cycles and the balance of Y and/or RE elements. The relationship between geodynamic position and type of magmatism, as well as the geochemical variations in the geospheres, especially mantle and crust of the earth, are described in greater detail.

Frankfurt am Main
November 1987
Wolfgang Töpper

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For an overview of the behavior of Y and/or RE in the hydrosphere, inspect the relevant chapters of textbooks or of papers dealing especially with RE geochemistry given in the following examples:

E. D. Goldberg, Minor Elements in Seawater (Chem. Oceanogr. 1 [1965] 163/96, 164/5, 169, 189/90).

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7.1   Origin of Yttrium and/or Rare Earth Elements in the Hydrosphere

7.1.1   Seawater

As can be seen from the following paragraphs, Y and/or RE can be supplied to seas and oceans in various ways and in quantitatively different amounts from the continent with river water, weathering products, and aeolian material, but also with products of submarine and surface volcanism, and, to a smaller extent, with cosmic material (in the open ocean) [1, pp. 223/4]; glacial runoff and abrasion are further minor sources [2]. Resolution of under-lying (sea-bottom) sediments, e.g., [3, p. 128] and see below or interstitial waters of marine sediments can also be RE sources [4].

Most of the RE (>99% according to [1, p. 243]) originate from terrigenous/continental sources (see, e.g., [5, 6]), derived from the weathering of igneous, sedimentary, and meta-morphic rocks [7], as is mentioned for RE (with suspended material) in the northern Indian Ocean and the Mediterranean Sea [1, pp. 251/2], or La in the Sargasso Sea and the tropical northern Atlantic Ocean [8]. A substantial part of Nd in seawater is of continental deriva-tion [9], as, e.g., in the Atlantic Ocean [36]. The major continental RE input from river water is in the suspended state [2, 10 to 12], the soluble input being only a few percent of the total RE discharged by rivers [11]. Degradation of particulate matter in river systems provides the initial source of marine Nd [30]. Runoff from Precambrian terrains into the Arctic Ocean is a possible source of relatively non-radiogenic Nd in the deep water of the northern Atlantic Ocean [15]. However, since the shelf area contains <10% of all sediments of the

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world's oceans and at intermediate depth about two orders of magnitude less than in the pelagic zone, it is assumed that the contribution of RE supplied by river discharge into seawater is not high [31].

Aeolian particles may supply RE into seawater [2, 10, 12, 13], as, e.g., in surface waters of the northern Atlantic [4], the Pacific [14], and the Indian oceans [5]. A significant transport of RE to the oceans may take place from the atmosphere by dust [13]. However, atmospheric dust is only of local importance (e.g., in the arid regions [12]) as source of RE in seawater [15], and atmospheric deposition could be a partial source of La and Ce in surface micro-layers of the southern North Sea off Lowestoft, Great Britain [16]. The amount of RE supplied as dry precipitates to the ocean from atmosphere constitutes ~10% of the amount carried in by rainwater [31]; compare also pp. 108/9.

Several processes have been proposed for the transfer of elements from submarine basalt magmas into the deep-marine environment. One such mechanism is the long-term, low-temperature weathering (halmyrolysis) of volcanic rocks exposed at the sea floor. Another is the mobilization of elements during the violent interaction of molten lavas with seawater to form palagonite tuffs. A third mechanism, often cited but never explicitly defined, is the action of "hydrothermal exhalations" or "volcanic emanations" that accompany submarine volcanic activity, which transport elements from the magma into seawater [37]. Submarine volcanism is a local source of Y and/or RE in seawater [1, pp. 223/4], [10], and locally hydrothermal solutions connected with the submarine volcanism supply these elements directly into seawater [1, p. 241], e.g., in the Bauer Basin, east of the East Pacific Rise, where the RE in seawater originally were associated with hydrothermal iron oxyhydrox-ide sediments [17]. Some indication of the influence of volcanic supply on dissolved RE in seawater off San Diego, California, can be shown by the increased Eu/Sm ratio of 0.27 compared to acid igneous rocks with 0.17 [1, pp. 247/8]. In view of the anomalous RE pattern for an Fe-rich deposit from the Dellwood Seamount, northeastern Pacific Ocean, which differs significantly from that of normal seawater, the RE have been derived from the underlying basalt by leaching with seawater invading along cracks and establishing a convecting system by which metals are transported to the surface and coprecipitated with Fe and Mn [35]. Substantial contribution (~20%) to the dissolved load of Nd from primary oceanic sources may exist [32], and mantle-derived material may be a source of Pacific Nd through seawater circulation at mid-ocean ridges, and reactions with volcanic ash [36]. But as derived from Nd isotopic composition ($\varepsilon_{Nd}(O)$, see p. 46), only a small part of it originates from sources with oceanic mantle affinity [13], or submarine volcanism, and hydrothermal systems play no dominant role as a source [3, p. 133]; note also that mid-ocean ridges are not an important source for RE [34].

Dissolution of the underlying sediments as the likely source of RE in seawater is shown for one deep-water sample (from 4550 m) in the equatorial Atlantic Ocean [18]; dissolution may occur by complex formation with organic, P-containing compounds [29], see p. 9. Release of RE from sediments into deep waters during early diagenesis is reported for the northern Atlantic Ocean in the Cape Madeira abyssal plain [4]. Some leaching of RE from the clay particles takes place during sedimentation in the slightly alkaline environment of seawater; Y and yttrian RE are the chief elements transferred to the water [33]. In near-shore and estuarine environments, clays may act as a source of dissolved RE, because they release the adsorbed metals on contact with seawater by exchange of Mg and Na ions [19].

Sediments suspended by tidal currents are the major source of suspended La, Ce, Sm, and Eu in the southern North Sea off Lowestoft, Great Britain [16]. Dissolution at the sediment-water interface, or resuspension of the sediment is an important injection process for particulate [155]Eu in Bikini Atoll lagoonal waters, central Pacific Ocean [20].

Man-made pollution by artificial radionuclides can supply Y and/or RE to seawater via (mainly) atmospheric fallout, as is reported, e.g., for ^{155}Eu in the Atlantic Ocean [21], ^{144}Ce and ^{155}Eu in the Gulf of Taranto, Italy [22], and ^{144}Ce in the estuaries of the French rivers Seine, Loire, and Gironde [23]. Wet deposition is the primary mode of ^{144}Ce transfer from the atmosphere to the ocean surface in coastal and offshore waters of the northern Pacific Ocean [24]. In the northern Adriatic Sea, ^{144}Ce originates partly from atmospheric fallout on land, where it could be collected by surface waters flowing into the sea [25]. In seawater at Makara, New Zealand, ^{144}Ce, ^{91}Y, ^{147}Nd, and ^{143}Pr originate from atmospheric fallout, and due to resuspension from coastal sediments and, possibly, river transport, additional amounts of old fallout may be introduced [26]. In addition to atmospheric fallout, artificial RE radionuclides in seawater originate from nuclear reactor discharge, e.g., ^{144}Ce in coastal waters of the English Channel [27] and of Mont Saint Michel Bay [28], or in the Loire and (by industrial pollution) Seine River estuaries, all France [23].

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7.1.2 Non-Marine Waters

Surface Waters. The origin of Y and/or RE in river water is mainly from detrital material dispersed in the water and derived from erosion or weathering of rocks, as follows from an investigation of soluble and detrital river loads in the four major world rivers Amazon, Congo, Ganges, and Mekong [1]. Contribution of RE by terrestrial material is also given for 11 Norwegian rivers [2], or the Gironde River, France [3]. Further, soil is mentioned as an important source of La for Lake Michigan water, USA [4], or as contributing to the RE content in Volga River water, USSR [5], and to the Sm content in fresh waters of the Mikurajima Island, Japan [6].

Also solution of Y and RE by direct contact with ore bodies or mineralized zones may release these elements into water, forming local concentration anomalies, as is observed in a streamlet near Ty Flehan, Brittany, France [7], and in surface water from a partly mineralized granite intrusion, Far East, USSR [8, 9].

Underground water is assumed as a source of La in surface water of an industrial region in the European USSR [10]. Derived from granites and metamorphic rocks, rare elements (including RE) are transported by ground and surface waters, but also by deep water traveling via fissures and veins, into salt lakes of the Eastern Pamir, USSR [11].

Temporarily, by resuspension of sediments, radionuclides of RE may enter the water of the Columbia River, Oregon and Washington [12] and of Lake Michigan, both USA [13]. See also, remobilized sediments containing radionuclides (e.g., [144]Ce or [144]Pr) derived from waste discharge at Vallabregues nuclear power plant, Rhone River basin, France [14].

Man-made pollution supplying Y and RE into surface water occurs by atmospheric fallout of artificial radionuclides (mainly from nuclear weapon tests) as is mentioned, e.g., for the Seveso River, northern Italy [15]; for Lake Trasimene, central Italy [16]; the water reservoir Lake Marathon, Athens region, Greece [17]; for the rivers Lahn near Giessen [18]

and Danube at Gundremmingen, Bavaria [19], both Federal Republic of Germany, and near Vienna, Austria [20]; and for surface waters of the European USSR [10] or the Dardanelle Lake, Arkansas [21]. Minor influence of atmospheric fallout on the [144]Ce content in river water is derived from equilibrium content between suspended material and bottom sediment for the Rhine River, Federal Republic of Germany [22]. In addition to atmospheric fallout, radionuclides of Y and RE are released by nuclear reactor discharge into water, e.g., of the Danube River near Gundremmingen [19], or of the Dardanelle Lake, Arkansas [21]. Direct contamination by fertilizers, most probably, leads to contents of Y, La, Ce, and in some cases Sm, Eu, and Lu in low-mineralized acid surface water (with pH~4.5) from springs near Ty Flehan, Brittany, France, which are connected with subsurface drainage of water-saturated top soil layers [7].

The origin of Y and RE in **ground, subsurface, and oil field waters** is attributed to the weathering and dissolution of the surrounding, RE-containing rocks, see, e.g., [23], or ores, see, e.g., [24 to 28]. Subsurface gasification of coal can change physico-chemical properties of subsurface waters and enrich them in rare elements (e.g., Y) from the condensation zone [25]. Elevated contents of La in formation and subsurface waters (not related to oil formations and situated above them) of petroleum pools, western Siberian lowlands, USSR, are attributed to the leaching of surrounding clay-containing rocks. Leaching is increased due to the saturation of country rocks with oil and hydrocarbon gases during oil accumulation and subsequent degassing through the roof, resulting in a decrease of the sorption capacity of clays [29].

In addition to the dissolution of surrounding rocks, the infiltration of atmospheric precipitates is a source of Y and RE elements. Thus, atmospheric precipitation as a source of Yb is assumed for ground waters of various northern taiga regions in the USSR, Canada, and USA (Alaska), the extent of uptake being reduced by congelation [30]. Industrial, urban, and agricultural pollution can be the source of artificial RE radionuclides in ground waters of Poland [31, 32]. However, no effect from nuclear fallout on [141]Ce and [144]Ce contents is observed in ground waters in the vicinity of a nuclear reactor facility, Ibaraki prefecture, Japan [33].

Rare earth element concentrations in **mineral and thermal waters** are usually explained by the leaching of surrounding RE-containing rocks and ores (see examples below); a volcanic source is mentioned occasionally [34]. In the case of leaching, the RE can enter the waters together with other components (HCO_3^-, SO_4^-, Ca^{2+}), as is exemplified by mineral waters of Eastern Siberia [36] or (with degree of solution depending on the type of water) by thermal waters of Kamchatka, Far East, USSR [35]. Pegmatites are the source rocks for the RE in carbonated, slightly acid mineral waters from central Afghanistan (with Y and La in concentrations of 5 to 10 µg/L each), where very active thermal metamorphic processes lead to the production of CO_2; this gas mixes with water, acidulates it and facilitates leaching of RE and other elements from rocks. In addition, the source areas for the waters (which lie at high elevations), together with numerous faults produce a pressurized system that allows water to penetrate to considerable depth, where pressure and temperature are high and, therefore, leaching of the RE from the country rocks is most rapid and leads to high contents [37]. Highest RE contents (>10 µg/L) occur also in waters (hydrotherms of various types), Bulgaria, being connected with metamorphites contacting marbles [40]. Further examples for RE origin by leaching of surrounding rocks are mentioned for the Transbaikal region, Eastern Siberia [38]; for the Misasa hot springs region, Japan, where granites are supposed to be the source of the RE [39]; and for thermal waters of the Geyser Valley and the Uzon Caldera, both Kamchatka, Far East, USSR, where the RE are attributed partly to the leaching of ores [34].

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7.2 Mode of Occurrence, Distribution and Content of Yttrium and/or Rare Earth Elements in the Hydrosphere

7.2.1 Mode of Occurrence

Seawater. In seawater, Y and RE occur with solid terrigenous suspended matter or sorbed onto the surface of suspensions, or together with colloidal substances of high–molecular weight organic and inorganic compounds, or in soluble ionic and complex form. The degree of sorption depends on pH (compare also pp. 20/1) [1]. Most of the elements belonging to the RE series are very insoluble in seawater [81]. Since seawater is probably naturally saturated with RE, the major part of them will be present as solids [82]. In estuarine water, for the most part the RE are associated with suspended matter [2], as, e.g., in the St. Lawrence River, Quebec, Canada [3]; or in the mixing zone with seawater of River Amur, Far East, USSR [4]; or in the Gironde estuary, France [42]. For the dependence of RE contents on salinity in the Gironde, see pp. 22/3.

Mainly present as structural components in various minerals of the suspended matter are La, Ce, and Sm in the Rhine River estuary, Netherlands [5]; or most likely associated with clay minerals or the terrigenous fraction are RE in the Patuxent River estuary, Maryland [6]. Ce and Eu are apparently associated with clays in the sea reach area of Thames estuary, Great Britain [7]. Suspended particles of bastnaesite occur in deep–ocean waters of the Atlantic and Pacific oceans [8].

Half of most RE in marine surface water is retained by 0.45 μm Millipore filters at an offshore station in the Gulf of Mexico [9]; less than 50% of RE is in the >0.7 μm suspension at two stations of the Indian Ocean (central part and continental slope of India) [10, p. 884]. Between 30 and 50% of Y and the lanthanides is sorbed on suspended matter in the Bauer

Basin, East Pacific Rise [83]. Between 20 and 25% of the radioactive Ce introduced into seawater is in the particulate state, having a diameter of >1.2 μm after the aging periods [11]. A substantial percentage of Nd can be adsorbed onto particles in surface seawater of the Drake Passage and of the southeastern and central Pacific Ocean [84]. Bound to suspended matter are Ce, Tb, and Lu in coastal seawater off Arasaki, Miura peninsula, Tokyo Bay, Japan [12], or Y and Yb in the Black Sea, USSR [13]. The major part of radioactive nuclides of Y and/or RE in seawater occurs in particulate form [14], especially in coastal waters where particulate [144]Ce reaches >90% in the English Channel [15] and 80% at Kashima-nada, Japan [20]. In natural seawater, 57.0 to 74.5% of total [144]Ce occurs as an electrofilterable form [16]; or about 60% of [144]Ce and 45% of [91]Y are in the suspended state. Identical [144]Ce and [91]Y concentrations among suspended and dissolved fractions were obtained by ultrafiltration and centrifugation for artificially introduced elements in seawater, the radioactive fraction which passed through a filter or remained in the upper part of the test tube being assumed as dissolved [17]. After penetrating into seawater, artificially added [91]Y and [141]Ce will exist chiefly in the adsorbed state (~60 to 80%). The absorption of radioactive isotopes by the suspension is complex with simultaneous ion exchange sorption and capture of colloidal forms which are formed after the introduction of the isotopes into seawater [85]. Between 18 and 100% of [155]Eu occurs in the particulate fraction of lagoonal waters, Bikini Atoll, central Pacific Ocean [18, p. 45]. Much lower amounts of [144]Ce (<10%) occurring in suspension are given for surface water along ~45°N latitude off the California coast [19]; see further, small amounts of [144]Ce in the open sea off Japan [20], and 11.4% of Y and 10.3% of La occurring in ocean water suspensates [21]. By experiments simulating deep underwater nuclear bursts, it has been confirmed that Y and Ce, as fission products, essentially occur in the particulate state (in duplicate tests, 93 and 98% or 94 and 95%, respectively), the colloidal state being minor (about 4 or 2.3 and 6.6%, respectively), and the soluble part negligible [22]; compare [23], [10, p. 884]. As follows from theoretical and experimental models, at equilibrium conditions about 50% of the radioactive Ce in seawater occurs in the suspended fraction, about 20% with the colloidal phase, and <30% is in solution [24]. Fallout [144]Ce (from the 1962 nuclear test in the Pacific) is distributed among the particulate and soluble states with 9.9 to 86.8, mean 38.7 and 8.9 to 27.7, mean 18 mμμc/L, respectively, for eight surface-water samples (April 1964) from the Gulf of Mexico [25, pp. 118, 122].

In contrast to the above statements, a predominance of the dissolved form in seawater for Y and La is stressed by A. P. Lisitsyn et al. [21], radioactive Ce introduced into seawater existing mainly in dissolved forms [11]. More than 80% of most RE is in the soluble part (Ce, Tb, and Lu being higher in the insoluble part) of coastal surface seawater near Arasaki, Miura peninsula, Japan [12]; compare also RE occurring mainly in the soluble form in waters of the Gulf of Mexico, where the ratios particulate RE/soluble RE (being lower than those previously reported for seawater of the Indian Ocean) were smaller for the heavier RE (see pp. 34/5), indicating that the particulate phase may be functional in the fractionation of RE in seawater [26]. For the same region 32% of [144]Ce is in soluble form (in April 1964) and 33% of [144]Ce occurs in soluble (including colloidal) form even after a period of approximately 18 months following the last (1962) nuclear test in the Pacific [25, pp. 118, 126].

Besides connection with the particulate suspended matter, Y and the RE may exist in seawater (for example in the Indian Ocean) as colloids (for orders of magnitude see the penultimate paragraph), complex compounds, or dispersed ions [10, p. 887]. Note that in prefiltered seawater (0.1 μ filter) from different depths of the Pacific Ocean, artificially added [141]Ce and [91]Y are not present solely in the suspended fraction at any pH [86]. Lanthanides, in the very low concentrations which occur in seawater, should be present very largely

as radiocolloids and rapidly become associated with any solid surface available [99]. As derived from ultrafiltration and centrifuging experiments (to describe radioactive waste behavior in seawater), ^{144}Ce and ^{91}Y may occur as negatively charged particles of colloidal aggregates (with an average radius of 0.44 and 0.20 µm, both ±0.05, respectively) as well as neutral aggregates of ^{91}Y with phosphates [17]; compare colloidal or soluble phosphate complexes of Ce^{3+} formed by reaction between seawater and artificially added Ce [27]. ^{155}Eu occurs as colloid in variable amounts in lagoonal waters of the Bikini Atoll, central Pacific Ocean [18, pp. 44/5]. As derived from experiments with seawater and model solutions to describe the state of radionuclides, the suspended fraction of ^{144}Ce can be viewed as a sorption colloid [28], which is formed mainly by Ce^{3+} [88] and releases ^{144}Ce to a true dissolved form in the presence of organic complexing substances [29]; for an influence of these complexes on the behavior during migration and precipitation, see p. 71. The speciation pattern of Y and RE cations in seawater is complicated since they are able to form stable complexes with a wide variety of ligands [89] and tends to be dominated by the formation of carbonate complexes with stability increasing with the charge of the central cation [90]; also, RE in seawater form stable and soluble complexes with CO_3^{2-} in a weakly alkaline medium [103]. The predominant species of trivalent lanthanides in seawater is the carbonate complex $Ln(CO_3)^+$, and significant but variable amounts of sulfato, chloro, and hydroxy complexes can be present together with traces of free Ln^{3+} ions [30]; see also, $LnCl^{2+}$, $LnSO_4^+$, LnF^{2+}, and $Ln[(CO_3)_4]^{5-}$ as predominant lanthanide complexes in seawater [91]. Further, a substantial part of RE existing as complexes with CO_3^{2-} and other ions present in seawater of the central, northern, and western parts of the Indian Ocean [10, p. 887]; or Ce^{4+} hydroxy complexes formed by reaction between seawater and artificially added Ce [27]. RE nuclides (probably forming oxides at the high temperatures associated with nuclear detonations) retain their particulate nature in seawater, primarily as hydroxides of the type $RE(OH)_3$ [14]. Although the ionic forms or easily dissociable species are the dominant existing states in seawater with a lowered pH (<6), radioactive Ce is hydrolyzed slowly at pH>6 and forms complexes with hydroxide, chloride, or other anions present in seawater, or exists as polymerized forms [11]. Ions of Y and RE are strongly hydrolyzed in seawater, hydrolysis being accompanied by polymerization of hydrolyzed ions and, under suitable conditions, by association of hydroxopolymers into colloidal particles [87]. Based on the stability constants of a great number of complexes, an equilibrium speciation of dissolved components in model seawater (pH 8.2) at 25 °C and 1 atm pressure has been calculated; the rounded values for trivalent Y and RE and the overall side reaction coefficient, log $\bar{\alpha}$, are given in the following (for additional details see original paper) [31, pp. 855/9, 874/81]:

trivalent cation	free ion	OH*)	F*)	Cl*)	SO$_4$*)	CO$_3$*)	log $\bar{\alpha}$
			percentage occurring as				
Y	15	14	3	7	6	54	0.81
La	38	5	1	18	16	22	0.42
Ce	21	5	1	12	10	51	0.68
Pr	25	8	1	12	13	41	0.61
Nd	22	9	1	10	12	46	0.66
Sm	18	10	1	8	11	52	0.75
Eu	18	13	1	10	9	50	0.74
Gd	9	5	1	4	6	74	1.02
Tb	16	11	1	8	9	55	0.80
Dy	11	8	1	5	6	68	0.94
Ho	10	8	1	5	5	70	0.99
Er	8	12	1	4	4	70	1.08

Table [continued]

trivalent cation	free ion	OH*)	percentage occurring as					log ā
			F*)	Cl*)	SO$_4$*)	CO$_3$*)	
Tm	11	21	1	5	6	55	0.94
Yb	5	9	1	2	3	81	1.30
Lu	5	21	1	1	1	71	1.32

*) For the complexes no individual ionic species is identified, for the data available do not justify any finer resolution or allow a discussion of the relative proportion of the various possible complexes.

Soluble complex compounds of the RE may also form with organic substances present in seawater [10, p. 887], or likely via complexing by organic debris [32], as is described for heavier RE present in seawater at concentrations of 10^{-10} to 10^{-11} M [33]; or variation of ^{91}Y content with depth may be due to interaction with certain complex-forming materials, possibly derived from the decomposition of organic matter [17]. See also, due to complexation with products of the decomposition of organic material, minimum contents of suspended, artificially added ^{91}Y at 500 m depth in Pacific seawater; artificially added ^{144}Ce is not affected so markedly [86]. As follows from an equilibrium speciation of RE in a model seawater (see p. 9) and its extension to additional ligands, humic acid complexation (being generally more significant in fresh water, see p. 13) may occur in seawater, and the nature of the humic acid ligand suggests that cations which will be complexed significantly by it should include the lanthanides, but no data are yet available to test this deduction [31, pp. 869, 871/2]. In alkaline medium (pH 9 to 10), Y and Ce are significantly solubilized by humic acid, Y forming strong non-ionic or anionic complexes to the extent of 90 to 100% of the element [33].

The occurrence of Y and/or RE, especially their radioisotopes, is also connected (surficially adsorbed) with marine organisms, whose element uptake depends on a number of factors (biological, environmental, physico-chemical); for details see original paper [14]. As a result of trapping by hydrobionts, >90% of ^{90}Y (initially occurring partly as hydroxocomplexes) converts to the coarse suspended fraction shortly after introduction into natural seawater not freed from suspended matter and hydrobionts [92]. Thus, for ^{144}Ce, plankton is the principal sorbent in vivo [34]. Hydroxy complexes of La, Ce, Sm, and Eu are adsorbed on the surfaces of fine detritus which apparently is concentrated by biological species (e.g., radiolaria) rich in Sr, as is observed for bulk plankton mixtures from both coastal and open-ocean waters, eastern Pacific Ocean [93]. Present in greatest amount in plankton is ^{144}Ce as a fission product with least solubility (together with ^{95}Zr) in open-ocean water at the Eniwetok test site, Pacific Ocean [94, 95]. Incorporated in practically all trophic levels of the Adriatic Sea, Yugoslavia, is ^{144}Ce (varying with the season) in plankton and other marine organisms of the northern part [35], mostly in zooplankton, followed in decreasing order by benthos, phytoplankton, and sediments of the Kvarna region [36]. Various types of biota contain ^{155}Eu in the lagoonal waters of the Bikini Atoll, central Pacific Ocean [18, pp. 19/20]. Accumulation of ^{144}Ce occurs in the soft body of mussels and of ^{91}Y in the skeleton of mussels, lobsters, and crabs (of the Black Sea?) [37]. Enrichment of RE occurs in marine organisms, especially algae, off the coast of Ibaraki prefecture, Japan [38]; ^{144}Ce being highest in green algae mixture, Gulf of Mexico [25, p. 118]; non-planktonic algae contain Y, La, and Ce in the Gulf of Kola, northwestern European USSR [39]. However, not more than 0.1 to 0.3% of total RE is associated with plankton of the Indian Ocean [10, p. 889], and no La concentration by phytoplankton occurs in the Black Sea [40]. In an adsorbed phosphatic phase rather than on Ca sites due to ion exchange, the RE may occur in foraminifera tests [41].

The behavior of RE radioisotopes in seawater in relation to a time-dependent adsorption (adsorbability) has been intensively investigated experimentally, thus giving hints of the degree of accumulation or the mode of occurrence in a natural environment. Besides the references [11, 14, 33] cited above, the following papers deal especially with the topics: adsorption of ^{90}Y on Teflon and influence of time on it [100], or of ^{91}Y on glass and Teflon and influence of time and temperature on it [101], both results being compared with the adsorbability of ^{90}Y purified from ^{90}Sr in [92]; adsorption on glass and Fluoroplast-4 and changes of hydrolysis products with time for ^{91}Y [102]; adsorption and changes of hydrolysis products with time for both trivalent ^{144}Pr and ^{144}Ce [87]; steady-state ratio between dissolved and suspended fraction of ^{91}Y and ^{144}Ce [86]; and sorption equilibrium between solid and liquid phases for ^{91}Y and ^{144}Ce and differences in behavior during sorption on living zooplankton [85].

Non-Marine Waters

In **river water**, Y and RE occur as solid terrigenous suspended matter, or sorbed on the surface of suspended matter, or as colloidal compounds with high-molecular weight organic and inorganic compounds, as well as in soluble ionic and complex form [1]. The main part of the RE (together with Fe and Al) in river water is associated (with only slight geographical variability) with suspended matter [43, pp. 188/90, 200] (and see below) for which an enrichment of the light RE is typical [44, 45]. More than three-fourths of the total RE carried by rivers occurs in suspended form; colloidal and dissolved forms are of minor importance [44]; note also that most of RE in river water are transported into seawater in suspended form and only a minor portion in solution. In the following are given the average Y and calculated summary contents of light (La to Eu) and heavy RE (Gd to Lu) suspended and dissolved in river water, the annual river discharge and the calculated average percentage of suspended and dissolved river discharge into seawater; susp. = suspension, sol. = solution [104]:

	average contents for susp. in g/t	sol. in mkg/L	discharge in 1000 t/yr. susp.	sol.	total	average percentage of river discharge susp.	sol.
Y	30	430	555	1.530	557	99.65	0.35
Σ light RE	213.80	1811	3949	6.441	3955	99.82	0.18
Σ heavy RE	14.12	201	261	0.714	261	99.73	0.27

Differences due to granulometric and mineral composition occur in the correlation between the contents of total RE and suspended matter for rivers coming from mountainous areas or flowing over plains (for details see original paper) [45]; compare [42]. From analyses for seven major world rivers (Amazon, Congo, Ganges, Mekong, Magdalena, Parana, Orinoco) and additional data from literature sources for other rivers, the following mean amounts of RE are transported in suspended or dissolved form; values given in parentheses are considered as a first approximation because of the scarcity of data and/or the wide variation of concentrations [43, pp. 175/88]:

transported as	La	Ce	Pr	Nd	Sm	Eu	
river-suspended, in 10^{-6} g/g	45	95	(8)	35	7	1.5	
river-dissolved, in 10^{-6} g/L	0.05	0.08	0.007	0.04	0.008	0.001	

transported as	Gd	Tb	Ho	Er	Tm	Yb	Lu
river-suspended, in 10^{-6} g/g	(5)	1.0	(1)	(3)	(0.4)	3.5	0.5
river-dissolved, in 10^{-6} g/L	0.008	0.001	0.001	0.004	0.001	0.004	0.001

In the suspended fraction are contained 95.3% of Y (mean for 17 rivers) or 96.6% of Yb and 99.9% of La (mean for 16 rivers each), as is found for the major rivers of the USSR (practically all large rivers), North and South America, and Europe; see original paper for the quantitative data (μkg/L) of these and other RE and of Y [46]. Note further that in the principal world rivers, 99.69% of the Y and 99.76% of the La occur in suspension [21]; about 96% of La and Ce and about 99% of Eu in the Main River, Federal Republic of Germany [47]; or about 98% of RE in the Gironde, France [48]. The predominance of the suspended form is shown further for RE and Y in the rivers Dordogne and Garonne (and their confluence area in the Gironde estuary, see p. 7), although there are greater differences in the percentages of soluble and detrital RE for the individual RE discharged [42]. Mainly associated with suspended particles are La, Ce, Eu, Sm, Yb, and Lu in river water of the upper Volga basin, USSR [98]. Present as small-sized particulate matter (<1 μm) are the RE in eleven Norwegian rivers (predominantly from the central and southern part) representing an average river water of Norway (possibly also for Scandinavia) [49, pp. 117, 120, 132, 137]. Mainly transported as particulate is La in the Thames River and its tributary, Kennet River, an increased dissolved transport being related to water hardness [50], see p. 50. Only about 30% of ^{144}Ce occurs with the suspended matter of the Don River near Rostov-on-Don, Ukraine, and an exchange with the individual states of solute forms (see p. 13) cannot be ruled out [51]; and ^{144}Ce is apparently associated with suspended matter of the Danube River, Romania [52]. Bound to the particulate fraction (>0.3 μm) are 97.3 and 98.4% of ^{152}Eu at McNary Dam site (Washington and Oregon sides, respectively), Columbia River [53].

The suspended matter carrying RE and/or Y consists mainly of clay minerals (illite) in a number of Norwegian rivers (as is indicated by factor analysis) [49, pp. 120, 126/8], or of alumino-silicates in the Gironde, France [48].

Table 1
Calculated equilibrium speciation of dissolved components in model fresh water at different pH from [31, pp. 856/60, 874/81].

tri-valent cation	percentage at pH 6 occurring as							percentage at pH 9 occurring as						
	free ion	OH[*]	F[*]	Cl[*]	SO$_4$[*]	CO$_3$[*]	log $\bar{\alpha}$	free ion	OH[*]	F[*]	Cl[*]	SO$_4$[*]	CO$_3$[*]	log $\bar{\alpha}$
Y	63	1	17	<1	14	4	0.20	<1	14	<1	<1	<1	85	2.57
La	73	<1	1	<1	25	1	0.14	2	10	<1	<1	<1	88	1.78
Ce	72	<1	3	<1	22	3	0.14	<1	5	<1	<1	<1	95	2.37
Pr	72	1	2	<1	23	2	0.14	1	9	<1	<1	<1	90	2.23
Nd	70	1	3	<1	24	3	0.15	<1	9	<1	<1	<1	90	2.33
Sm	68	1	3	<1	25	4	0.17	<1	14	<1	<1	<1	86	2.49
Eu	71	1	3	<1	21	4	0.15	<1	18	<1	<1	<1	82	2.48
Gd	63	1	5	<1	22	9	0.20	<1	14	<1	<1	<1	86	2.92
Tb	67	1	6	<1	22	4	0.18	<1	32	<1	<1	<1	68	2.67
Dy	65	1	6	<1	21	7	0.19	<1	46	<1	<1	<1	54	3.01
Ho	65	1	7	<1	19	8	0.19	<1	48	<1	<1	<1	52	3.08
Er	63	1	7	<1	19	10	0.20	<1	78	<1	<1	<1	22	3.54
Tm	66	1	8	<1	20	6	0.18	<1	86	<1	<1	<1	14	3.51
Yb	58	1	7	<1	17	17	0.24	<1	62	<1	<1	<1	38	3.59
Lu	59	1	8	<1	15	17	0.23	<1	92	<1	<1	<1	8	4.21

[*] For the complexes, no individual ionic species is identified, for the data available do not justify any finer resolution or allow discussion of the relative proportion of the various possible complexes.

The speciation of the trivalent elements (mainly the lanthanides) in river water tends to be dominated by the formation of carbonate complexes [90]. As follows from calculations of equilibrium speciation of dissolved components in model fresh waters (with pH 6 and 9) at 25 °C and 1 atm pressure (data see Table 1, p. 12), the RE mainly occur as free cations or hydroxide and carbonate complexes, with minor amounts of fluoride, sulfate, and chloride complexes [31, pp. 855/60]; compare percentages for ionic forms and various complexes of Y and Ce in model systems of ordinary and highly-colored river waters [54]. Less than 25% of the Ce and <33% of Eu occur in dissolved form (as determined by dialysis) in the Glomma River at Fetsund, Norway [55]; about 5% of RE is present in the dissolved load of the Gironde estuary, France [48]. For ^{144}Ce in Don River water, near Rostov-on-Don, Ukraine, an occurrence in cationic (about 50 to 60%), anionic (about 30 to 40%), and neutral forms (about 10 to 13%) is discussed (which differs, especially for the anionic and neutral forms, from literature data for the dissolved part in atmospheric depositions, compare p. 109). In cationic form, it occurs as hydrolyzed Ce^{3+} ions ($Ce(OH)_3$) and as positively charged complex ions; in the anionic form (negatively charged complexes and polymeric ions) it may be connected with organic acids (citric, oxalic, tartaric, etc.) [51], compare [56], or possibly (stable within pH 2 to 8.6) with humic acids [57]. In water (with pH 7.3 and a high color index) of the Moskva River spring region, European USSR, complexes with fulvic acids occur for Ce, Y, Yb, and ^{144}Ce (weakly soluble ones with the high-molecular and a number of soluble cationic and anionic ones with the low-molecular weight fractions of the acids) [58]. Additionally, Y forms complexes with phenol and other soluble organic substances [59]; for the stability of fulvic acid complexes with Y, Ce, and Yb, see [60], and for the percentage of individual fulvate (and other) complexes of Y and Ce in model systems for ordinary and highly-colored river water, see [54]. The cationic form accounts for 1.1 and 1.6% of ^{152}Eu at the McNary Dam site (Washington and Oregon sides, respectively), Columbia River; in addition, 1.6% occurs in non-ionic form at the Washington side [53]. With aging in fresh water, the electroneutral species of ^{144}Ce as well as colloidal or particulate and more or less adsorbable species are formed which, in the initial dilute HCl solution, show cationic species [96].

High RE concentrations in **lake waters** may be associated with humus complexes or high-molecular weight colloids as in Lake Trehørningen, Baerum [61], or, assumed, in the saline bottom layer of Lake Rørholtfjorden, both Norway [62]; compare also higher concentration factors for La in phytoplankton (3.0), benthos (2.6), zooplankton (2.5), and fish (1.5 to 1.8) of Lake Michigan, USA [63], or a tendency for increasing concentrations of ^{144}Ce and ^{144}Pr in aquatic plants with increasing nuclide content in the Beloyarsk(oe) fresh water reservoir of a nuclear power plant (Sverdlovsk region?), USSR [64]. Whereas high accumulation in the biomass occurs for ^{144}Ce (51%), ^{91}Y accumulates only at 8%, as follows from experiments with solutions prepared from lake (or fresh) water. The other modes of occurrence are with the suspended matter (40% for Ce, 92% for Y) and in solution (9% for Ce, none for Y) [97]. In the RE-rich brine waters (produced by evaporative concentration) of eastern Pamir lakes, Central Asia, USSR, an occurrence of carbonate and fluorocarbonate complexes of RE is assumed [65]; compare also mineralized waters p. 14.

In **ground waters**, the RE (including Y) may occur as simple cations, compound ions, or complex compounds, predominantly with CO_3^{2-}, F^-, or humic organic matter [66], for an influence of these forms on the behavior of Y and RE during migration and precipitation, see Chapter 7.3. For example, in subsurface waters of the Ukrainian Shield, USSR, Y and La occur as complex compounds, for La solely hydrogencarbonates [67]. In ground water associated with bauxites, the RE form carbonate complexes, Y being present only if chloride is high [68]. In alkaline waters, e.g., of the Lovozero massif, Kola Peninsula [69], and of Central Asia, all USSR, the RE predominantly occur as carbonate and fluoride com-

plexes [70]. In neutral or slightly alkaline waters (pH 6.5 to 8) of the Urals, the Transuralian region, and of northern Kazakhstan, the RE possibly occur as simple cations, compound ions, or (pseudo)colloids [71]; or in ground waters of the Monticello area, New York, Ce and Y might be in true solution or occur as colloidal material [72]. Organometallic complexes are the supposed principal type of occurrence of RE in ground water from crystalline schists of the Piedmont area, Virginia. If the RE occur at the determined concentrations of 10^{-7} to 10^{-11} M as quasi-colloids, they probably would be filtered out, or sedimentated out of solution while the waters move through soil and sapropelite [73]. See also, organometallic compounds extracting RE from ground water directly in contact with petroleum, Azerbaid-zhan [74].

The type of occurrence of Y and RE in **mineralized and/or thermal waters** is as free ions or as complex compounds, the relative amounts being variable, as can be seen from the following: In mineral waters, southern part of Eastern Siberia, an important correlation between RE concentrations and HCO_3^-, SO_4^{2-}, and Ca has been observed [75]. Subsurface waters (pH between 2.0 and 7.8, E_h +96 to -700 mV) from complex ores and chalcopyrite deposits of the Alaverdi region, Armenia, contain Y and Yb (in complex ore waters only) as sulfate complexes or as trivalent free ions, the ratio between both forms being slightly influenced by pH and the type of water [76]. In the thermal springs of Plombières and Bains, Vosges, France, La occurs mainly as free ions and complex compounds (e.g., $La(OH)^{2+}$ or LaF^{2+}) [77]. Thermal waters of Belgium contain RE, besides being in solution, in varying amounts in suspended matter; thus, Ce and Eu are lower in suspension at the localities St. Ghislain, Ghlin, Douvrain, and Stambruges, whereas the stagnant warm waters of Baudour have an elevated content of Ce (5.5 µg/L) in suspended matter compared with the amount in solution (<0.8 µg/L) [78]. However, thermal waters ($<100\,°C$) of regionally different type from the northern, central, and lower Paratunsk River basin, Kamchatka, Far East, USSR, contain RE always in the soluble state [79], as is the case for the various waters of the Geyser Valley and the Uzon Caldera (with pH 1.5 to 6.5 and up to $100\,°C$), or the carbonate hot springs of the Nalachevo area (with pH 6.0 to 6.5 and 35 to $74\,°C$), all Kamchatka. Stable carbonate complexes are assumed to cause the substantially higher RE contents (up to tenfold) in the Nalachevo waters compared with chloride-Na-, sulfate-Na-, or sulfate-type waters (RE being lowest in the first type) of the other regions (where the RE, depending on pH of the water, may occur as free ions or hydroxo complexes) [80].

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7.2.2 Relationship Between Content and/or Composition of Rare Earth Elements and the Chemistry of Water or Other Factors

7.2.2.1 Seawater. General

Since the RE metals are strictly lithophile elements, the principal factor determining their distribution in the hydrosphere must be the suspended matter [1]. Further, solid–state chemistry controls concentration of La in seawater while complexation in solution seems to be less important [2], and Eu enrichment seems to depend on the chemical species in which the element occurs in seawater of the central Pacific Ocean, southeast of Hawaii, hydroxides showing the greatest enrichment and shortest residence times [3]. In shallow-sea areas, Ce, perhaps mostly involved in suspended solid particles, behaves apparently in the same way as other RE, while in the deep-sea areas Ce is subjected to selective removal relative to the other RE [4]; see also Chapter 7.3. Rare earth contents in suspended matter are correlated with the amount of suspension in surface seawater which decreases from coastal to open ocean (see pp. 34/5). Variations in contents of individual RE are due to the variable composition of the suspended terrigenous matter with different sorption ability (see p. 26). In the open ocean, maximum enrichment of intermediate RE (Nd through Dy) occurs in suspended matter with maximum amounts of the pelitic fraction [5]. In the oceans, the concentrations of the dissolved and suspended forms of RE are much lower than those in rivers; for the suspended form this is due to the much lower amounts of the suspended material itself (see pp. 25/6) and to much lower RE contents in oceanic suspensates compared to river suspensates [6]. In coastal suspended matter with variable RE composition, total RE are enriched with the light RE following the nature of RE composition of terrigenous material from continental regions. In the shelf areas most of river-suspended matter is deposited and only the pelitic fraction and dissolved RE are transferred further into the central parts. Thus, in the peripheral zones a sharp change of RE composition occurs with RE concentrations in suspension and solution becoming reversed. The duration of contact of the pelitic suspended fraction with seawater provides considerable sorption of RE and leads to a redistribution between coastal and open-ocean water, Ce being preferentially sorbed by terrigenous silicate suspended matter, while contents of intermediate RE (Nd through Dy) and Y increase considerably in water relative to contents in suspension and bottom sediments [7, pp. 149/50, 162/5]. Higher contents of Y and/or RE in coastal compared to open-ocean surface water are due to a more profound effect of the input of terrigenous detritus on coastal seawater [5, 8], while in the open ocean other sources (e.g., atmospheric fallout) can be more important [9]. Physical factors such as gravity, turbulence, and adsorption to other matter govern the spatial distribution of particulate RE in the hydrosphere. In contrast to removal by sedimentation (see pp. 74/5), part of the RE becomes adsorbed to small organic and inorganic debris suspended in water and, because of turbulence produced by wind and ocean currents, this particulate matter remains in the mixed or shallow layers for some time, and eventually may become associated with living organisms [10].

The relative abundances of RE are distinctly different in various continental source mate-

rials, seawater, and sediments, and the abundance patterns can serve as "fingerprints" that identify sources of the elements in seawater. Since the scavenging residence time for RE ($\sim$400 yrs.) is shorter than the oceanic mixing time (1600 yrs.), RE and Nd isotopes always reflect elemental sources [11]. So, composition of RE in seawater is expected to respond rapidly to variations in the inputs of RE to the marine environment due to their very low solubilities and mobilities, resulting in short residence times in seawater (compare Chapter 7.3). Since residence times are less than mixing times of the oceans, RE are capable of maintaining distinctive abundances in regions receiving abnormal inputs. Therefore, shelf waters are distinctly different from open-ocean waters, and even open-ocean waters vary laterally and vertically [12]. Based on literature data (e.g., [7, pp. 149/50, 166/70], [13]) the following summary of RE characteristics in different marine environments is given [9]: (1) Contents of dissolved RE on the whole decrease laterally from coastal to open ocean. Average total RE contents are 0.0891 mkg/L in shelf water, 0.0664 mkg/L in bottom troughs of the coastal zone, and 0.0262 mkg/L in the open ocean, i.e., about one fourth that in shelf water. (2) In the open ocean, contents of dissolved RE regularly increase with depth; average total RE contents are 0.0248 mkg/L at 0 to 100 m, 0.0232 mkg/L at 1000 m, 0.0256 mkg/L at 2000 m, and 0.0310 mkg/L for bottom water at 3000 to 5700 m. (3) The change of RE composition (normalized to clay from platform) from coastal to pelagic, and from surface to deep waters, is characterized by increased relative amounts of heavy RE and La and a decrease of the relative amount of intermediate RE with a minimum for Sm. (4) Except for the upper shelf water, seawater is characterized by a distinct Ce deficiency, doubling from coastal to open-ocean water and generally increasing with depth; the Ce deficiency is most evident at intermediate depth (about 2000 m) in the open ocean.

With regard to the influence of the preceding factors it seems inappropriate to give an average RE composition of seawater, but the following contents have been calculated and are used in the literature: Goldberg [14] gives, in mg/L, Y 0.0003, La 1.2×10^{-5}, Ce 5.2×10^{-6}, Pr 2.6×10^{-6}, Nd 9.2×10^{-6}, Sm 1.7×10^{-6}, Eu 4.6×10^{-7}, Gd 2.4×10^{-6}, Dy 2.9×10^{-6}, Ho 8.8×10^{-7}, Er 2.4×10^{-6}, Tm 5.2×10^{-7}, Yb 2.0×10^{-6}, Lu 4.8×10^{-7}; and Holland [15] gives, in µg/kg, Y 0.001, La 0.0034, Ce 0.001, Pr 0.0006, Nd 0.0028, Sm 0.0004, Eu 0.0001, Gd 0.0007, Tb 0.0001, Dy 0.0009, Ho 0.0002, Er 0.0009, Tm 0.0002, Yb 0.0008, Lu 0.0001. As mean content for coastal seawater Balashov [7, p. 141] gives, in 10^{-5} mg/L, Y 1.99, La 1.38, Ce 1.60, Pr 0.193, Nd 0.765, Sm 0.159, Eu 0.033, Gd 0.151, Tb 0.031, Dy 0.149, Ho 0.041, Er 0.133, Tm 0.029, Yb 0.128, Lu 0.027.

Due to the variance through geological time in Nd isotopic composition (refer also to Chapter 9) and the short cycling time of RE in the oceans, compared to mixing between the oceans, the ^{143}Nd/^{144}Nd ratio is variable in seawater and reflects the source terrane. Therefore, this ratio is widely used as a tracer for studying the transport of RE in oceans, or the origin of different water masses [16], and as a tracer of ocean currents for short-time scales or of mixing in and between the oceans [17, p. 223]; instead of the ratio, its normalized coefficient $\varepsilon_{Nd}(O)$ is often used; for definition see [17, p. 228] and compare also "Seltenerd-elemente" A5, 1981, pp. 170/1. For examples using differences in Nd isotopic composition, see pp. 45/7. Particulate Nd concentration in the nepheloid (turbidity) zone (which contains pelagic clay swept back up to the water column and may extend 1000 m above the sediment-water interface) is much higher than the average in seawater, thus suggesting that continental cation exchange between pelagic clay and seawater, particularly in the nepheloid zone, may control the Nd isotopic composition of seawater [18].

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7.2.2.1.1 Influence of the Chemical Composition of Seawater

In a subalkaline medium (as seawater) and, in particular, in the presence of complexing agents, yttrian RE are considerably more stable in solution than cerian RE [1]. Generally, increasing chlorinity, alkalinity, and pH (>8.5) and decreasing sulfate content favor the formation of stronger solution complexes of heavier lanthanides. The importance of pH and alkalinity is indicated by the magnitude of the stability constants of the tetracarbonate complex $Ln[(CO_3)_4]^{5-}$ (see original paper), one of the major lanthanide complexes in seawater. These effects are particularly sensitive for Eu through Dy to heavier RE, the prime effect apparently being the increase of carbonate ion activity (small increases in pH strongly increase the amount of carbonate available for lanthanide complexing) and the tendency for heavier RE to form the tetracarbonate complex. Significant complexing of RE under normal seawater conditions is not typical, except with strong depletion of sulfate under reducing conditions. As calculated for a hypothetical model solution, 50% complexation would only occur in those brines for which the Cl/SO_4 ratio greatly exceeds that of normal seawater, which seems to be important only under high chlorinity and alkalinity conditions [2].

To clarify especially the **influence of pH** of the seawater on distribution and mode of occurrence (refer also to pp. 7/9) of Y and/or RE, radioisotopes of these elements are used in laboratory experiments. In the following, results of experiments using predominantly natural seawater samples are given briefly (for details see the original papers): For [91]Y introduced in prefiltered seawater from 10 miles off Sevastopol, Crimea peninsula, USSR, its chemical forms are stable with time at pH ≤ 3. At pH between 4.35 and 8.0, adsorbability of [91]Y on glass and Teflon increases with age of solution (see p. 32) with a maximum after about 24 h at pH 8.0 or on the fifth or sixth day at pH 4.35 [3]; see also adsorption experiments with ^{90}Y added to natural seawater not freed from suspended matter and hydro-

bionts, showing the sorption maximum on fresh sorbents shifted with increasing pH to the side of lower storage times [4]. Radioactive Ce added at pH<6 to prefiltered coastal seawater from Nakaminato City, central Japan, and to artificial seawater occurs predominantly in ionic or easily dissociable forms; at pH>6 it forms complexes with hydroxide, chloride, or other anions present in seawater, or exists as polymerized forms [5]. The amount of ^{144}Ce and ^{91}Y retained by an ultrafilter increases with pH of the seawater. According to ultrafiltration and centrifugation experiments, these elements, introduced at any pH into prefiltered and acidified surface seawater of the Pacific Ocean, are not present solely in the suspended fraction, and the amount in suspension is not reduced at a pH>7 (as is observed in doubly-distilled water) and Ce concentrations $>7 \times 10^{-12}$ M, since mononuclear Ce hydrolysis products preferentially interact with foreign impurities, thereby forming suspended particles (see pp. 24/5). However, in the pH region >7, the behavior of Ce^{3+} is totally different in nature, Ce^{3+} being oxidized to the tetravalent state, and a true colloid of difficultly soluble Ce^{4+} hydroxide or phosphate should be formed [6, 7]; see also oxidation of Ce^{3+} as a function of pH for ^{141}Ce added to settled, aged seawater of the coastal Atlantic Ocean, southeastern USA [8, p. 237]. Centrifugation experiments show that at pH>6.5 the content of suspended ^{144}Ce (added to the solution at $<10^{-10}$ mol/L) changes, apparently due to an accumulation of finely-dispersed, non-sedimenting, ^{144}Ce-containing particles [9]. The dependence of the state of ^{91}Y on acidity of seawater is similar to that of ^{144}Ce [6, 7], although Y does not change valence, and at the concentrations studied it cannot form an independent hydroxide phase at pH<9, while, possibly, Y^{3+} can form a true colloid of difficultly soluble compounds with, e.g., PO_4^{3-} or HPO_4^{2-} [6] (see also p. 9). In surface seawater 5 km off the coast of Ibaraki prefecture, central Japan, without HCl treatment before filtration, considerable amounts of RE exist in the residue on the 0.22 μm filter, while in seawater treated with HCl before filtration, the greater part of RE remained in the dissolved state [10].

Although Y and RE are assumed to belong to those elements whose variations in abundance in seawater are independent of salinity [11], and changes in salinity do not affect the isotopic composition of Nd in seawater [12] or $\varepsilon_{Nd}(O)$ may be decoupled from either temperature or salinity [13, p. 6002], there are statements that **salinity or chlorinity** influences content and composition of RE in seawater as well as in estuarine zones as can be seen from the following. Taking into account the marked drop of sorption of trace elements from waters of appreciable salinity and the virtual absence of RE and other trace elements in chemogenic deposits of terminal drainage basins, an increase of absolute and relative contents of these elements in concentrated brines is assumed as mineralization increases. With increasing mineralization of natural waters already at the stage from fresh to brine (at a total salt content of 3.5%), the relative content of RE drops markedly, which mainly is due to their absorption by sorbents and organisms. Therefore, river waters are relatively richer in the elements studied than seawater [14]. A non-linear relationship between concentration and salinity (non-conservative behavior) is observed for RE in the mixing zone of river and seawater (river-sea barrier) [15]. In the zone of direct contact of river and seawater (e.g., Gironde and Volga estuaries), total RE concentrations in fresh water of $\sim 550 \times 10^{-5}$ mkg/L are about one order of magnitude higher than in coastal seawater with 20×10^{-5} mkg/L [16, p. 149]. Within the estuarine zone the lanthanides are removed from solution but, due to their low distribution (or partition) coefficients K_y (ratio between the mean concentration in water (given in μg/L or μg/kg dissolved solids) and in the solid phase (given in μg/kg)), the particulate concentration is not seriously affected. Only the leachable fraction will be modified. Based on literature data, the log K_y values (describing the ease with which elements are transferred from solid to solution phase) for RE are as follows; susp. = suspension [17]:

	log K_y*) for distribution between water and solid phase			
	river/rock	river/susp.	sea/rock	sea/deep–sea clay
La	−1.92	−1.96	−5.69	−5.73
Ce	−2.04	−2.08	−6.48	−6.55
Nd	−1.98	−1.95	−5.64	−5.67
Sm	−1.96	−1.95	−5.70	−5.70
Eu	−2.05	−2.16	−5.63	−5.73
Gd	−1.92	−1.81	−5.52	−5.60
Tb	−2.03	−2.01	−5.57	−5.55
Ho	−2.21	−2.01	−5.45	−5.25
Er	−1.98	−1.89	−5.22	−5.08
Tm	−1.71	−1.62	−4.75	−4.85
Yb	−1.95	−1.95	−5.19	−5.12
Lu	−1.66	−1.77	−4.90	−4.95

*) Concentrations given in μg/kg for both components.

With increasing salinity (0.1 to 28‰) a gradual decrease of RE concentrations in particulate matter is observed in the Gironde estuary, France, which never exceeds 25 to 35% at 28‰ salinity. Comparing measured RE concentrations in waters of various salinites with the theoretical dilution curve of river water with seawater, an uptake of RE from solution by as much as 50% is observed. As can be seen from Table 2, light RE are removed from solution as soon as the river water reaches the estuarine area, while the heavy RE, being more strongly chelated, remain longer in solution (compare also [18, p. 77]), and the Ce/La ratio remains nearly constant throughout the estuary and is much higher than in seawater. Owing to the very low soluble vs. detrital RE ratio, a removal from solution will not give any significant enrichment of the particulate phase [19]; for details on the removal mechanisms, see Chapter 7.3 and for relation of RE concentration and chlorinity, see below. Likewise, when salinity increases up to 28‰, a decrease of the suspended form of 25 to 35% and a decrease of the dissolved form by more than 50% are found for the estuaries of Rhone and Gironde, both France, heavy RE remaining in solution longer due to the formation of more stable complexes [15]. Up to 12‰ salinity, RE concentration shows an overall constancy (within 30%) in suspended matter of waters from three depth zones of the Zaire River mixing zone, indicating that they remain strongly bound to the suspended sediment. The RE contents are as follows [20]:

depth zone and salinity	content in ppm						
	La	Ce	Sm	Eu	Tb	Yb	Lu
surface; 2.1‰	51	97	7.7	2.1	0.55	3.6	0.43
halocline; 5.4‰	40	76	6.6	1.9	0.79	2.7	0.31
near–bottom; 11.6‰	46	64	7.7	1.9	0.52	2.8	0.34

Within the core of Mediterranean outflow water, Sm and Nd concentrations appear to imitate salinity in the northern Atlantic Ocean, high Sm and Nd contents corresponding to high salinity portions and vice versa [13, p. 6004].

The content and composition of RE in estuarine and coastal seawater might be dependent upon chlorinity as is exemplified in the following. From the confluence of the rivers Garonne and Dordogne (chlorinity 0.008‰) to Pointe de Grave (chlorinity 15.8‰), RE in suspension of the Gironde estuary, France, show uniform concentrations with coefficients of variation

Table 2
Concentrations of Y and RE at Various Salinities (sal.) in the Gironde Estuary System, Northwestern France, from [19].
Concentrations are given for suspension in mg and for solution in 10^{-10} g/L.

type of occurrence	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ratio Ce/La
Garonne and Dordogne rivers, 0.1‰ sal.																
suspension	30	44	93	8.2	35.8	6.2	1.08	6.1	0.90	—	0.90	2.4	0.44	2.8	0.42	2.11
solution	431	475	790	73	379	78	14.8	85	12.4	—	14.4	42	6.1	36.4	6.4	1.66
Gironde estuary, 0.42‰ sal.																
suspension	27	45	95	9.7	37	6.2	1.17	7.7	1.04	—	0.99	3.5	0.46	3.1	0.41	2.11
solution	—	197	320	36	139	30	6.0	—	—	—	—	—	—	32	6.2	1.62
Gironde estuary, 7.0‰ sal.																
suspension	22	44	84	8.8	32	6.0	1.07	5.5	0.88	—	0.85	2.7	0.37	2.6	0.39	1.91
solution	150	55	113	15	98	12	3.7	18	2.6	—	3.6	—	—	15	2.9	2.05
Gironde estuary, 28.3‰ sal.																
suspension	19	34	54	5.9	23	3.8	0.78	4.4	0.66	—	0.69	2.0	0.32	2.9	0.34	2.18
solution	93	78	110	9.0	51	—	1.31	9.8	1.26	—	1.60	7.1	1.21	5.3	0.85	1.41
open ocean, 35.5‰ sal.																
suspension	—	15	35	—	—	1.5	0.6	—	—	—	—	—	—	—	—	2.33
solution	133	34	12	6.4	28	4.5	1.3	7.0	1.4	9.1	2.2	8.7	1.7	8.2	1.5	0.35

<5% for La, Sm, and Eu, 5 to 10% for Ce, and 10 to 13% for Tb and Yb. The contents for individual RE are tabulated below, the suspended matter is separated by ultrafiltration or centrifugation (marked by an asterisk) [21]:

sample No.	chlorinity in ‰	content in suspension in µg/g						
		La	Ce	Sm	Eu	Tb	Yb	Lu
08	0.008	45.5	100	7.80	1.40	0.92	2.8	0.49
09	0.30	45.5	100	7.60	1.45	0.96	2.7	0.49
10	0.87	46.5	100	7.40	1.45	0.76	3.5	0.40
31*	1.10	46.0	70	7.15	1.45	1.3	3.2	0.47
11	1.26	45.0	95	7.00	1.30	1.2	2.8	0.51
14	1.59	43.5	80	6.50	1.30	1.0	2.7	0.44
06	2.84	45.5	95	7.05	1.50	1.0	2.5	0.41
25	3.48	43.0	90	6.90	1.35	1.1	2.5	0.49
16	4.82	45.5	95	7.40	1.40	1.0	2.7	0.46
19	6.69	45.0	95	7.30	1.40	0.94	2.6	0.37
20	10.5	41.5	90	6.85	1.30	1.2	2.5	0.40
21	12.3	43.5	90	7.35	1.35	0.86	2.8	0.49
07	15.8	43.5	75	6.85	1.35	0.89	2.4	0.39
average		44.6	90	7.17	1.40	1.0	2.75	0.45

In contrast, for coastal surface seawater off Arasaki, Miura peninsula, Japan, the RE concentration is lower with higher chlorinity. The contents in solution (HCl filtration) and in insoluble parts (residue) for two samples are tabulated, the content for sample No. 2 being determined with pH adjusted by HCl solution immediately after and several days after the sampling date (the lower figures suggest adsorption of RE on the surface of the containment) [22]:

fraction of sample and chlorinity	content in µg/L								
	La	Ce	Sm	Eu	Tb	Dy	Tm	Yb	Lu
No. 1; 18.54‰									
solution	0.030	0.0509	0.0048	0.0014	0.0014	0.0049	—	0.0040	0.0004
insoluble	0.010	—	0.0006	0.0002	—	0.0003	—	—	—
No. 2; 19.25‰									
solution	0.017	0.0133	0.0015	0.0006	0.0005	0.0025	0.0030	0.0012	0.0002
insoluble	0.005	0.0201	0.0009	0.0006	0.0045	0.0009	—	—	0.0012
solution	0.006	0.0136	0.0007	0.0004	0.0009	0.0009	—	0.0013	0.0002
insoluble	0.004	0.0215	0.0010	0.0005	0.0028	0.0010	—	—	0.0008

The sorption or hydrolysis behavior of RE relative to seawater salinity was derived experimentally with radioisotopes, under the special conditions of the original papers: The primary effect of seawater on the state of [144]Ce is that less suspended [144]Ce is formed. It is not possible to decide whether this is due to the desorbing effect of dissolved salts, to partial complex formation by the hydrolyzed ions with some natural ligands, or to the effect of the high ionic strength of the solution. The absence of a reduction of [144]Ce in the suspended fraction at a pH>7, in contrast to doubly-distilled water, may be due to

the presence of foreign substances which inhibit polymerization, i.e., mononuclear Ce hydro-lysis products preferentially interacting with foreign impurities, thereby forming suspended particles [6]; refer also to [7]. The reduction of a portion of the suspended fraction of ^{144}Ce (added at 10^{-10} mol/L to stabilized seawater (pH 6.65)) with increasing electrolyte concentra-tion (salts of Na, K, Mg, and Sr) may be due to the competition of the electrolyte ions for the sorption centers of the suspended matter. With respect to desorbing action, the ions form the series $Sr^{2+} > Mg^{2+} > K^+ > Na^+$. The process of sorption is dependent upon the relation $\log K = A + B \cdot \log C_i$, where K is the fraction of the suspended quantity (or K_{ads}), C_i is the concentration of the electrolyte, and A and B are constants [23]. This linear depen-dence of adsorption on the concentration of electrolyte ions results from the formation of sorption radiocolloids. The isotherm of ^{144}Ce retention is described by such an equation when solutions based on seawater purified from suspensions are used. The nature of salt cations present in seawater strongly influences the value of A, which is probably associated with the characteristics of the competitive ions (e.g., the charge of the radionuclide ion), whereas B remains almost constant [24]. And with increasing salt background of an indiffer-ent electrolyte in seawater, the adsorption of ^{144}Ce onto colloidal impurities (forming stable sorption colloids) is more actively inhibited than in distilled water and NaCl solution. This causes the sedimentation isotherm in model solutions to shift toward the alkaline region [9]. In solutions without a salt background, the fraction of coarse forms of ^{144}Ce is greater than in seawater, and sorption takes place more actively. Thus, it may be assumed that in seawater hydrolysis takes place less rapidly due to the high salt background [25]. A reversible change with salinity occurs for ^{144}Ce forming suspended particles in centrifugation experiments, with ^{144}Ce being added to a mixture of fresh and seawater (Amur River and open Pacific Ocean) freed of coarsely dispersed suspension by filtration. Thus, at a definite salinity, ^{144}Ce which undergoes hydrolysis tends to form suspended particles and may be transferred to the sludge (see pp. 79/80), and an increase in salinity leads to a decrease in the amount of ^{144}Ce in suspension. If similar processes occur in nature, possibly the erosion of radionuclides from the sludge of an estuary is associated with a salinity change due to high- and low-tide phenomena [26]. Refer to RE concentrations not changing in water regularly with the tidal changes, but being strongly influenced in bottom sediments in water with different salinity and pH [27]; or with increasing salinity, ^{155}Eu showing higher fractional solubility (mostly at salinities $> 15‰$) in experimental river water–fresh water mixtures for the estuarine zone of Anasco River, Puerto Rico [28].

Hydrolysis products of Fe influence the physico–chemical state of radioelements in sea-water, as is shown in experiments with simultaneous addition of 25 µg/L of stable Fe and ^{144}Ce or ^{91}Y, respectively, into seawater of the tropical Pacific Ocean. Subsequent ultrafiltra-tion showed that in the presence of Fe almost 90% of ^{144}Ce and ^{91}Y is transferred to the suspended fraction, due to a typical process of coprecipitation (see p. 80), compared with 45% of radioyttrium and 60% of radiocerium in natural seawater without additional Fe. The formation of the suspended fraction begins in a more acid region than in experiments without addition of Fe. The influence of direct sorption of radionuclides on ferric hydroxide is negligible, as follows from experiments with seawater freed of suspension (pH 8) to which 25 µg/L of stable Fe and, ten hours later, the studied isotopes were added. Separation of dissolved and suspended fractions by ultrafiltration shows the amount in the suspended fraction to be 79.6% for ^{144}Ce and 81.7% for ^{91}Y [29].

Another group of factors influencing content and composition of RE in seawater is the **amount and/or** (mainly mineralogical and granulometric) **composition of suspended matter** (of abiogenic or biogenic nature; for the latter see pp. 28/30). Due to much lower amounts of suspended material in the oceans than in rivers (0.2 against 510 mg/L, respectively), the contents of hydrolyzed elements such as Y and La occurring in suspended form are

low in the ocean waters [15]. Thus, a correlation between the amount of suspended matter in surface seawater (depending on climatic and facial factors; see pp. 33/4 and 34/44, respectively) and RE contents in suspended matter is reported for the Indian Ocean, where minimum contents of suspended matter (<1 mg/g) in the southern part are associated with minimum RE_2O_3 contents (0.9 to 1.3 mkg/L), and maximum amounts of suspension in coastal seawater of the Needle Cape, South Africa, correlate with maximum RE_2O_3 contents (5.1 to 10.2 mkg/L); waters containing 1 to 3 mg/g suspended matter show RE_2O_3 contents between 2.6 and 7.9 mkg/L and those with >3 mg/g suspended matter between 3.8 and 10.2 mkg/L. Similarly, in the northern Indian Ocean contents of RE in suspended matter increase with increasing amounts of suspension [30, p. 250]. Some covariance between contents of suspended solids and Ce occurs in surface seawater of the Atlantic Ocean (with similar chlorinity and sampled between October 1963 and June 1964); the corresponding contents are [8, pp. 231/2]:

location	chlorinity in ‰	contents	
		mg/L solids	μg/L Ce
inlet of Ocean City, Maryland	17.2	15	0.85
54 km from entrance to Chesapeake Bay	18.2	~5 [*]	0.29 [*]
Chesapeake Bay near Annapolis	8.2	4.5	0.18
6 km off Cape Kennedy, Florida	20.0	1.9	0.14
23 km off Bermuda Island	20.3	0.1	0.014

[*] Mean for duplicate analyses treated differently, the variance is between 1 and 12 mg/L for solids and between 0.12 and 0.58 μg/L for Ce.

Content and vertical distribution of suspended matter influence RE content in waters of the northwestern and southeastern Black Sea, USSR (pp. 43/4). For a change with depth between particle distribution and Nd concentration in the Pacific Ocean, see pp. 42/3. Suspended material considerably influences ^{144}Ce concentration levels in seawater, Japan [31].

Mineralogical and granulometric compositions of suspended matter determine the relative abundance of the individual RE in natural waters [32]. Thus, the variable composition of suspended terrigenous matter with different sorption ability causes variations in contents of Y and of individual RE in marine suspended matter. For example, the pelitic fraction (<0.01 mm in size), having the highest sorption ability shows maximum enrichment of intermediate RE (and Ce) in the southern Indian Ocean, as is indicated by a correlation between percentage of the pelitic fraction in suspension and the Nd/La, Sm/La, and Ce/La ratios. In addition, the Nd/La ratio correlates with the subcolloidal fraction (<0.001 mm in size) which, like the pelitic fraction, consists mainly of clay minerals. Intermediate RE are also enriched, but to a greater extent in surface-suspended matter of the eastern Mediterranean Sea, the enrichment of Y being intermediate between the values for Dy and Ho. The differences between Indian Ocean and Mediterranean samples can be explained by the type of clay mineral present: hydromica predominates in the former, and montmorillonite (having two to four times higher sorption ability) constituting 30 to 50% or more of the Nile River bottom sediments influences the latter [30, pp. 256, 258/9]. Note also that suspended minerals present determine the relation between Sc and La in particulate matter of several depth-profiles of water in the Gulf of Maine [33]. Lateral variations in RE concentration occur in the Gironde estuary, France, due to constant mixing of river-borne detrital material (with definitely higher RE contents, except for Lu) and carbonate-rich marine suspended matter causing a seaward decrease of RE concentrations in the particulate matter [19]; and the relative impoverishment of Black Sea water in La, Ce, and Pr may be explained by settling of the heavier particles in river estuaries (see p. 33) [32]. Rare earth elements

are most likely associated with the clay mineral or terrigenous fraction of colloidal and particulate matter from 0.5 m depth in the Patuxent River estuary, Maryland, as is indicated by an Al content-related enrichment factor (near unity) $EF = (X/Al)_{sample}/(X/Al)_{reference}$ (with X = concentration of the element under consideration and the average crustal concentration used as a reference). Colloidal samples were collected by ultrafiltration in February 1979 at five and in July 1979 at six stations (station 6 being near the mouth of the river) covering a salinity range from zero (station 1) to 12 g/kg (stations 5 and 6); particulate fractions (>0.4 μm in size) were collected for summer samples only. Tidal variations in the suspended load are minimized by sampling on single high slack tide runs following the tidal crest. Winter colloidal material varies from an Al-rich product at the head of the estuary to a carbonaceous product near the mouth, contents of Al, Fe, and C decreasing with increasing salinity (Al and Fe by a factor of 500, C only by a factor of 10). In contrast, summer colloidal material is comparably C-rich and Al-poor throughout the estuary without a considerable seaward decrease of the colloidal material. It is composed largely of submicron clay particles and diatom fragments plus some polymeric organic material in fresh to brackish water, and composed entirely of filamentous organic polymers in brackish water. The summer particulate fraction, relatively low in C and high in Al and Fe, contains numerous microorganisms (mainly diatoms) and clay mineral particles. The RE compositions of the winter colloidal and summer particulate fraction at station 3, both high in Al content, show a North American shale-normalized pattern typical of crustal rocks. In the summer colloidal fraction, although relative RE abundances are also similar to shale, the absolute contents are all lower, emphasizing that the clay component comprises a smaller part of the sample relative to carbon. Total RE contents are lower in summer colloidal compared to winter colloidal material by a factor of nearly 10, which is consistent with the respective ash contents of 8 and 68% on dry weight basis. The contents for individual RE in colloidal (C) and particulate matter (P; size >0.40 μm) for the winter and summer samples are as follows [34]:

station	content in μg/g dry weight						
	La	Ce	Sm	Eu	Tb	Yb	Lu
winter *)							
1–C	80	140	12	2.4	—	3.55	0.60
2–C	76	137	12.5	2.2	—	3.41	0.49
3–C	65	138	9.8	1.9	—	3.87	0.66
4–C	51	109	7.7	1.56	—	2.9	0.43
5–C	9	12.4	1.12	0.24	—	<0.5	—
summer *)							
1–C	20	31	2.18	0.53	—	1.3	—
2–C	9.2	15	1.1	0.30	—	0.59	0.10
3–C	7.0	11	0.87	0.21	—	0.46	0.06
4–C	9.5	12	0.83	0.17	—	0.68	—
5–C	7	16	0.70	0.3	—	—	—
6–C	5	5.8	0.37	0.13	—	0.38	—
1–P	57.7	108	8.7	1.7	0.77	2.55	0.37
2–P	52	94	6.2	1.75	0.91	2.9	0.29
3–P	55	96	6.5	1.6	0.74	1.9	0.28
4–P	56	104	6.9	1.75	0.69	2.6	0.23
5–P	24	63	4.1	0.97	—	—	0.13
6–P	8	16	1.6	0.13	—	—	—

*) Size of colloidal material is between 1.2 nm and 0.40 (summer) or 0.45 μm (winter).

No significant differences occur for La, Ce, and Sm between four size fractions (ranging from about 30 to 0.5 µm) of suspended matter in one sample of the Rhine estuary at Nord-Hollands Kanaal (station 2), Netherlands, just above the region of maximum salt intrusion and in two samples of the Dutch Wadden Sea (stations 3 and 4). The element contents of fraction I ($\approx$ 30 µm) in relation to salinity and total suspended matter content (susp.) are as follows [35]:

station	susp. in mg/L	salinity in ‰	content in µg/g		
			La	Ce	Sm
2	23.5	<0.5	26	62	4.8
3	1.3	29.2	22	64	3.8
4	2.0	30.7	19	52	3.1

Red clay consisting of minute particles of various composition is the best sorbent for [144]Ce (99.7 to 99.8%), foraminiferal ooze (including also coarser particles of silt size) has a lower overall specific surface and thus a lower capacity to extract Ce, and "iceberg" ooze with a still wider range of particle size (coarse particles predominating) adsorbs only 97 to 97.2%. Diatom tests exhibiting a small specific surface show the lowest extraction ability (89.4%) [49]; compare also p. 33 for an influence of size fraction on [144]Ce uptake. Appreciable fractions of [141]Ce added to seawater stored at room temperature for various time periods are associated with particles having sizes from >1 to 0.01 µm; combined filtration and centrifugation show a connection with samples >0.005 µm [8, pp. 233/6].

Admixtures of organic matter and marine salts are further factors which decrease concentrations of RE in marine suspended matter [16, p. 151], note also [36]; or organic material which does not concentrate La and Lu dilutes the terrigenous fraction of marine suspended matter, as is indicated by the very low element contents in seawater compared to sedimentary rocks [37]. Refer also to the Gironde estuary, France, and the equatorial Pacific Ocean [18]. Deep-water or sea-floor enrichment in RE may occur via dissolution and mineralization of biogenic suspended matter [18, pp. 78, 84/5, 87] as, e.g., in near-bottom waters of the Black Sea (station 201, off Poti, Greater Caucasus) [32]; for data see pp. 43/4. Injection of a light RE-enriched fraction released from dissolving biogenic particles at, or near the sea floor probably causes the changes in shale-normalized RE pattern of Sargasso Sea waters (pp. 38/9). The change of the state of [91]Y added to water samples from different depths of the Pacific Ocean is explained by the reaction of [91]Y with decomposition products of organic material, whereas [144]Ce added to these waters is not affected so markedly by those substances that cause almost complete solution of [91]Y at the 500 m horizon [6]; see also [7] and p. 9.

Besides the above-mentioned factors, there are **biological factors** (organisms) that influence RE distribution, especially of its radioisotopes, in seawater, as is exemplified only briefly in the following. In general, the ability of organisms to incorporate elements depends on the form in which elements occur and on the mode of nutrition. Thus, autotrophic organisms absorb RE with difficulty due to their particulate nature. And organisms in lower trophic levels concentrate them to a higher degree than do organisms in higher trophic levels, a selectivity probably due to differences in the external surfaces of organisms [38]. In plankton from the three world oceans, differences in the distribution of single RE elements possibly are due to the components of plankton which selectively accumulate RE; especially Eu and Gd are enriched and otherwise enrichment decreases with increasing atomic number [39].

In the Indian Ocean (at depths 0 to 100 m) plankton with a RE content of $0.7 \times 10^{-2}\%$ and non-moletile plankton with 1.1 to $3.3 \times 10^{-2}\%$ RE_2O_3 (or, recalculated to one liter of water, 0.001 to 0.003 γ/L) does not significantly contribute to the total RE content of seawater (0.3 to 1.4 γ/L RE_2O_3). A direct relationship between distribution of RE and organisms is not observed, as follows from comparison of RE contents in seawater and biomass of the same oceanographic stations [40]. Since plankton traps the main part of dissolved RE in seawater, at the same time the composition of RE changes to higher intermediate and heavy RE (and Y) contents. In regions of intense planktonic activity, total RE contents in suspended matter can sharply decrease, even in coastal seawater [16, p. 165], e.g., in the southern Indian Ocean (at Princess Ragnhild Coast, Antarctica) with low RE contents in suspension (0.0009 mkg/L RE_2O_3) and intense biosynthesis; maximum contents of biogenic compounds (amorphous SiO_2, C_{org}, $CaCO_3$) occur in suspension. Mainly $CaCO_3$ and amorphous SiO_2 and RE show a reverse relationship in the suspended matter, i.e., the biogenic components of the southern Indian Ocean do not show any RE enrichment and serve as diluents of mineral components, containing the major part of RE, in surface-suspended matter. However, they cannot fully explain the low RE contents of suspension, since maximum concentrations of biogenic elements do not exceed 60% of total suspended matter and, therefore, can reduce RE contents only by two to four orders of magnitude [30, pp. 250, 252/4]. Otherwise, since in surface seawater biogenic components can constitute more than 50% (up to 90%) of total suspended matter and since plankton contains a mean of 0.55 g/t RE, a considerable part of suspended RE can be bound to biogenic components [18, pp. 84/5]. For diatoms and foraminiferal plankton the following RE contents occur [41]:

	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
				contents in ppm					
foraminiferal plankton	0.146	0.238	(0.034)	(0.0064)	0.0034	(0.0186)	0.008	—	0.0015
diatom	5.77	8.21	6.71	1.56	2.404	1.78	1.69	0.998	0.859

A strong biological retention of radioisotopes is indicated by the vertical distribution of [144]Ce within the surface layer of waters around Japan (p. 43), and retention in the bodies of plankton swarms may partly explain secondary maxima of [144]Ce and [147]Pm in vertical profiles at various depths in the equatorial Atlantic Ocean. In most cases, these maxima are enriched in [147]Pm vs. [144]Ce. The lanthanide fraction of a fallout event can be accumulated in the skeletons of a diatom population so long as grazing proceeds at a minimum rate [42]. For the effect of plankton on the state of [144]Ce added to both seawater from a depth of 10 m and seawater saturated with respect to uranine, studied in experiments with solutions in vivo (exposed under natural conditions) and in vitro (kept in the dark, the plankton chlorophyll is degraded), see [25]. At practically all trophic levels, [144]Ce is incorporated in the northern Adriatic Sea along the west Istrian coast [43], and concentrations in benthic organisms are much lower than those in plankton, where [144]Ce is one of the dominant radionuclides [44]. Biological accumulation may partly explain the great variability of the physicochemical state of [155]Eu in lagoonal waters of the Bikini Atoll, central Pacific Ocean [45]. In the Aegean Sea, the adsorption of added [91]Y by suspension after two days is 50 times that of zooplankton [46]. An effect of pH on the accumulation of [91]Y by marine organisms occurs via its mode of occurrence (at pH<3 ionic, >3 hydrated, and 8 to 8.2 hydrolyzed forms); the same holds for the trivalent ions La, Ce, Pr, and others [47]. Plankton samples of the coastal region of Nice, France, show the highest [141]Ce + [144]Ce + [144]Pr activity (1320 pCi/g · sec) in the size fraction <60 μm containing in addition to planktonic organisms a great amount of fine-grained detritus (mean size 10 to 20 μm) with 2800 pCi/g · sec. While the plankton absorbs and rejects radioelements very quickly, the detritus, on the contrary, accu-

mulates radioelements, which is important in the transfer of radioactivity in the food chain [48].

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7.2.2.1.2 Influence of Physical Factors and/or Facies

Besides the influence of the chemical composition of seawater (see proceeding paragraph), there are several factors more physical in nature that influence the distribution and/or composition of RE in seawater environments. Thus, the **pure chemical properties of Y and RE** may be of importance; e.g., variations in ionic radius or oxidation-reduction reactions (followed partly by a differential mineral uptake, see also p. 73) may cause variation of the relative RE concentration in seawater via differential solubility or ion exchange

processes. For the RE, such processes are known to be minimally effective, for RE complexes are typically weak and show only modest variations in strength within the series, and Ce and Eu are expected to exhibit stable ions other than trivalent [1] and may fractionate from the trivalent RE as a result of redox potential [2]. With this possible exception of Ce and Eu, the similar chemical properties of RE allow for only limited fractionation during their passage through the ocean. Thus, although absolute concentrations may vary between marine phases, relative concentrations will vary only slightly from one phase to another [3, p. 286]. There is also an ordered variation in stability constants of RE complexes which may cause fractionation of light relative to heavy RE [2]. Differences in the stabilities of soluble complexes of light and heavy RE, heavy RE being more strongly complexed, lead to an enrichment of heavy RE in seawater with respect to sediments [4 to 7], as is stated, e.g., for the Black Sea [8], for the northwestern Atlantic Ocean [9], for the Pacific Ocean off the coast near San Diego, California [10], and for the estuaries of Rhone and Gironde rivers of France [11] (for the Gironde see also [12, p. 77]). In addition, differential adsorption on solid phases leads to the monotonic enrichment of heavy RE in seawater [5], the lighter members showing greater reactivity owing to their increased basicity with respect to incorporation in, or on, solid phases [4], as is stated, e.g., for the northwestern Atlantic Ocean [9], or the Pacific Ocean off the coast near San Diego, California [10]; and for the Gironde estuary, France [12, p. 77]; and for the Gulf of Mexico, the fractionation of RE by the particulate phase being indicated by smaller particulate/soluble ratios for the heavy than for the light RE [13]. The negative Ce anomaly in seawater may be the net effect of the insolubility and adsorption of oxidized tetravalent Ce onto marine solids [14]; the oxidation having taken place in the ocean rather than in the weathering profile or in rivers as is supported by the similarity of the La/Ce ratio in filtered water of the Gironde River to that of shale [3, p. 292]. The oxidation of Ce to tetravalent and the reduction of Eu to divalent states are potentially singled out from all other processes affecting their distribution. However, thus far there is no clear evidence for the reduction of Eu in seawater [9]. No redox fractionation of Eu seems to occur in the upper 1200 m of the northwestern Atlantic Ocean, as Sm, Eu, and Gd are strongly correlated [15], and a significant Eu anomaly is absent at all depths. The Sm/Eu ratio of 4.6 is close to that for shales (4.7), although one might expect Eu anomalies to develop in strongly reducing environments such as anoxic basins or hydrothermal vents [9]. Concentration of Eu relative to the other RE is normal in Pacific seawater off the coast near San Diego, California [10]. However, at one station in the northern Atlantic Ocean, the intensity of a negative Eu anomaly is different at different depths (see p. 38). Experiments on age changes in adsorbability of radioisotopes differing in valence ($^{144}Ce^{3+}$ and $^{144}Ce^{4+}$) on Teflon from seawater show that during the entire period of aging the adsorbability of $^{144}Ce^{4+}$ changes negligibly and remains lower than that of $^{144}Ce^{3+}$, while in desorption experiments the values of the residual activity for the former are actually always greater than for the latter. According to theoretical considerations (lower basicity of Y compared to Ce), the state of maximum adsorbability at pH 8 on Teflon for $^{91}Y^{3+}$ is reached considerably earlier than for $^{144}Ce^{3+}$, and the height of maximum adsorbability is considerably lower for Y than for Ce. Consequently, at the same concentration of hydroxyl ions, the probability of prolonged existence of unstable, intermediate hydrolysis products is lower the more strongly the element under consideration is hydrolyzed [16]. Ions with large ionic radii are absorbed most strongly. Therefore, ^{141}Ce added in trace amounts to mixtures of different adsorbents with fresh seawater is adsorbed most completely, regardless of the nature of the adsorbent, compared to ^{91}Y. This relationship is preserved even if the element is present in the form of complex ions, as it can be the case in seawater [17]. The existing state of RE greatly affects their concentration factors in marine organisms, as is shown by a comparison of concentration factors calculated from the amount in the dissolved state and from the total amount, respectively. If only the dissolved form is assumed

available to marine organisms, values about one order of magnitude higher are obtained, especially for Ce, Eu, and Tb [18]. The original form when introduced into seawater and the size of the particles influence the uptake of ^{144}Ce by aquatic organisms [19].

The **geographical position of a water basin or** the prevailing **climatic/meteorological conditions** may also influence the distribution of RE in seawater. Thus, unlike that of open-ocean water, the chemical composition of land-locked seas is strongly influenced by the inflow of river water, and RE contents, therefore, ought to be determined not only in different regions of the sea, but also in the different components of its water-salt balance, i.e., river and rainwater. Due to the characteristics of its shorelines, the Dnieper-Bug estuary in the Black Sea serves as a settling area for the suspension brought in by rivers from the southern Russian Platform, while the suspension carried by the Rioni River from the Greater Caucasus is delivered directly to the sea. The settling of suspended matter in the estuary is the main reason of low RE concentration (suspended plus dissolved) in the nearby Karkinit Gulf which is 2.5 times lower than in the southeastern part of the Black Sea (station 201, off Poti), although the RE content in the river waters is of the same order, as can be seen from the following; tentative figures for La are given in parentheses [8]:

source of water	content in 10^{-6} ppm						
	ΣRE	La	Ce	Pr	Nd	Sm	Eu
Dnieper-Bug estuary	1760	210	580	69	350	90	8
Karkinit Gulf	1362	(100)	230	46	350	97	21
Rioni River near Poti	1882	380	600	85	320	110	14
Black Sea off Poti	3102	(200)	800	110	800	240	65

source of water	content in 10^{-6} ppm						
	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Dnieper-Bug estuary	97	16	110	29	100	14	72	15
Karkinit Gulf	96	17	140	37	100	16	92	20
Rioni River near Poti	82	14	96	25	77	11	57	11
Black Sea off Poti	260	40	280	70	210	30	165	32

In the Baltic Sea, relative seclusion combined with a considerable effect from land runoff and the smaller volume of water are responsible for a higher average ^{144}Ce level in the spring of 1981 (16 Bq/m^3) as compared to that in the North Sea (11 Bq/m^3) [20]. An influence of climatic factors on RE content in marine suspended matter occurs for different parts of the Indian Ocean and the eastern Mediterranean Sea. Intense terrigenous supply from tropical humid zones and the foothills of the Himalayas causes higher RE contents in unfiltered surface seawater (1.1 mkg/L RE$_2$O$_3$) in the northeastern Indian Ocean (south of the Gulf of Bengal) compared to the northwestern (Arabian Sea; 0.6 mkg/L RE$_2$O$_3$) and southern parts (0.0009 to 0.0102 mkg/L RE$_2$O$_3$) being accompanied by arid and antarctic zones with a lower terrigenous input; and due to a lower terrigenous input from the arid zones of Africa and the Orient, RE contents in the Mediterranean are lower by one order of magnitude compared to the northeastern Indian Ocean (see table below). Minimum input from arid areas is further shown by the sharp enrichment of heavy RE in seawater off San Diego, California, with a RE(Ce)/RE(Y) ratio of 0.3 (based on data of [10]), i.e., predominance of dissolved RE and absence of any essential input of terrigenous suspended matter which would be characterized by the reverse relationship. The contents of RE$_2$O$_3$ for individual sites are as follows; susp. = suspended [21]:

location and climatic zone	content of		
	susp. matter in water; mkg/L	RE_2O_3 in dry susp. matter; g/t	RE_2O_3 in susp. matter; mkg/L
northeastern Indian Ocean			
coastal India; tropical humid	2.5	350	0.90
open ocean	1.4	175	0.25
southwestern Indian Ocean			
coastal Africa; arid southern	1.241	6.4	0.0079
open ocean; humid moderate	0.33	4.0	0.0013
open ocean; arctic southern	1.768	1.6	0.0028
open ocean; arctic southern	1.950	2.6	0.0051
open ocean; arctic southern	0.753	3.2	0.0024
coastal Antarctica; arctic southern	0.859	1.0	0.0009
southeastern Indian Ocean			
coastal Antarctica; arctic southern	3.101	3.3	0.0102
open ocean; arctic southern	2.033	1.9	0.0038
open ocean; arctic southern	1.245	2.4	0.0030
open ocean; arctic southern	2.245	1.5	0.0034
eastern Mediterranean Sea			
open ocean; arid northern	0.20	110	0.022

Notice also a lower La content (partly based on data from [21]) in surface-suspended matter in the equatorial region than at moderate latitudes of the Pacific Ocean [12, pp. 84/5]; an addition of weathering products of crystalline rocks (primarily feldspar, mica, quartz, and others) to the clay fraction of aeolian suspension in arid climatic zones and mountain regions decreases RE contents in the marine suspended matter [22, pp. 150/1]. For a different influence of atmospheric fallout over the Indian and Atlantic oceans, varying with the latitudinal distribution of aerosol and being considered the main factor determining RE concentration in seawater, see [23] and pp. 116/7. The lower abundance of lithophile elements, like RE, in summer vs. winter colloidal material of the Patuxent estuary, Maryland (see pp. 26/7), possibly reflects slower erosion when the watershed is under an active vegetation cover [24]. Marine meteorological conditions seem to affect markedly the distribution of radioactive RE in estuarine water [25]. An influence of seasonal changes on [144]Ce contents in plankton and other marine organisms is shown for the northern Adriatic Sea along the west coast of Istria, with the highest activities occurring in late spring and summer [26].

Lateral differences in content of RE and Y **between coastal or shelf zones and the open sea** have been mentioned and can be seen in the following examples for individual oceans. Compared to the Gironde estuary, France, the RE composition in surface shelf water of the Atlantic Ocean is strongly diminished in light RE (absolutely and relatively to the heavy RE); the Ce deficiency is especially increased [12, pp. 77/8]. In seawater from the peripheral parts of the Atlantic Ocean (Gulf of Mexico), the percentage of RE occurring in suspension or solution is different from that in water from 1000 m depth of the North American shelf as is corroborated by the following:

location, reference, and type of occurrence	Y	La	Ce	Sm	Eu	Tb	Dy	Ho	Tm	Yb	Lu
Gulf of Mexico [27]											
dissolved	—	—	—	19.5	14.5	—	42.5	—	—	53	—
suspended	—	—	~100	80.5	85.5	—	57.5	—	—	47	—
North American shelf [28]											
dissolved	70	76.3	—	32	28.5	21	—	49	58	53.5	43
suspended	30	23.5	—	68	71.5	79	—	51	42	46.5	57

Contents of La, Sm, and Lu in seawater from a coastal (northwest arm of the Atlantic Ocean in Halifax, Nova Scotia, Canada) and two open-sea locations are [29]:

location, water depth, and salinity	content in µg/L La	Sm	Lu
northwest arm of Atlantic Ocean	0.013	0.010	0.008
Gulf of St. Lawrence; 20 m; 27.626‰	0.013	0.008	0.009
Cabot Strait; 150 m; 34.145‰	0.011	0.008	0.006

It is not known whether there is a dependence of the degree of the Ce depletion on distance from shore, Ce being normal in three samples from the Strait of Gibraltar and depleted by a factor of about 5 in eight open-ocean samples from the mid-Atlantic Ocean. The largest differences in concentration occur among the light RE (La through Eu) where the ratio between the maximum and the minimum value for La and Ce is about 6; the corresponding ratio for the heavy RE (Gd through Lu) is approximately 1.5. The particulate matter separated from two samples from the Strait of Gibraltar has a RE pattern different from that of the water samples. The RE concentration in this phase is less than 0.5% of the content of seawater [30]. One surface seawater sample taken from 23 km off Bermuda, Atlantic Ocean, has a much lower Ce content of 0.014 µg/L than two coastal seawater samples with 0.12 and 0.85 µg/L. A composite of samples taken at depths of 900 and 2000 m, Bermuda, shows 0.004 µg/L, comparable to that (observed by [10]) for seawater off the coast of San Diego, California [31].

In near-shore waters of the Indian Ocean, contents of RE_2O_3 in unfiltered surface seawater are higher (mean 3.1 mkg/L) than in offshore waters with 0.3 to 1.4 mkg/L. Despite regional climatic differences (see pp. 33/4), RE are much more abundant in suspended matter of all coastal areas than in the open sea, and the concentration in open-sea suspensions is only 28 to 37% of that in coastal areas, as can be seen from the following data for different parts of the Indian Ocean; one sample each if not otherwise stated [21]:

	RE_2O_3 content in mkg/L for suspended matter coastal zone	open sea
northeastern part	0.9	0.25
southwestern part	0.0079	0.0029 (4 samples)
southeastern part	0.0102	0.0034 (3 samples)

Three unfiltered surface samples, two from the coast of India and one from Colombo Bay, Sri Lanka, show a sharp increase of RE_2O_3 contents (2.4 to 4.7×10^{-7}%) as compared

with two surface samples of equatorial and central Indian Ocean water (1.0 and 1.4×10^{-7}%, respectively). Following the general trend, RE_2O_3 contents in suspension (separated on 0.7 μ-membrane filters after separation of the larger plankton) also increase in near-shore waters (4.7 γ/L at the continental slope of India), compared to the central ocean sample (1.4 γ/L) [32].

Assuming that the dissolved RE in seawater comes from crustal rocks through weathering processes and that the average dissolved RE distribution is that of sediments, then the RE in a Pacific seawater sample from 100 m depth, about 15 km west of San Diego, California, have been further fractionated in a monotonic fashion in favor of the heavy RE (due to increasing stability of heavy RE complexes or to differential adsorption on solid phases), Lu being enriched by a factor of about 2.6. The light RE (La through Sm) have not been fractionated within experimental error, although a possible 20% fractionation for Sm is suggested. Contents of RE in the above mentioned sample are La 29, Ce 13, Pr 6.4, Nd 23, Sm 4.2, Eu 1.14, Gd 6.0, Dy 7.3, Ho 2.2, Er 6.1, Tm 1.3, Yb 5.2, and Lu 1.2 μg/L [10].

The physico-chemical form in which a particular trace element or radionuclide occurs in the marine environment may be dependent on whether it originates from coastal or open-ocean waters, e.g., ^{144}Ce is in particulate form in coastal waters of the Irish Sea at Windscale, but only 21% of the total concentration of ^{144}Ce is present in particulate fractions in open-ocean water [26]; 80% of the ^{144}Ce is in the particulate form in coastal seawater, Kashima-nada, Japan, and a small part is particulate in the open sea [33].

As is shown in the following, besides **vertical differences in** seawater for **content** (see pp. 39/45) **or composition of RE** (see next paragraph), **or for Nd isotopic composition** (see pp. 45/6), there are also **differences for individual water masses** within, or between single oceans (see examples in the following paragraphs and pp. 46/7). Note also, RE and Y belong to the category of elements whose variation in abundance is not clearly dependent on depth or oceanic basin [34]. Owing to variable concentrations of dissolved RE in river runoff, shelf waters have variable RE contents, and the average RE concentration increases in deep parts of open-ocean water (see table on p. 37). The following is stated for individual RE elements: Transition from surface to deep shelf waters is accompanied by a decrease of Ce concentrations and an increase of La, Y, and heavy RE. Only at the transition from surface to intermediate depth in open-sea water is a dependence on depth evident for Y and Yb. On the whole, open-ocean water has a more homogeneous RE pattern than coastal seawater, since stratification of RE with depth weakens, due to a more homogeneous composition of suspended matter and regeneration of RE composition by dissolution of organic carbonate and silicate components of suspension, indicated by decreasing Y/Sm and Yb/Sm ratios at intermediate depths of 1000 to 2000 m. Therefore, the specific vertical stratification of contents of dissolved RE in seawater reflects the dependence of composition of suspended matter on distance from shore (see pp. 34/6). Contents of Y and calculated mean contents of light and heavy RE (for individual data see original paper), besides ratios indicating RE composition, for different seawater regions (in general?) in relation to depth are given in the table on p. 37 [22, pp. 168/70]. Rare earth elements can easily be enriched in the deep-ocean water relative to surface water by slight dissolution from any settling particles, since the ratio of RE concentrations in oceanic pelagic clay and in seawater is large ($>10^7$). However, the amount of dissolution is limited by solubility, and is small compared to the total flux of sediments to the ocean floor [56].

Different groups of RE distribution patterns have been found for seawater from various depths and water masses. Thus, sixteen samples from widely spaced stations and from depths >900 m in the central Atlantic Ocean between 16° N latitude and the equator show

element or ratio	content of dissolved RE in 10^{-7} mg/L						
	shelf water		trough[1]	open ocean (central zone)			
	<350 m	1000 m	>3000 m	<100 m	1000 m	2000 m	3000 to 5700 m
Y	173	157	268	107	119	130	135
Σ(La to Eu)	533.1	403.92[2]	302.9	101.90	77.00	85.96	126.94
Σ(Gd to Lu)	58.36	56.01	92.97	38.77	31.20	39.95	44.26
La/Sm	5.2	19.2	10.9	6.6	6.2	7.8	8.2
Ce/Sm	13	7.6	7.3	5.7	4.3	3.7	3.9
Yb/Sm	0.4	0.9	1.46	1.3	1.9	1.9	1.45
Y/Sm	7.7	12.7	21.2	22.2	29.0	30.5	23.1

[1] Near-shore deep-sea troughs between 3000 and 7500 m. — [2] Ce and Nd only tentatively.

six types of RE patterns (type A to F). Based on weighted linear regression analyses it is shown that eleven samples from depths between 1800 and 2500 m at all studied stations and from 4000 to 5000 m at two stations in the eastern basin, all being from the same water mass (the North Atlantic deep water), have an identical RE pattern of type A (taken as a normalizing standard) with an average enrichment factor of 2.3 for Y and an average depletion factor of 5 for Ce, provided that both elements are distributed normally relative to the other RE in chondrites. This Ce anomaly is in good agreement with the value of 4.8 (deduced from the data of [10]) for Pacific seawater off San Diego, California. The regression lines through a set of normalized data can be looked upon as the lanthanide pattern of that sample relative to the average distribution given by type A. The data of the remaining samples, normalized to type A, show that eight samples have patterns best fit by single straight lines, three of which have negative slopes (type B pattern) and result from samples collected at a depth of 4000 to 5000 m at two stations in the western basin, and five of which have positive slopes (type C pattern) and result from samples collected between 900 and 1000 m at two stations in the western and one station in the eastern basin. Both patterns are significantly different from the type A pattern. Of three samples which have normalized patterns best represented by two lines, one has a type D pattern and was collected at a depth of 900 to 1000 m at one station in the eastern basin, and two have type E patterns and were collected at one station in the western basin at 900 to 1000 m depth. The normalized patterns of two mud-containing samples from one station in the western basin at 4000 to 5000 m depth resemble that of the North American shale composite, obviously reflecting contamination, and are referred to as type F patterns. According to the different types of RE patterns, the calculated mean contents of Y and RE are as follows for sixteen [1] and an additional eight analyses of Atlantic seawater; n = number of analyses [30]:

element	content in 10^{-4} µg/L					
	type A[1] n = 11	type B n = 3	type C n = 5	type D n = 1	type E n = 2	type F n = 2
Y	134.3	156.0	135.8	127	122.5	25150
La	34.9	57.3	31.0	10.0	27	23700
Ce	15.5	29.7	17.7[2]	6.2	11.6	67150
Pr	6.6	11.1	7.5	4.9	4.2	7395
Nd	30.5	38.3	26.0	22	16.5	29350
Sm	4.6	6.9	5.2	3.4	3.4	6665
Eu	1.4	2.0	2.6	0.9	1.0	1595

Table [continued]

element	type A[1] n = 11	type B n = 3	content in 10^{-4} µg/L type C n = 5	type D n = 1	type E n = 2	type F n = 2
Gd	7.3[3]	9.0	7.7	5.6	5.6	5945
Tb	1.8	1.6	1.4	—	1.0	843
Dy	9.2	10.7	8.8	5.2	6.7	4710
Ho	2.3	2.7	3.0	1.8	2.2	1012
Er	8.8	10.3	8.9	8.6	7.8	2680
Tm	1.8	1.7	2.2	1.7	1.7[4]	380
Yb	8.3	9.3	10.7	6.2	8.7	2175
Lu	1.5	2.1	3.2	1.3	1.8	344

[1] Average content given in the original paper is calculated by taking the arithmetic mean of the logarithm of the absolute abundances of each element, the antilogarithms of these results are in µg/L: Y 133, La 34, Ce 12, Pr 6.4, Nd 28, Sm 4.5, Eu 1.3, Gd 7.0, Tb 1.4, Dy 9.1, Ho 2.2, Er 8.7, Tm 1.7, Yb 8.2, Lu 1.5. — [2] Three samples only. — [3] Nine samples only. — [4] One sample only.

Based on data in [35 to 37], the following four types of shale-normalized RE patterns are given for Atlantic Ocean waters: (1) shelf water, e.g., from the Barents Sea, Arctic Ocean, and the Strait of Gibraltar, has a pattern almost identical to that of water from the Gironde River, France, with absolute RE concentrations, however, being significantly lower; (2) Antarctic bottom water (AABW) differs from shelf water in three aspects, namely the concentrations of RE are significantly lower, the heavier RE (Sm through Lu) exhibit a strong monotonic increase with increasing atomic number, and Ce is strongly depleted relative to the trivalent RE; (3) North Atlantic deep water (NADW) closely resembles AABW, the main differences being a decrease in contents of the individual RE, a steeper slope to the monotonic heavy-RE increase, and an increase of the Ce depletion relative to the other RE; and (4) Antarctic intermediate water (AAIW) shows a RE pattern similar to that of the other water masses, but it has the pattern most strongly fractionated from river water, i.e., it is the most strongly depleted in RE, it has the strongest heavy RE enrichment, and the strongest Ce deficiency. The three major water masses are stratified such that the RE concentrations increase slightly with depth more or less continuously. Due to insufficient analyses, a trend for Pacific seawater is not ascertained; however, concentrations of RE in the deeper water are significantly higher than in the Atlantic, suggesting that the increase with depth may be more strongly developed [3, pp. 290/2]. Other shale-normalized RE patterns for seawater samples, Cape Madeira abyssal plain, Atlantic Ocean, show the following characteristics: (1) surface seawater with a flat and shale-like pattern showing slightly negative Ce and prominent negative Eu anomalies; (2) water below the mixed layer (~100 m) with a pattern showing heavy RE enrichment becoming less significant with increasing depth, a negative Eu anomaly developing, and a less striking negative Ce anomaly than previously reported (see [10]) which at first strengthens and then weakens. Consequently, except for its Ce anomaly, the deepest sample begins to resemble surface water; and (3) seawater between ~900 and 1500 m (representing Mediterranean outflow water) showing a typical seawater pattern which is, however, anomalous relative to waters below and above in displaying stronger negative Ce and weaker negative Eu anomalies and higher heavy RE and lower light RE contents, thus leading to a more marked heavy RE enrichment [2]. At selected depths of the Sargasso Sea, shale-normalized RE patterns show three major features: (1) heavy RE are enriched relative to the light RE, the Lu/La ratio in the upper water column being about four times higher than in shales. With Ce disregarded,

RE patterns are very similar in the upper 1000 m. However, from about 1000 m downward, a minimum tends to develop at about Sm and Eu, possibly due to injection of a fraction enriched in light RE released from dissolving biogenic particles at or near the sea floor; (2) at all depths, a significant Eu anomaly is absent; and (3) in the mixed layer, Ce is two- to threefold enriched relative to La and Pr, representing the first finding of a distinct positive Ce anomaly in seawater which is explained by injections of Ce from reducing inshore sediments. The anomaly drops off rapidly with depth until the transition from positive to negative values at about 250 m, and at greater depth a typical three- to fourfold depletion develops, indicating enhanced removal of dissolved Ce^{3+} due to oxidation to the highly insoluble Ce^{4+} state [9].

Rare earth distribution patterns and seawater masses show a strong relationship, differences in lanthanide distribution and total abundance between different water masses being small but significant [1]. Due to the mixture of inland and ocean waters, a RE composition in coastal seawater, being intermediate between river and Pacific Ocean waters, with a slight Ce deficiency in one of two samples, occurs for surface seawater of the coast off Arasaki, Miura peninsula, Japan [45]; refer to a RE pattern very close to that of shales in near-shore, filtered seawater 5 km off the coast of Ibaraki prefecture, suggesting the contribution of terrestrial material [18]. The age of a water parcel may be reflected to some extent by the degree of fractionation of RE, the water mass with the most strongly fractionated RE pattern then possibly being the oldest. The trend in fractionation of RE patterns for the Atlantic Ocean from shelf water to Antarctic bottom water, and from North Atlantic deep water to Antarctic intermediate water may reflect the relative time water has been isolated from continental sources [3, p. 292]. Variations from one water mass to another in RE concentrations are expected, inasmuch as the mixing times of such waters are probably of the order of or greater than the residence times of RE [10]. Mixing of a specific water mass with other water masses having different overall or relative (or both) lanthanide concentrations changes relative and overall concentrations of lanthanides in seawater [1]. Ocean currents may be responsible for transporting RE between water masses, e.g., between the Scotia Sea and southern Atlantic Ocean [42, p. 234]. The characteristic current system in the northern Pacific Ocean is responsible for different ^{144}Ce concentrations in its eastern and western parts, coastal surface waters near La Jolla, California, have lower contents (0.05 pCi/L) than in the western part [47]. Closely following the pattern of turbidity, ^{144}Ce shows a maximum content in a zone of very turbid water in the St. Lawrence estuary, Quebec, Canada [48]. Bulk surface seawater samples from the southern North Sea, off Lowestoft, Great Britain, show a marked decrease of particulate RE between 3 and 6 km offshore (La 1.5 and 0.32, Ce 3.3 and 0.18, Sm 0.22 and 0.025, Eu 0.089 and 0.0056 µg/L, respectively). A marked decrease in turbidity occurs at about 5 km from shore [49].

For two analogous depth profiles of the northern Atlantic Ocean, the summary contents of light and heavy RE given in the table on p. 40 can be calculated (for the individual data see original paper) from samples of prefiltered water, Cape Madeira abyssal plain (28°01′ N, 25°59′ W) [2], and from unfiltered water, Sargasso Sea (33°58′ N, 58°05′ W) [9]. Additionally, contents of Nd and Gd varying between 10 to 40 and 3 to 10 pmol/kg, respectively, at different depths have been noted for the Sargasso Sea [15]. For variation with depth in Nd and Sm content and ^{147}Sm/^{144}Nd ratio in Sargasso Sea water, see p. 43. The depth profile at Cape Madeira is characterized by a deep-water enrichment, all RE showing significant increases towards the bottom, a mid-water extrema at about 1000 m, and low but non-zero concentrations at the base of the mixed layer (about 100 m). In addition, light RE show surface maxima. The deep-water enrichment varies in magnitude systematically throughout the RE group, the proportional increase towards the bottom being higher for

content in 10^{-12} mol/kg seawater

depth in m	Sargasso Sea Σ light RE[1]	Σ heavy RE[2]	depth in m	Cape Madeira Σ light RE[3]	Σ heavy RE[4]
10	109.98	8.27	0	143.93	17.37
49	99.05	9.11	100	45.91	15.81
98	60.90	7.33	200	60.47	14.50[5]
147	50.70	8.73	600	65.26	18.98
491	47.20	7.91	700	76.79	19.30
638	43.70	7.34	900	56.68	20.41
783	45.14	7.75	1000	49.12[6]	6.00[7]
981	45.43	9.57	1500	56.18	21.63
1179	59.86	9.32	2500	86.15	23.17
1379	48.70	7.66	3000	82.98	22.48
1719	47.70	7.33	4500	164.77	25.60
2486	11.22[6,8]	9.37			
2874	29.60[6]	9.67			
3264	72.78	11.46			
4328	148.07	14.38			
4378	144.46	14.28			
4427	156.90	13.53			

[1] Comprises La, Ce, Pr, Sm, and Eu. — [2] Comprises Tb, Ho, Tm, Yb, and Lu. — [3] Comprises La, Ce, Nd, Sm, and Eu. — [4] Comprises Gd, Dy, Er, and Yb. — [5] Without Gd. — [6] Without La. — [7] Only Dy. — [8] Without Ce and Pr tentatively.

the light than for the heavy RE, e.g., Yb or Dy are enriched by a factor of about 1.4 at 4.5 km depth relative to the base of the mixed layer, whereas Nd and La are enriched by factors of 3.6 and 4.2, respectively (compare also [38], where enrichment factors are given as La 2.26, Ce 1.55, Nd 1.95, Sm 1.78, Eu 1.39, Gd 2.11, Dy 1.28, Er 1.25, Yb 1.35). As in deep water, surface enrichment of RE varies with atomic number; however, the light RE are enriched (e.g., La by a factor of 2.8 compared to the base of the mixed layer), whereas heavy RE are not enriched or are slightly depleted. Due to their similarity, surface- and deep-water enrichments show a striking correlation; the enrichment of Ce and Eu are anomalous compared with values obtained from interpolations between their respective neighbors. Both the fractionation of light from heavy RE (or vice versa) at the surface and bottom boundaries of the water column and the anomalous behavior of Ce and Eu are compatible with the chemistry of the RE. Possibly, certain parts of this vertical profile may be hydrographical signals. Thus, surface values could reflect input of continental RE by horizontal air streams (advection), and deep-water values could mean that North Atlantic deep and bottom water originally forms with very high RE contents. It is more plausible that the mid-water extrema reflect a distinctly different composition of Mediterranean outflow water (at about 1200 m) from that of the adjoining Atlantic water masses, i.e., a larger heavy RE enrichment, a more negative Ce anomaly, and a less negative Eu anomaly [2]. For changes with depth of the RE distribution pattern of Cape Madeira and Sargasso Sea samples, see pp. 38/9. Advective transport will be the major means of influencing the vertical distribution of long-lived radioisotopes (including ^{144}Ce) within three water columns of the Atlantic Ocean at 36° N, 68° W [46]. In the Gulf of Maine, La contents (being strongly correlated with Sc) in particulate matter for samples taken during various months of 1969 and 1970 vary with depth and are mostly enriched close to the bottom [39]. Contents of dissolved Y and the calculated sums of light and heavy RE (for the individual RE, see

original paper) in relation to depth for shelf waters of Gibraltar [35] and the Barents Sea near Novaya Zemlya, European USSR [36] are as follows; additionally, ratios are given indicating the RE composition:

| | Content in 10^{-5} mg/L | | | | |
| | Gibraltar | | Barents Sea | | |
element or ratio	10 to 15 m	350 m	50 m	100 m	225 m
Y	1.33	2.42	1.96	1.68	1.74
Σ(La to Eu)	1.615	2.519	6.176	7.59 [2]	7.998 [2]
Σ(Gd to Lu)	0.433	0.464	0.65 [1]	0.60	0.601
La/Sm	7.5	6.4	8.0	—	—
Ce/Sm	10.0	7.2	16.8	—	—
Yb/Sm	0.91	1.16	0.49	—	—
Y/Sm	19.5	20.0	10.3	—	—

[1] Without Tb. — [2] Without Sm.

Three clearly defined layers occur in the upper 120 m of the Atlantic Ocean between 22°45′ N, 63°06′ W and 15°22′ N, 20°56′ W. The top, well-mixed layer has the highest value of specific activity of ^{155}Eu which is practically constant, while in the layer of rapid temperature fall, the activity sharply decreases depending on half-life. Below this thermocline activity remains practically constant. The positions of these layers are directly related to the position of the thermocline [52]. Much higher concentrations of ^{144}Ce occur at the surface than at depth for one station in the Gulf of Mexico, off Panama City. Particulate and soluble ^{144}Ce concentrations for different depths are as follows [55]:

| depth in m | content in mμμc/L | |
	particulate	soluble
0	47.0	23.0
400	6.6	1.3
750	1.7	3.0

Throughout the water column at 36° N, 68° W in the Atlantic Ocean the ratio of soluble to insoluble ^{144}Ce is the same, but vertical profiles of ^{144}Ce concentrations as measured on three successive days show a variance with depth [53]:

date	depth in m	^{144}Ce content in dpm/m³	date	depth in m	^{144}Ce content in dpm/m³
8–27–70	7 ± 2	1010 ± 100	8–29–70	surface	900 ± 60
	20 ± 3	990 ± 80		10 ± 1	960 ± 90
	39 ± 5	700 ± 60		25 ± 1	810 ± 70
	65 ± 5	360 ± 40		43 ± 1	680 ± 90
	88 ± 6	260 ± 90		69 ± 1	300 ± 50
				92 ± 1	240 ± 80
8–28–70	surface	860 ± 90			
	11 ± 1	840 ± 70			
	26 ± 1	1050 ± 70			
	46 ± 2	440 ± 60			
	72 ± 1	240 ± 30			
	97 ± 1	210 ± 40			

Increasing concentrations occur with depth for Sm and Nd at one station in the north-eastern Atlantic Ocean (station 95) as well as for Nd at one station in the northwestern Atlantic Ocean (station 30), the latter showing in bottom water (4850 m) the highest Nd concentration as yet reported in seawater. At station 95, between 800 and 2000 m, Nd and Sm contents oscillate due to the influence of the Mediterranean water outflow, high contents corresponding to the high-salinity ranges and vice versa. Below 2000 m, Nd shows an approximately linear increase with depth (see table below). In general, these Sm and Nd profiles at station 95 are similar to those reported for filtered seawater from the northeastern Atlantic Ocean at the Cape Madeira abyssal plain (see [2]), a region also influenced by the Mediterranean outflow, but concentration levels at comparable depths are 20 to 30% lower at station 95. The $^{147}Sm/^{144}Nd$ ratios also differ, varying between 0.106 and 0.126 with one outstanding value of 0.173 at 200 m at Cape Madeira, while at station 95, without exception, the ratios vary between 0.117 and 0.134, pointing to an absence of any surface enrichment. In contrast, the eastern Atlantic sample studied by [2] may possibly be related to higher levels of dust fallout from the Sahara [40]. Generally increasing Sm and Nd contents are reported for the Drake Passage and the southeastern and central Pacific Ocean (see table below). For the three vertical profiles studied (stations 315 and 327 in the Drake Passage and station 31 in the central Pacific), an approximately linear increase of Nd content with depth occurs (in contrast to the differences in Nd isotopic composition at different localities, see p. 45), the concentration gradient at station 327 being about a factor of 3 lower than at station 315. The sample from 30 m at station 31 has the lowest Nd concentration yet measured in seawater. Samples where Sm concentration was measured yield a constant $^{147}Sm/^{144}Nd$ ratio of about 0.11 at all levels. As indicated in potential temperature vs. salinity diagrams for the three above mentioned stations, the Nd distribution is not dependent on factors that directly influence local temperature and salinity variations. Concentration as well as isotopic composition of Nd may depend on scavenging by particles, resolution from particles, and resolution from sediments at the sea bottom, since the regular change of Nd contents with depth cannot be simply due to scavenging [43]; compare pp. 69/71. The contents of Nd and Sm and the $^{147}Sm/^{144}Nd$ ratios for the above mentioned locations are as follows; latitude and longitude are given here only by their degree values:

location, station number, and latitude and longitude	depth in m	content in 10^{-12} g/g Nd	Sm	ratio $^{147}Sm/^{144}Nd$	Ref.
Atlantic Ocean					
95; 36° N, 10° W	surface	1.80	0.376	0.126	
	200	2.01	0.417	0.125	
	500	2.26	0.473	0.126	
	800	2.48	0.528	0.128	
	1000	2.34	0.519	0.134	
	1000	2.35	—	—	
	1150	2.61	0.532	0.127	
	1300	2.49	0.533	0.129	
	2000	2.46	0.498	0.122	
	3000	2.84	0.556	0.118	
	4000	3.33	0.644	0.117	
30; 36° N, 61° W	200	1.96	—	—	
	1100	2.60	—	—	
	4850	9.01	—	—	
101; 36° N, 08° W	650	5.16	—	—	[40]

Table [continued]

location, station number, and latitude and longitude	depth in m	content in 10^{-12} g/g Nd	Sm	ratio ^{147}Sm/^{144}Nd	Ref.
Sargasso Sea					
OCE 63-1-1; 29° N, 76° W	300	2.00	0.462	0.140	
OCE 63-2-2; 27° N, 70° W	2200	2.57	0.516	0.121	
OCE 63-2-3; 27° N, 70° W	3400	3.19	0.623	0.118	[41]
Pacific Ocean					
315; 61° S, 62° W	50	1.85	0.347	0.109	
	800	2.30	0.432	0.113	
	2000	3.25	0.610	0.113	
	3600	4.21	0.800	0.115	
327; 56° S, 66° W	50	1.19	—	—	
	650	1.31	—	—	
	1900	1.93	—	—	
261; 47° S, 83° W	3900	3.69	0.683	0.112	
292; 60° S, 89° W	5050	4.09	—	—	
31; 20° S, 159° W	30	0.411	—	—	
	2800	2.57	—	—	
	4500	3.68	—	—	[43]
SW-1; 36° N, 122° W	1000	3.2	0.63	0.118	
SW-4a; 0° N, 86° W	2500	2.2	0.4	0.112	[42]

An approximately fourfold increase with depth occurs for some RE in seawater (at 31°10′ N, 120°54.5′ W) off San Diego, California; it is difficult to say whether inorganic scavenging or biological uptake is responsible. The respective contents in μg/L of Ho, Yb, and Lu are 1.7, 4.3, 2.0 at 100 m and 7.2, 28.0, 6.4 at 4000 m depth [10]. The vertical distribution of ^{144}Ce at six stations around Japan in the Pacific Ocean and Japan Sea shows a sharp decrease from 0 to 500 m and approximately uniform concentrations in layers below 500 m. The mean concentrations in deep waters (0.11 to 0.18 μμc/L) are one-fifth to one-twentieth of those in the surface layers. This pattern of vertical distribution of ^{144}Ce seems to indicate strong biological retention within the surface layer and rapid decrease in deep layers due to the decrease of fallout and the decay during vertical transport [54]. Deep lagoonal waters of Bikini Atoll, central Pacific Ocean, generally have higher ^{155}Eu concentrations than surface waters, the particulate concentration also being higher at the deep stations (>70%) [51]. RE_2O_3 contents are also higher in deep waters than in surface waters at several places in the Indian Ocean (see table on p. 44). The more detailed profiles at stations 4575 and 4618 show a gradual decrease of RE content with depth, reaching a maximum in bottom water, and resemble that of the biogenic elements Si and P. The RE content in suspended matter also increases with depth, but since the content of suspension does not change, it is supposed that the suspended particles adsorb the RE from seawater during sedimentation [32].

As described for ocean water [44], in Black Sea water (station 201, off Poti, Greater Caucasus) the relative abundance of heavy RE increases with depth due to a more intense complexing of heavy compared to light RE. The maximum at 10 m may be caused by biomass

location, sample number, latitude and longitude	sampling depth in m	RE_2O_3 content in 10^{-7}%
Arabian Sea		
4712; 15°11'7" N, 68°33'6" E	surface	(0.3)
4721; 16°50'0" N, 68°33'6" E	surface	1.0
	3500	2.4
northern part of Indian Ocean		
4618; 6°24'1" N, 75°48'1" E	surface	1.3
	50	2.5
	200	3.1
	1870	3.5
	bottom	4.1
central part of Indian Ocean		
4575; 29°42'9" S, 89°85'0" E	surface	1.4
	100	1.0
	1000	1.6
	2600	3.8
4582; 16°03'0" S, 90°05'9" E	1000	1.9
	3800	2.2
4594; 1°59'2" S, 86°41'5" E	surface	1.0
	1000	2.0
Malabar coast of India		
4619; 9°17'2" N, 75°57'0" E	surface	2.4
	90	4.5
4620; 8°34'2" N, 75°38'4" E	surface	4.7
Colombo Bay, Sri Lanka	surface	3.5
Java deep; 10°08'6" S, 108°00'4" E	3000	4.4
	6200	2.5

concentrating RE, or by retention of minute suspended particles resulting from an increase in density of seawater with depth. A further decrease of contents between 10 and 300 m corresponds to the vertical distribution of suspended matter, and the increase in near-bottom water may be due to the decomposition of organic matter, higher contents of suspended matter, and/or enrichment of the suspended particles in RE during their passage through water. The calculated summary contents (suspended and dissolved) of light (La to Eu) and heavy RE (Gd to Lu) vary with depth as follows; for individual data see original paper, La contents are only tentative [8]:

	content in 10^{-6} ppm				
	0 m	10 m	20 m	300 m	1720 m
Σlight RE	2215	2320	1022	504	900
Σheavy RE	1087	1111	492	239	757

With increasing depth, mean ^{144}Ce levels decrease gradually in the Baltic Sea (in the spring of 1981) from 16 Bq/m^3 at the surface to 11 Bq/m^3 at 50 m depth. The variances are 4 to 47 and 7 to 30 Bq/m^3, respectively [20].

The isotopic composition of Nd in the Atlantic Ocean (Sargasso Sea) varies with depth, with ε_{Nd}(O) values at or below 1000 m being very uniform (-13.5 ± 0.4) and two near-surface samples (300 and 50 m) having values of -10.9 and -9.6, respectively. All deep-water samples reported above are from water masses associated with North Atlantic deep water, which is suggested to have a uniform Nd isotopic composition, at least in its western part. Such values for surface waters may vary, depending largely on other sources for their observed isotopic composition. Isotopic distinctions must be related to the sources of surface waters, mechanisms of their injection into the oceans, and their circulation patterns and mixing mechanisms within the oceans [41]. In contrast, fairly uniform ε_{Nd}(O) values at different depths, being independent from geographical location, are reported for two stations in the Drake Passage, one south of the Antarctic polar front (-8.4 to -9.1 at 50 to 3600 m depth), where Nd composition is independent of its concentration, and one north of the Antarctic polar front (-9.2 and -8.2 at 650 and 1900 m depth, respectively). At two stations, one in the Humboldt Plain, far north of Drake Passage, and one in the Bellinghausen Plain within the Antarctic circumpolar current, ε_{Nd}(O) values are determined as -7.9 at 3900 m and -8.2 at 5050 m depth, respectively. The Antarctic polar front has no observable effect on the distribution of Nd isotopic composition. A decrease with depth in ε_{Nd}(O) from $+0.3$ at 30 m to -8.1 at 4500 m is reported for one station in the south-central Pacific Ocean. The indistinguishable ε_{Nd}(O) values for deep-water samples of the south-central Pacific and of the Drake Passage indicate that both represent Antarctic bottom water underlying middle and deep Pacific water. One sample from a depth of 2000 m in the north-central Pacific with a ε_{Nd}(O) value of zero compared to -4.5 at 2800 m in the south-central Pacific indicates considerable differences in Nd isotopic composition between waters within the central Pacific as well as between the central Pacific and the Drake Passage. The changes in Nd isotopic composition with depth in the northern Atlantic (see [41]) and south-central Pacific Ocean show well-defined isotopic characteristics which can be used to characterize water masses and which are unaffected by changes in salinity due to evaporation or dilution by rainwater [43]. Values of ε_{Nd}(O) can be, in principal, decoupled from either salinity or temperature. The isotopic composition of Nd at station 95 in the northeastern Atlantic Ocean in the vicinity of the Mediterranean water outflow is within the range of ε_{Nd}(O) values reported for the Sargasso Sea (see above), ε_{Nd}(O) varying with depth by 2.7ε units. In the upper 500 m, ε_{Nd}(O) ranges between -11.4 and -12.5, and below 500 m it increases to more radiogenic values, reaching a maximum of -9.8 at 1000 m. It lowers again below 1000 m, remaining constant down to 4000 m. This shift in the samples at 800 and 1000 m, corresponding to about 2ε units and associated with the Mediterranean outflow core, indicates a source of Nd different from that in adjacent waters (compare also pp. 46/7) and is a direct result of Mediterranean water (ε_{Nd}(O) $\geqq -9.8$) intruding into a nearly uniform layer of northern Atlantic water (ε_{Nd}(O) ≈ -12). One additional sample from the eastern Atlantic Ocean (Gulf of Cadiz) with ε_{Nd}(O) -9.9 at 650 m depth represents Mediterranean outflow water (as follows from theoretical considerations). A depth profile from the western Atlantic Ocean at 36° N, 62° W is almost indistinguishable from that of the Sargasso Sea. Its uniform deep-water values of -14.0 at 1100 m and -13.6 at 4850 m are lower than those in the deep layers of station 95 with ≈ -12. Both ε_{Nd}(O) ranges are assumed to characterize North Atlantic deep water. All these data indicate a source at the surface which is distinct from that for the respective deep waters, demonstrating lateral and vertical transport of RE [40]. Accounting for variations of 2ε units in Atlantic seawater by addition of Nd from mid-oceanic ridge basalt or oceanic volcanic sources to continental material as represented by the

North American shale composite ($\varepsilon_{Nd}(O) = -14.4$) would require doubling of the oceanic contribution [42, p. 234].

There are distinct Nd isotopic variations in seawater, and $\varepsilon_{Nd}(O)$ values observed are characteristic of the ocean basins. While the difference in the absolute abundance of ^{143}Nd between the Atlantic and Pacific oceans is only $\sim 10^6$ atoms/g seawater, the isotopic effects can readily be measured [41], [42, pp. 231, 234]. The small but distinct range of $^{143}Nd/^{144}Nd$ ratios in seawater within each ocean basin is a function of the residence time of Nd in seawater, of the kinetics of any important exchange process, and of intra- and interocean mixing times. Continental-derived detrital material is the dominant control of the Nd budget in seawater within each ocean basin (see also [42, pp. 229, 234]) and highlights the differences between them, as is inferred from $^{143}Nd/^{144}Nd$ ratios in surface pelagic clays, showing the same general relationship as those in ferromanganese depositions, i.e., the median ratio of Pacific clays being higher than the median of Indian Ocean clays which, in turn, is higher than that of Atlantic clays [50]. The exchange and mixing of water masses can possibly be traced through Nd isotopic composition, since oceans are not well mixed with respect to Nd isotopic composition as a result of the short residence time of Nd and its distinct source characteristics having different $\varepsilon_{Nd}(O)$ values [43]. Within each ocean basin a rather thorough mixing of Nd is suggested by the rather restricted range of $\varepsilon_{Nd}(O)$ values for seawater and ferromanganese nodules in the Atlantic and Pacific oceans; however, a better understanding is required [41]. Different $\varepsilon_{Nd}(O)$ values in the Atlantic and Pacific oceans can be due to different values of the continental sources directly supplying RE and being responsible for at least 80% of Nd in the former and a minimum of 50% in the latter [41]. The more negative values in the Atlantic point to the dominance of an old continental source (with a low average Sm/Nd ratio) relative to young, mantle-derived materials for Nd injections [43]. Another possibility is that $\varepsilon_{Nd}(O)$ values of the continental sources are the same for both oceans with the Pacific having much larger contributions (as much as 50%) from oceanic mantle sources (with $\varepsilon_{Nd}(O) = +10$; see [42, p. 232]) mixed with Atlantic water (≈ -12) with only small direct contribution from older continental sources. However, no marine materials (sediments or water) yet have been analyzed with $\varepsilon_{Nd}(O) > 0$, indicating that submarine volcanism (or hydrothermal systems) cannot play a dominant role. The far greater drainage of fresh water into the Atlantic relative to the Pacific is a third alternative. Dilution of Nd from continental sources draining into ocean basins combined with Nd having $\varepsilon_{Nd}(O) > 0$ from volcanic mantle sources is the most likely explanation for negative $\varepsilon_{Nd}(O)$ values in seawater [41]. At least at the station studied in the south-central Pacific, the source of Nd near the surface is more radiogenic than is indicated by ferromanganese sediment data in this area (compare [50], [42, p. 225]) or from seawater in the eastern Pacific (compare [41]). Values of $\varepsilon_{Nd}(O)$ close to -9 in the Drake Passage, the only region where significant transport of water occurs between the Atlantic and Pacific oceans, are intermediate between northern Atlantic and mid-depth Pacific values and closer to Atlantic and similar to, or possibly slightly lower than values inferred from ferromanganese sediments for the Indian Ocean. Therefore it is concluded that one-half to two-thirds of Drake Passage water is of Atlantic and at most one-half of Pacific origin. These values do not agree with those based on the estimated salt budget for the Drake Passage or on heat-transport considerations. Rather uniform $\varepsilon_{Nd}(O)$ values with depth in the Drake Passage, in contrast to the northern Atlantic (compare [41]) and south-central Pacific Ocean (see p. 45) indicate slow addition of Nd to southern ocean waters from other source terranes (Atlantic, Indian, and Pacific oceans) relative to residence time and vertical mixing of Nd in the southern ocean. The profiles investigated in the northern Atlantic and south-central Pacific consist of water layers with different sources. The Pacific apparently represents mixtures of southern ocean water with what is inferred to be more typical shallow or interme-

diate Pacific water, as is indicated by the change in Nd isotopic composition with depth in these profiles. The Atlantic data suggest a layer of water, possibly of Mediterranean origin, underlain by northern Atlantic deep water with some mixing [43]. Presumably, injection of waters with distinct Nd isotopic composition results in the eastern Atlantic in more radiogenic values of $\varepsilon_{Nd}(O)$ of about -12 than in the western Atlantic Ocean with -13 to -14. These injected waters possibly can be from the Mediterranean outflow and also, in part, a larger southern component (Antarctic bottom water) with $\varepsilon_{Nd}(O)$ values of -9 (see also [43]). Due to complex mixing processes between Mediterranean outflow core and surrounding waters, samples within the core do not show a linear correlation between Nd and nutrients, as it is evident for adjacent waters [40]. Using a box model to describe steady-state conditions for Nd in the Mediterranean Sea, the sources of soluble and relatively radiogenic Nd, necessary to shift the isotopic composition of incoming Atlantic water, are supposed to be rivers draining a relatively young continental terrain possibly characterized by late Precambrian basement and younger volcanic terrains as well as Nd remobilized from deep-sea sediments with significant young volcanogenic components (volcanic ash layers) in the Mediterranean basin. Possible sources of relatively non-radiogenic Nd (low $\varepsilon_{Nd}(O)$ values) in deep waters of the northern Atlantic Ocean are runoff from Precambrian shields of North America and Asia into the Arctic Ocean ($\varepsilon_{Nd}(O)$ is expected to be ≤ -25) and mobilization of RE in deep-sea sediments into the overlying water column which is thought to be necessary to bring the dissolved oceanic RE budget into balance. The isotopic differences described for deep waters of the eastern and western Atlantic basin (see p. 45) may reflect sediments that have an "older" component in the western relative to the eastern basin, if Nd in deep waters is supplied from sediments. However, the presence of different sources of RE with the same Nd isotopic composition (e.g., the $\varepsilon_{Nd}(O)$ value of -9.8 at 1000 m depth in the Mediterranean outflow being indistinguishable from the maximum of -9.6 in near-surface water of the Sargasso Sea and of -9.4 in the western Atlantic) requires caution in identifying water masses on the basis of Nd isotopic composition alone [40]. Rapid mixing of the water column in lagoonal Bikini Atoll waters, central Pacific Ocean, is indicated by constant [155]Eu concentrations in deep and surface waters at a few stations [51].

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7.2.2.2 Non-Marine Waters

River and Lake Waters

As is exemplified by the following paragraphs, the relationship between content and composition of RE and Y in surface waters depends on several factors. Besides differences introduced by the source material or area, the physico-chemical state of (dissolved or suspended) Y and RE and the chemistry of the water (especially pH or alkalinity) are of major importance.

With increasing **alkalinity** (pH between 6 and 9) and mineralization (content of mineral matter), the contents of Y and RE increase (Ce and La strongly, Y slightly, and Yb insignificantly) in alkaline waters (having generally higher RE contents; refer also to the table on p. 56) along with contents of F and CO_3 ions [1].

With decreasing pH, La concentrations in river water generally increase [2]. At different pH, the calculated speciation of trivalent Y and RE cations in model fresh water at 25 °C and 1 atm pressure shows different amounts of the important dissolved components (for details see pp. 12/3). Thus, at pH 6, free ions predominate with minor amounts of sulfate, carbonate, and fluoride complexes, while at pH 9 carbonate complexes for Y and the light RE and hydroxide complexes for the heavy RE occur [3]. The pH also influences the exact composition of the various soluble and insoluble coordination compounds of trivalent Ce, Yb, and Y with fulvic acids in surface water [4], and the association between humus and trace elements depends to some extent on pH. In water of Lake Trehørningen, Baerum, Norway, which was concentrated experimentally by evaporation under reduced pressure at 35 °C and pH > 3 to 4, complexing of La and Ce with humus is very strong (since retention by ultrafiltration is very high and the fraction centrifuged out or retained by ion exchange membranes is very low). If the solution is acidified to a pH of 2 to 3, results of ion exchange indicate that a substantial part is released from the organic complexes [5]. In unpolluted lakes of northern and southern Sweden (20 and 18 lakes with pH > 5.3 and > 4.7, respectively), mostly having low total salt content and some of them very acid, no significant differences are found for Sm and La levels in water samples collected during March and April. The concentrations, range and mean, in µg/L are: La < 0.1 to 1.1, 0.39 ± 0.31 and Sm 0.02 to

0.26, 0.08±0.07 for 18 samples from northern Sweden; La<0.1 to 1.0, 0.38±0.26 and Sm 0.03 to 0.14, 0.07±0.03 for 16 samples from southern Sweden [6]. Two lake waters with comparable pH (9.4 to 9.6) but different mineralization (63890 and 103710 mg/L) from areas of granitoid massifs, USSR, contain 0.10 and 0.45 mg/L ΣRE, respectively [1]; refer also to mean total RE contents of 0.119 and 0.45 mg/L in alkaline mineralized lake waters (pH~10) of Tuz-Kul' and Sasyk-Kul', respectively, in the eastern Pamir, USSR [7]. A relationship between water hardness and La content occurs at four stations in the rivers Thames and Kennet, Great Britain, where between 22.5 and 62.0% of La is carried with the soluble fraction [8, pp. 261/2], a higher percentage than that given for the Garonne River, France [9]; refer also to p. 12. Possibly due to admixture of seawater, La and to a lesser degree Ce, is enriched to contents of 1.5 mg/L La and 2.2 mg/L Ce in the Astrakhan lighthouse area, Volga River mouth, USSR, compared to average contents in the suspended matter of the river of 1.05 mg/L La and 2.0 mg/L Ce [10]. In Ca-Na- and Ca-hydrogencarbonate surface waters of granite intrusions in the Far East, USSR, anomalous contents of Y and Yb derived partly from ore bodies occur [11]. The saline anaerobic bottom layer (up to 12.5 m thick, maximum salinity of 17‰) of the stratified Lake Rørholtfjorden, Norway, has higher RE contents than the upper fresh water layer (135 m), the average enrichment factors (saline to fresh water) being La 9, Ce >4, Sm 7, Eu 1.3. In a vertical lake profile, contents of some RE and pH values vary as follows; saline water zone is below 135 m [12]:

depth in m	pH	RE contents in µg/L				
		La	Ce	Sm	Eu	Yb
1	5.9	0.6±0.2	0.6±0.1	0.17±0.05	<0.02	<0.4
10	6.0	0.6±0.2	<0.3	0.16±0.05	<0.02	<0.4
30	5.7	0.6±0.2	<0.3	0.18±0.03	<0.02	<0.4
50	5.7	0.7±0.2	<0.3	0.17±0.03	0.012±0.001	0.49±0.09
70	5.7	0.6±0.2	<0.3	0.17±0.02	0.014±0.001	<0.4
90	5.6	0.8±0.2	<0.3	0.12±0.02	0.011±0.001	<0.4
110	5.6	0.7±0.2	0.5±0.2	0.17±0.03	<0.02	<0.4
130	5.6	0.9±0.3	0.3±0.1	0.11±0.01	0.0009±0.001	<0.5
135	5.6	0.5±0.2	0.5±0.1	<0.2	<0.01	<0.5
137	6.6	3.2±0.3	1.3±0.2	1.6±0.2	0.015±0.001	<0.3
139	6.6	7.3±0.7	0.9±0.1	0.9±0.1	<0.02	0.46±0.06
141	6.6	7.1±0.6	1.1±0.1	0.8±0.1	<0.02	0.71±0.09
143	6.6	6.8±0.5	1.2±0.1	<0.8	<0.02	<0.3
145	6.6	6.6±0.6	1.1±0.1	1.2±0.1	<0.02	<0.2

Relative to the **amount of suspended terrigenous material** in rivers, total RE contents (suspended and dissolved) vary more than 500-fold, this relationship being even more evident for RE in suspension [13, pp. 149/51]. For river-suspended matter an enrichment of light RE is characteristic [14]. The average RE composition for suspended matter of nine water samples, Gironde River, France, is Y 27.5, La 54.8, Ce 103.4, Pr 10, Nd 37.7, Sm 6.32, Eu 1.24, Gd 6.05, Tb 0.92, Dy 3.77, Ho 0.98, Er 2.75, Tm 0.42, Yb 2.8, Lu 0.41, ΣRE(+Y) 259 g/t [15]. Contents of individual RE in suspended matter of other rivers are given in the following summary:

South America
Magdalena — La 37, Sm 6.4, Eu 1.4, Yb 3.7; Parana — Sm 9.1, Yb 3.5, Lu 0.57; Orinoko — La 50 ppm [9]. Amazon — La 48, Ce 112, Sm 9.7, Eu 1.8, Yb 3.7, Lu 0.60 ppm [16].

Africa

Congo — La 47, Ce 104, Eu 1.5, Tb 1.6, Yb 2.4, Lu 0.38 ppm [16]; La 50, Ce 90, Eu 1.6, Gd 2.5, Tb 1.6, Yb 2.6, Lu 0.37 ppm [9]. Zaire — La 53, Ce 74, Sm 7.7, Eu 1.7, Tb 0.56, Yb 2.8, Lu 0.36 ppm [17].

Asia

Ganges — La 42, Ce 98, Nd 48, Sm 9.7, Eu 1.2, Tb 0.7, Tm 0.35, Yb 3.2, Lu 0.51; Mekong — La 48, Ce 93, Pr 8.5, Nd 47, Sm 5.4, Eu 1.5, Gd 5.3, Tb 0.9, Ho 0.9, Er 2.7, Tm 0.45, Yb 3.2, Lu 0.58 ppm [16].

Europe

Rhine — La 31.1, Ce 53.5; Main — Y 45, La 31.0, Ce 55.5; Neckar — La 35.0, Ce 48.4 ppm [18]. Thames — La 28.9, Ce 97.9, Sm 5.4 [19]; La 29.0, Ce 105.2, Sm 7.0 µg/g [8, p. 266].

A direct correlation between content of suspended matter and total RE content occurs in some rivers of southwest France (Dordogne and Garonne-Gironde) and the USSR (Volga and Rioni, western Caucasus). Due to differences in granulometric and mineral composition of particles which depend on morphology of the area, data of Rioni River do not fall on the straight correlation line observed for the other rivers. Rioni water near the river mouth, at Poti, is therefore enriched in La, Ce, Pr, Nd, and Sm; summary mean contents are Σ(La to Eu) 1509.0 and Σ(Gd to Lu) 373.0×10^{-6} ppm [20]. The calculated mean contents of light (La to Eu) and heavy RE (Gd to Lu) and of Y for these rivers are as follows; susp. mat. = suspended material:

river and location		susp. mat. in mg/L	Y	content in 10^{-5} mg/L Σ light RE	Σ heavy RE	Ref.
Volga delta		38.75	105	507[1]	69[2]	[10]
Dordogne	above Libourne	2	—	56.3	4.6[3]	
Garonne	above Bordeaux	7	24	151.1	12.6[3]	
	below Bordeaux	1590	4500	29960.0	2339.0[3]	
Gironde	middle course	1141	320	21440.0	1719.0[3]	
	Pointe de Grave	22	41	306.9	24.5[3]	[15]

[1] Without Eu. — [2] Only Gd, Dy, Er, and Yb. — [3] Without Dy.

Variations in the suspended load, highly associated with river flow rate, possibly cause the high coefficient of variation for La (217%) in the soluble fraction in the Thames River, Great Britain [8, pp. 261, 265].

The amount and composition of suspended matter (which show relationship to weathering or climatic factors, see p. 54) strongly influence the distribution of ^{144}Ce in surface waters [21]. Thus, differences in grain-size distribution and composition of suspended matter influence contents of Ce radionuclides in various rivers of the Federal Republic of Germany, and tidal action mixes inland water-suspended matter of higher radionuclide content with marine suspended matter lower in radionuclides [22, pp. 159/62]. In contrast to normally decreasing radioactivity of ^{144}Ce per liter of water with decreasing content of suspended matter per liter in the mouth of the River Elbe, Federal Republic of Germany, the specific activity of ^{144}Ce/g suspended matter behaves in the opposite way, e.g., it increases downstream (between the mouth of the River Oste and lightship "Elbe 1") and shows clear differences in ^{144}Ce concentrations at 5 m water depth during falling and rising tides [23].

Based on a compilation of water–rock partition coefficients for chemical elements (predominantly used to discuss river input to ocean, pp. 21/2, or overall composition of river water and seawater, p. 200) it follows that **solid state chemistry,** especially complex stability, controls element content and distribution in river water. Thus, from diagrams of electronegativity function vs. partition coefficients between river water and crustal rock [24, 25] or between river water and river–suspended matter it can be seen that the degree of affinity for the solid phase decreases with increasing electronegativity on passing from the RE to the halides (for the definition of function and coefficients see original papers) [26]. Sorption of part of RE on river–suspended matter causes a decrease of dissolved RE concentrations in river water compared to ground and subsurface waters [13, p. 147]. The increasing stability of organic and inorganic complexes of the RE explains the observed increase of the soluble/ detrital RE ratio from La to Lu in the rivers Garonne and Dordogne, France [16]. A more profound effect of these complexes on the RE pattern in filtered surface water of five Pacific Northwest rivers, USA/Canada (and, in addition, different RE patterns of the sedimentary rocks affecting the rivers, see p. 53) can be the reason for differences as against dissolved RE patterns for the Dordogne and Garonne rivers, with RE patterns very similar to the sedimentary type rock abundance pattern used for normalizing. The Pacific Northwest rivers also show a pattern similar to the sedimentary type rock (within a factor of two) but also similar to the seawater RE pattern with the dissolved RE increasing (relative to sedimentary rocks) as atomic number increases, and the heavy RE are more abundant than the light RE in previous observations in river water [2]. In addition to Y content, in the following are given calculated summary contents of light (La to Eu) and heavy RE (Gd to Er, Yb, Lu) and element ratios indicative of RE composition for the French rivers [15]:

river and location		dissolved content in μg/L			ratio	
		Y	Σlight RE	Σheavy RE	La/Yb	Ce/Sm
Dordogne	above Libourne	—	181.3	19.9[1]	13.1	10.5
Garonne	above Bordeaux	43.1	181.5	20.5[1]	13.1	9.9
	below Bordeaux	—	72.8	3.3[2]	6.2	10.7
Gironde	middle course	15	29.7	4.2[3]	3.7	9.4
	Pointe de Grave	9.3	24.9[4]	3.0[1]	9.2	—

[1] Without Dy. — [2] Yb and Lu only. — [3] Gd, Tb, Ho, Yb, Lu only. — [4] Without Sm.

The corresponding data for the Pacific Northwest rivers are [2]:

river	dissolved content in ng/L		ratio	
	Σlight RE	Σheavy RE	La/Yb	Ce/Sm
Fraser	399.9	78.7[1]	—	6.1
Columbia	166.4	13.8[2]	6.7	1.3
Rogue	119.4	18.3[2]	4.0	5.7
Klamath	59.5	13.8[3]	4.9	8.1
Sacramento	40.9	8.8[3]	3.2	4.6

[1] Gd, Tb, Ho, Er only. — [2] Gd, Tb, Ho, Yb, Lu only. — [3] Gd, Tb, Ho, Er, Yb, Lu only.

Differentiation of RE in Volga River water, USSR, does not significantly affect the elements from La through Dy, and only the relative contents of the heavy RE (Er through Lu) increase by a factor of almost two [10]. As is suggested by RE patterns for river water, Afon Gwesyn

catchment, mid–Wales, Great Britain, the relative hydration energies of individual RE and not the composition in the weathering material mainly control fractionation of RE on weathering into solution [27].

For an influence of source area morphology on RE amount in suspension or solution, see p. 84 and on RE composition in river waters, see below.

The **rock composition in the catchment area and processes of weathering and soil formation** determine content and composition of dissolved RE in river water. Regional differences in the composition of the source rock cause small differences of RE content and composition in suspended matter whose composition, in general, is fairly close to that of platform clays [28]. Mainly sedimentation in continental regions determines composition of RE in suspension, since the RE composition (suspended and dissolved) in river water is close to the average composition of sedimentary rocks (RE(Ce)/RE(Y) ratios being 2.75 to 4.2 and 3.1, respectively), and average RE contents in river-suspended matter (259 g/t) are close to that of platform clays (196 g/t) [13, pp. 147, 149/50]. An RE composition resembling that for average shales has been found for the chondrite-normalized RE pattern of Nippara River water (the upper stream of Tama River), Tokyo area, Japan [29], and for shale-normalized RE patterns of the dissolved and total load of Gironde River water, France. Since rocks other than shales crop out in the latter drainage area which may have different RE patterns, it is concluded that either contribution from these rocks is insignificant or that their relative contributions are such as to reinforce the shale pattern for both the dissolved and the suspended load [30]. Higher contents than in the world average sedimentary rock type of heavy relative to light RE in the sedimentary rocks affecting five Pacific Northwest rivers, USA/Canada, can cause a predominance of heavy RE in the rivers as compared to the Dordogne–Garonne river system, France [2]; see p. 52. Different characteristics of the source area lead to different RE concentrations in the Volga and Ural rivers, RE being found in all samples of the Volga River but only a trace of Ce in water of the Ural River, although the content of suspended material is practically the same in both rivers. Sedimentary rocks and soils, the main sources of clastic material carried by streams on the Russian Platform, have RE contents about tenfold higher than weathered ultramafic rocks which characterize the source area of the Ural River [10]. For the influence of climate on RE content for both regions, see p. 54. Concentrations of RE in the dry residue of Neva River water, Leningrad area, USSR, do not exceed Clarke contents in sedimentary rocks; the observed fractionation (with light RE being lower in river water) is consistent with the weathering scheme of RE minerals [31]. The hydrogeochemistry of acidic intrusions of the Far East, USSR, is reflected in waters by anomalous concentrations of the elements characteristic of a given intrusion. Thus, anomalous contents of Y and Yb occur in surface waters of two granite intrusions and waters in the vicinity of stocks and dikes of acidic and intermediate igneous rocks [11]; additionally, acid granite 1 and granite 2 are characterized by their La contents [32]. Related to the presence of apatite and fluorite are local concentration anomalies of Y in a streamlet cross-cutting a sulfide mineralization near Ty Flehan, Brittanny, France [33].

In relation to the stage of weathering (as defined by [28], refer also to "Rare Earth Elements" A6a, 1988, p. 10) of the drained rocks, dissolved RE coming into rivers from ground waters can show different composition (distribution patterns): (1) enrichment of Y and heavy RE in waters draining rocks with the initial (alkaline) stage of weathering ("Y waters"); (2) enrichment of light RE in waters draining rocks with a late (acid) stage of weathering ("La waters"); and (3) a V-shaped pattern with relative maxima both at La and Y–Yb due to mixing of the above two types. For all three types, in general, a Ce deficiency occurs due to its retention by hydrolysis in the weathering crust. For example,

entirely corresponding RE distributions in weathering crust and fresh water have been mentioned for the Volga basin, European USSR, and the Gironde basin, France [13, pp. 136, 139/40]. Higher relief and a smaller amount of vegetation for the Garonne basin, resulting in a larger detrital erosion, which manifests as a lower soluble/detrital RE ratio in the discharge area of the Garonne than of the Dordogne, can explain the discrepancy occurring between the two rivers [16]; for the calculated mean contents of dissolved light (ΣLa to Eu) and heavy RE (ΣGd to Lu) and Y and for ratios indicative of RE composition, see p. 52. In contrast to the Gironde and due to quite different processes of weathering and soil formation (extensive glacial erosion on the Scandinavian peninsula), leading to a different chemical behavior of Ce relative to the other RE in waters, soils, and sediments, surface waters of eleven Norwegian rivers show only a slight depletion of Ce relative to the other RE (Ce/Sm = 2.1). The range and weighted mean content of some RE for the river waters are: La <0.1 to 3.5, 0.40; Ce <0.06 to 2.1, 0.20; Sm <0.02 to 0.66, 0.095; Eu 0.006 to 0.040, 0.0098; Dy <0.01 to 0.11, <0.02; and Yb <0.01 to 0.5, <0.2 µg/L [34].

Different degrees of erosion lead to differences in the transfer of ^{144}Ce-containing soils into various rivers of the Federal Republic of Germany [22, pp. 161/2]. Probably due to inflow–outflow circulation in Lake Trasimene, central Italy, ^{144}Ce from fallout is concentrated in the outflow area [35].

Differences in climate determine the relationship of transport of RE in suspension and in solution in Volga and Ural rivers, both European USSR. The RE are found in all samples of the Volga River flowing in a humid zone, which is characterized by a predominance of chemical over mechanical denudation (1.75:1), while only a trace of Ce is found in water of the Ural River in an arid zone with a predominance of mechanical over chemical denudation (1.25:1) [10]. The average concentration of RE in solid discharge of the Amazon River, Brazil (6×10^{-2} mg/L), is three orders of magnitude higher than the concentrations in rivers of moderately humid climatic zones [13, p. 149]. Considerable concentration of dissolved organic material and HCO_3^- ion in surface waters of the humid zone explain the greater solubility of heavy compared to light RE [36]. Surface waters in a weakly humid zone (47°30′N latitude) show somewhat higher ^{144}Ce levels than waters in a more intensely humid zone (58°N latitude). The distribution of ^{144}Ce between soluble and suspended phases, however, shows only slight differences [21].

Content and distribution of **RE radionuclides** in surface waters is **influenced** especially **by seasonal or meteorological conditions,** but also by **living organisms,** as may be seen from the following few examples. Thus, rainfall in the catchment area of some rivers, Federal Republic of Germany, can cause the observed different ^{144}Ce levels in water. Especially the disappearance of ^{144}Ce in suspension during the first quarter of 1982 in the Rhine River near Koblenz is ascribed to seasonal or meteorological conditions [22, pp. 161/2, 164/5]. However, due to dilution, a decrease of ^{141}Ce concentration does not occur in Dardanelle Lake, Arkansas, since introduction of ^{141}Ce by rainfall occurs over a wide area and, therefore, concentrations are the same, no matter what the source of the water [37]. Season-dependent high river flow causes resuspension of Eu and Ce radionuclides into the Columbia River at McNary Dam site, Washington and Oregon, in spring and early summer [38], and of ^{144}Ce during summer into Lake Michigan [39]. Maximum La contents (1762 ppb) in the Columbia River at Hanford, Washington, in April 1962 are due to the introduction of waters from the Spokane tributary [40]. Higher contents during the winter months, due to greater rainfall, are reported for ^{144}Ce in the water reservoir Lake Marathon near Athens, Greece, concentrations varying between 0.27 and 0.78 pc/L [41].

The presence of living organisms influences the distribution of ^{144}Ce in surface waters, since ^{144}Ce can be carried by biota [21], e.g., an enrichment by a factor of 130 (relative

to water free of coarse sediments) occurs for [144]Ce in fish flesh, upper Danube near Gund-remmingen, Bavaria [42]; or plankton intensively concentrates ^{90}Y in the lakes Nehmitz and Stechlin, German Democratic Republic, the radioactivity in the ash being 136 to 300 and 136 to 327 pCi/g, respectively [43]. In water of the eutrophic lake Linsley Pond, North Branford, Connecticut, none of the RE is detected, suggesting that submerged rootless plants quickly extract RE from water [44].

An influence partially of **pollution** has been mentioned for some surface waters. Thus, for La in the Thames River, Great Britain, considerably higher dissolved contents at a downstream station (3.7 µg/L) compared to upstream (0.001 µg/L) are related to the signifi-cant increase in effluent discharge of industrial origin. The content of La in suspension in the Thames River is 38% higher than in its tributary Kennet River, which receives metal input primarily from natural sources [8, pp. 258, 265/6, 272]. Contents of some RE in Norwe-gian unpolluted and rather polluted surface water are as follows (in µg/L): Lake Trehørn-ingen, Baerum (May 1974), La 0.145, Ce 0.33 and Nitelva River, Lillestrøm (February 1974), La 0.21, Ce 0.48; the slightly polluted Glomma River, Fetsund, shows (February 1974) La 0.12, Ce 0.42, Eu 0.11 [45] and (November 1973) La 0, Ce 0.24, Eu 0.046 [46]. Lowest RE contents in the most highly polluted, and high RE contents in water with a small number of artificial pollution sources are reported for the Yodo River and its main branches (rivers Kizu, Uji, and Katsura), Japan [47, 48] and are, therefore, considered to be of natural origin [47, 49]. No impact of pollution on RE contents is found for the Neva River, Leningrad area, USSR [31].

Ground and Subsurface Waters

Content and composition of RE in ground and subsurface waters are dependent on pH and chemical type of the water, see, e.g., [50 to 55] and the following examples. With increasing pH, both the total content and the portion of light RE in the total RE content increases for alkaline waters of, e.g., the Kola Peninsula (Lovozero massif) and Central Asia, both USSR. The total RE content in these waters is $\leqq$500 to 601 µg/L, with maximum concentrations at pH>8 to 9.5 [51, 53]; compare for alkaline waters 500 to 680 µg/L with maximum values at pH>8 [54]. Ground water (mainly of the siliceous–hydrogencarbonate–Ca type, pH 5.8 to 7.9) of granite rocks, Baikal mountain region, USSR, contains as a mean for 34 samples (of which 62% contain RE) 0.0002 mg/kg each of Y and Yb [56]. Slightly acid (pH 6.8) subterranean mine waters of the HCO_3^-–Na–Ca type of an undisclosed alkaline massif (USSR?) have average and maximum contents of La 0.17 and 0.5, Y 0.06 and 0.1, and Ce 0.29 and $-$% of the dry residue, respectively. The slime fraction of the spring water contains Y$\leqq$0.1, La$\leqq$0.03, and Ce$\leqq$0.01% [57]. Acid to strongly acid mine waters of the Fe–Zn–SO_4^{2-} type, Kutna Hora ore district, Czechoslovakia, contain La at about 1 mg/L [58]. In very acid waters (pH nearly 3) of coal-bearing strata, central part of the Donbass, Ukraine, the RE contents are in the range of 0.n mg/L [55]. In relation to their chemical type, ground waters of the Transcarpathian region, Ukraine, contain La up to 0.096 mg/L in Cl^-–HCO_3^-–Na-type, up to 0.076 mg/L in HCO_3^-–Cl^-–Na-type, up to 0.075 mg/L in Cl^-–HCO_3^-–Na–Ca-type, and only 0.006 mg/L in HCO_3^-–Na–Ca-type waters [59]. For well and spring waters (pH~6.64, temperature ~15°C, and HCO_3^-–Cl^-–Ca–Na type) from an area with small U and Cu-U occurrences near Monticello, New York, statistically derived mean content and standard deviation are: Y 0.784±0.605, Ce 15.7±3.79, and Dy 0.0216±0.138 ppb [60]. Refer to higher contents of Y and Yb in subsurface waters occurring in regions containing ore mineralizations as, e.g., in the low-mountain regions of the south-eastern part of western Siberia [61] or in Afghanistan where highest amounts of Y in the waters are related to granitoid-type (maximum 0.5; mean 0.3 mkg/L) and rare metal pegma-tite-type mineralizations (maximum 0.2 to 0.3; mean 0.1 mkg/L); contents of Yb are at back-

ground level, 0.1 mkg/L [62]. Ground waters with different composition from fractures in agpaitic nepheline syenites (USSR?) contain Y, La, Ce, and Yb in relation to pH and mineralization (content of mineral matter) for six samples as follows [1]:

content in mg/L

mineralization	509.5	627	346	225.5	178	141
Y	0.016	0.0163	0.0093	0.0106	0.0196	0.0096
La	0.0275	0.2633	0.0761	0.212	0.1958	0.078
Ce	0.4178	0.3825	0.2076	0.338	0.3382	0.122
Yb	0.0015	0.0021	0.0015	0.0013	0.0007	0.0007
pH	>9.4	>9.4	9.1	9.1	9.1	7.8

The RE contents in subsurface waters of the HCO_3^--Ca, partly HCO_3^--Mg type from coal-containing depositions of the Russian Platform (artesian Moscow basin) are different for samples from the Lower and Middle Carboniferous rocks; range and mean content with number of analyses given in parentheses are [63]:

	content in mg/L for subsurface waters of the	
	Lower Carboniferous	Middle Carboniferous
La	0.06 to 4.9; 0.65 (17)	0.0005 to 1.0; 0.5 (5)
Ce	0.4 to 9; 1.0 (29)	0.04 to 1.7; 0.3 (8)
Sm	0.03 to 0.5; 0.17 (4)	0.008 (1)
Eu	0.006 (1)	0.008 (1)
Tb	0.3 to 0.07; 0.04 (12)	—
Lu	0.0002 to 0.0070; 0.0012 (8)	0.0005 to 0.0020; 0.0008 (5)

Rare earth element content in stratal waters*) of various petroleum deposits, western Caspian Sea region, Azerbaidzhan, depends on salinity and chemical type of water (Ca chloride–Na type at the Neftechalinsk and Surakhansk deposit, hydrocarbonate–Na type at the other ones), with highly saline waters having high RE contents. Mean ΣRE contents, given in $n \cdot 10^{-6}$ g/L, are 2.05 for seven analyses from Neftechalinsk; 1.45 for six analyses from Binagadinsk; 1.17 for five analyses from Balakhany–Surakhansk; and 0.62 for five analyses from Siazansk [64]. Refer to contents of Y and Yb in stratal waters below petroleum layers of the Dniepr–Donets basin, Ukraine, dependent on the age of the country rocks, their lithology, and the position of the water within the basin. Neither element occurs in waters extracted from clay stratum [65]. Mean contents of 1.34 γ/L La occur in formation waters of petroleum pools and of 29.0 γ/L La in subsurface waters not related to oil formations and situated above them, western Siberian Lowland [66]. Waters from condensation zones of subterraneously gasified coal, USSR, are enriched in Y, in addition to other rare elements, the Y contents being 0.006 and 0.01 mg/L for the Nadugol'nyi and Uspinski formations, respectively [67].

Old fossil ground water (22000 to 29500 yrs.) with pH between 6.3 and 7.5 and low salinities, supposed to be in solution equilibrium with surrounding rocks, Kufra basin, Libyan Sahara, contains in 10 out of 48 samples 0.2 to 3.4, mean 0.3 ppm Y [68]. Old ground and subsurface waters (5000 to 10000 yrs.) of the upper Volga river basin, USSR, are higher than surface river waters in Ce, Sm, Eu (except for subsurface water), Lu and lower in La and Yb [69]:

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*) Erroneously given as ground water in the English translation.

	mean content in mkg/L					
	La	Ce	Sm	Eu	Yb	Lu
ground water	1.5	2.5	0.1	0.03	0.008	0.0002
subsurface water	9.4	12.0	0.12	0.0005	0.0026	0.0002
river water	15.0	2.0	0.08	0.008	0.009	0.00005

Ground waters of the Perch Lake basin, Ontario, Canada, compared with the recharge area (sample GWO), have highest RE contents in wells adjacent to the lake's shore (samples GW–DT and GWK). The lake itself has the lowest concentrations. No explanation for this is given; the change in valence due to more reducing conditions adjacent to the lake shore quoted for other elements behaving in the same way seems not to occur with RE. The ground water samples taken during the winter months have the following contents [70]:

	content in µg/L			
	GWO	GW–DT	GWK	lake water
La	0.42	3.3	2.3	0.10
Ce	4.3	35	25	0.90
Eu	0.084	0.67	0.53	0.020
Nd	3.0	21	—	0.51
Tb	0.056	0.35	0.29	0.013
Yb	0.083	0.28	0.65	0.0089
Lu	0.081	0.23	0.21	0.014

In ground water from deep boreholes (>1700 m) of the Crimea peninsula and the Carpathians, both USSR, the La content differs from that in argillaceous rocks of the same depth interval. Five ground water samples, Crimea peninsula, contain 4 to 30, mean 12, and two samples, Carpathians, have 10 and 40 ppm La [71].

Moreover, for different types of ground and subsurface waters the following contents of Y and/or individual RE have been given without special discussion in the literature: Mean content of 0.23 mg/L Yb in ground waters (pH 6.68) of the northern taiga region (mainly of the USSR) [72]. Ground waters (pH 6.0 to 8.7, temperature 15.3 to 18.3 °C, and Ca-HCO_3^- type) of the Musashino area, central Honshu, Japan, show the following range and mean: for La 0.009 to 0.087, 0.027; Sm 0.0006 to 0.035, 0.006; and Eu 0.0007 ppb [73]. Two ground water samples (containing <50 ppm total solids) from wells of the Virginia Piedmont area of crystalline schists, west of Washington, D.C., contain 0.8 ppb Y, 0.4 ppb La and 0.03 ppb Yb and 41 ppb Y, 12 ppb La, 0.5 ppb Ce, 0.7 ppb Nd and Dy each, 0.8 ppb Er, 0.3 ppb Tm, 1.6 ppb Yb, and 0.3 ppb Lu [74]. Ground waters of the upper Arman' region, Magadan province, Far East, USSR, show range and mean for La of 0.7 to 3.5, 1.4 µg/L (108 sample points) and for Yb 0.05 to 0.76, 0.23 µg/L (for 44 sample points) [75]. Ground waters of the industrial region of Warsaw, Poland, contain Ce at <2 to 10 and Yb at ~6 to 18 µg/dm³ [76]. Stratal water ("plastovykh vodakh" of the Russian original), with Y 0.006, La 0.02 mg/L and water in fractures of crystalline rocks with Y 0.009, La 0.03 mg/L, occur in the Ukrainian Shield, USSR [77].

Mineral and Thermal Waters

The pH and chemistry of mineral and thermal waters influence concentration and composition of Y and/or RE as is exemplified in the following.

Contents of RE in water of the Tatsumatojigoku and Umigigoku hot springs, Japan, are higher in acid than in neutral or alkaline waters [78]. Acid H_2S-containing alum springs of Japan (Moto-yu and Gyōnin-no-yu) show higher RE contents than simple hot or low-H_2S springs (Kita, Benten, Omaru, Sandoyoga I, or Takao, respectively) (see table below). In the simple hot springs, contents of Ce and La are almost equal while in the acid alum springs Ce is about three times higher than La. In the Moto-yu spring, the abundance of each RE becomes gradually lower with increasing atomic number, showing almost the same tendency as in the case of the average earth's crust values [79]. The contents of individual RE in these and other acid hot springs of Japan are as follows:

locality, temperature, and pH	content in µg/L					Ref.
	La	Ce	Nd	Sm	Eu	
Nasu district[1]						
Moto-yu; 63 °C; 2.0	1.79	5.51	8.03	1.44	0.28	
Gyōnin-no-yu, 52 °C; 2.2	3.13	7.09	3.89	1.36	0.27	
Kita et al.; 93 to 65 °C; 4.0 to 5.7	0.30	0.32	0.11	0.07	0.016	
Takao; 39 °C; 5.4	0.034	0.031	—	0.004	0.003	[79]
Misasa[2]; 76 °C; 6.9	0.018	—	—	0.0059	0.00051	[80]
Yunotsu[2]; — ; —	0.08	—	—	0.02	0.005	[81]
Ikeda[3]; — ; —	0.13	—	—	0.07	0.008	[81]

locality, temperature, and pH	content in µg/L						Ref.
	Gd	Tb	Ho	Tm	Yb	Lu	
Nasu district							
Moto-yu	2.13	0.32	0.40	0.11	0.41	0.13	
Gyōnin-no-yu	3.72	0.34	—	2.08	1.38	0.32	
Kita et al.	0.07	0.02	—	0.013	0.066	0.017	
Takao	0.031	0.005	—	0.002	0.011	0.010	[79]

[1] For Nasu and Kusatsu, La 1.2 to 5.7, Sm 0.8 to 2.6, and Eu 0.2 to 2.6 γ/L are given additionally [82]. — [2] Hot spring. — [3] Mineral spring.

Due to pH dependence of RE accumulation, carbonated (pH > 8) and sulfurous thermal waters (pH ~ 6) of the Pyrenees and the Massif Central, both France, show different total RE concentration (see table on p. 59) and composition (with characteristic distribution patterns; see original paper). Compared to the carbonate waters with high amounts of heavy RE and positive Eu anomalies, sulfurous thermal waters are enriched in light RE, as is corroborated by the mean Dy/Eu ratio of 18 for the former and 0.5 to 3.5 for the latter. Anomalously high RE concentrations in sulfurous thermal waters of the Pyrenees are due to very large amounts of organic matter in those waters [83]. Deep-seated Na-chloride waters of the Geyser Valley and Uzon Caldera, Kamchatka Peninsula, USSR, with a relatively low total RE content (0.6 µg/L) become enriched during near-surface mixing with acid sulfate solutions in these elements by a factor of three (1.6 µg/L) in the most acid waters (pH 1 to 2), whereas in carbonate-type hot springs (pH 6 to 6.5, temperature 50 to 74 °C) of the Nalachevo area, Kamchatka Peninsula, the RE concentration increases by a factor of five (up to 10 µg/L) in sulfate waters [84, 85]. In various radioactive mineral springs (pH 6.3 to 9.5, temperature

locality; type of water; and pH	range and mean in ppb			
	La	Sm	Eu	Dy
Massif Central				
alkaline	0.218 to 1.107; 0.522	0.010 to 0.328; 0.116	0.002 to 0.022; 0.009	0.005 to 0.062; 0.028
acid	0.045 to 0.348; 0.202	0.007 to 0.024; 0.015	0.023 to 0.963; 0.323	0.030 to 0.248; 0.096
Pyrenees; alkaline; 8.5 to 9.5				
Thuès–les–bains	0.15 to 0.35; 0.165		0.0009 to 0.0085; 0.0038	0.0011 to 0.0073; 0.0038
Ax–les–thermes	0.012 to 0.331; 0.096	0.007 to 0.051; 0.0135	0.0074 to 1.0610; 0.1966	0.0011 to 0.0067; 0.0038
Usson–Escoububre Carcanéires	0.055 to 0.075; 0.067		0.0027 to 0.248; 0.0106	0.0016 to 0.0032; 0.0023
Pyrenees and Corsica				
alkaline	0.042 to 2.069	0.003 to 0.645	0.0006 to 0.267	0.0011 to 1.440
Pyrenees; acid; 6.2	0.65 to 2.43; 1.340	0.006 to 0.050; 0.0277	0.0035 to 0.0155; 0.0084	0.0676 to 0.3118; 0.1651

6 to 94 °C) of the western United States, the contents of Y and Yb are determined by duration of water circulation and thus tend to increase with increasing salinity. Their very small contents (Yb 0.02 to 2.4, Y 0.29 to 2.0 µg/L) are caused by their association with minerals being relatively insoluble in most near–surface environments but whose solubilities are increased by the presence of saline solutions [86]. Only small amounts of La and Ce occur in low-mineralized, slightly alkaline SO_4^{2-}–Na–Ca–type waters (temperature 17.5 °C, low Si and high NO_3^- contents) from the Chashma radon source near Leninabad, Tadzhikistan, USSR [87].

Depending on type of water and location, waters from several health resorts, eastern part of Eastern Siberia, contain 60 to 96 mg/L RE(Y), total RE content being between 200 and 460 mg/L [88]. Waters from springs and health resorts of the Transbaikal region, USSR, having 0.06 to 1.05 mg/L total RE content (20 to 60% being yttrian RE), show maximum content in water with maximum HCO_3^- content (Cook spring), and La and Ce subgroup elements are highest in HCO_3^-–Ca–type waters [89]. Cold mineral waters (CO_3^{2-}–Fe type) of the southern part of Eastern Siberia have highest RE contents while warm SO_4^{2-}–Na–type mineral waters are lowest. Total RE contents vary between 0.20 and 0.25 mg/L, the relative composition being Ce 20 to 40, Tm 0.6 to 1, and (Eu + Tb) 0.2 to 0.4% [90]; note also 100 to 480 µg/L total RE content for cold and warm carbonate–type waters of the same region, with lowest concentrations in SO_4^{2-}–HCO_3^-–Ca–Mg– and SO_4^{2-}–Na–type waters and highest concentrations (270 to 480 µg/L) in hydrogencarbonate–Na or Ca–type waters [91]. Highly mineralized Cl^-–Ca–type water of Lugela, Georgia, USSR, contains La 310.7, Ce 352.7, Pr 71.2, Nd 195.1, Sm 45.2, Gd 28.4, (Tb + Y) 25.4, and Dy 16.9 γ/L, these contents being much lower than their Clarke contents in the earth's crust [92]. Correlations between concentrations of RE and Ti, Al, V, Ga, and Zr have been found in thermal waters of central Afghanistan [93]. Volcanic hot waters from Santorini, Italy, contain small amounts of Eu,

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Tb, and Yb which increase with seawater concentrations in the influx areas [94]. Low-mineralized waters of the spas in western Czechoslavakia contain, in µg/kg water: Y, 3; Ce, Nd, Dy, Er, and Yb, 0.3 to 0.5 each; La and Pr, 0.1 to 0.2 each; and Ho, Tm, and Lu, 0.05 to 0.1 each [95].

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7.3 Migration, Removal, and Precipitation of Yttrium and/or Rare Earth Elements in the Hydrosphere

7.3.1 General

The form in which rare elements (including Y and La) migrate in natural waters varies with their acid–base properties (ionization constant, ionic potential, electronegativity) and with the hydrogeochemical conditions in the medium (e.g., pH). In spite of complexing, these elements are the least mobile and the poorest migrants in water. In all types of natural water, the concentration of complex–forming elements is always much lower than their Clarke content in the lithosphere [1]. Since the pH of hydrolysis of Y, La, Ce, and Yb is generally about 7 and the solubility product of their hydroxides is small, they have an insignificant migration ability in natural waters [2]. The mobility or migration ability of an element may be expressed by its coefficient of migration in water (ratio of the average contents in water and in the earth's crust) which is $\sim 1 \times 10^{-5}$ for RE in river water [3], or by its coefficient of thalassophility (ratio of the element content in seawater and the Clarke content in the lithosphere) which is in the order of $n \times (10^{-5}$ to $10^{-7})$ for RE [4] or 1×10^{-5} for Y and La each and 4×10^{-5} for Ce [5]. Among the RE, La is the most similar to Ca. Taking the migration ability of Ca as 100%, the calculated respective ability for La and Y is 0.15% and 0.1% in seawater and 19.7% and 2.7% in hydrogencarbonate–Ca surface water [6]. According to their $Me_{susp.}/(Me_{susp.} + Me_{sol.})$ ratio, describing the mobility of a metal in water, elements can be arranged in a series from low mobility (with a high ratio) to high mobility. During transfer from river through coastal to open–ocean water, the ratio decreases, since the main part of terrigenous (clastic) suspended material is deposited at the coastal and peripheral parts of the oceans, and thus in the central part soluble forms predominate with only minor terrigenous material. Certainly, dissolved organic matter forms complexes with the elements and thus increases their solubility in seawater. For some RE, the following series of mobility in river and seawater is given by the ratio $Me_{susp.}/(Me_{susp.} + Me_{sol.})$ (susp. = suspended, sol. = soluble) [7]:

	element	mobility in %
river water	La, Y	95 to 99
	Ce	80 to 95
seawater	Ce, Lu	20 to 50
	Y, Eu	10 to 20
	La	5 to 10

A higher solubility of RE is favored in all carbonate solutions with alkali metals compared to hydrogencarbonate solutions for which an essentially weaker solubility of the light RE occurs, and complexation of RE is higher in K– than in Na–carbonate solutions. Thus partitioning of RE occurs due to different solubilities in alkaline hypergene carbonate and hydrogencarbonate solutions, heavy RE having a higher solubility and a higher ability to migrate in comparison with the light RE [8]; refer also to a more extensive migration of yttrian RE due to higher solubility of hydrogencarbonate and organic complexes compared to the analogous complexes of the cerian earths [9].

Generally, trace elements may be removed from water and concentrated/deposited by several means. They may be: (1) adsorbed to clays, hydroxides, or organic carbon; (2) contained in the lattice of degraded clays; (3) precipitated as a sulfide; (4) removed by organisms and subsequently entombed in the sediment; (5) physically concentrated as heavy mineral placers (e.g., zircon, monazite, etc.); or (6) combined in the form of organometallic complexes [32]. Obviously, the third and sixth mechanism is of no importance for the RE as can be seen from the examples given in the following sections of this chapter. To quantify the removal of individual RE from seawater, or the net effect of Ce oxidation during removal, a modified version of a vertical scavenging model (using a diffusion–advection process and having been developed for other trace elements in [10]) leads to scavenging rate constants Ψ_{RE}/Ψ_{Lu} (Ψ = first-order scavenging rate constant) relative to the most conservative element (least changed in content) Lu, and does not need the various assumptions (e.g., an absolute value of the upwelling velocity) necessary for derivation of an absolute scavenging rate constant (given in years) in the original version [11].

Based on a surface complex formation model describing the adsorption of ions at hydrous oxide interfaces, it is shown that for tri– and tetravalent cations (including Y, La, Ce, Pr, Nd, and Lu), which usually form hydroxyl complexes in natural waters, the partitioning between solid and liquid phases in the oceans (C_{op}^i/C_{sw}^i = concentration ratio of element i in oceanic pelagic clay and seawater) or in rivers (C_p^i/C_r^i = concentration ratio of element i in river-suspended particles and river water) shows a broad maximum or even a slightly negative correlation with the relative bond–strength between cations (M^{z+}) and the oxygen of the hydrous oxide surface, or with the first hydrolysis constant $^*K_1$ for the reaction $M^{z+} + H_2O \rightleftharpoons h\text{-}O\text{-}M^{+(z-1)} + H^+$ (as is shown in simplified plots of log $^*K_1$ vs. log C_{op}^i/C_{sw}^i or log C_p^i/C_r^i with the details of complex formation of cations in water and on the hydrous oxide surface ignored; data for C_{op} from [12] and for C_r from [13]). The log $^*K_1$ is highly correlated to the ionization potential I (minimum amount of energy required to remove the least strongly bound electron from a gaseous atom or ion) and moderately correlated to the ionic potential or surface charge of ions. The ratio C_{op}/C_{sw} and the mean residence time in the ocean (τ) of an element are inversely related if τ is defined as $(V \cdot C_{sw})/(S \cdot C_{op})$ with V = volume of the ocean and S = mean sedimentation rate of pelagic clays; for other definitions of residence times, see following paragraphs. The surface complex formation model appears to work quite well both in river and marine environments [14].

The RE concentrations in seawater are far below the solubility product of their hydroxides, they are in an undersaturated state [15]. Compare also that lanthanides belong to the catego-

ry of depleted elements in the oceans according to their relative oceanic enrichment factor <0, calculated as log(concentration in seawater)-log(concentration in river water) [16]. Elements with the highest degree of undersaturation would be the most reactive in the marine environment [17] which is evidenced by their short **residence times in seawater.** Calculated according to $t_A = A/(dA/dt)$ (with A = total amount of the element in the oceans, dA/dt = the amount of the element introduced into or precipitated from the oceans per unit of time, assuming a steady state and a supply of 2×10^{15} g/yr. of material with a RE content similar to that of igneous rocks), the residence times in years are as follows: La 440, Ce 80, Pr 320, Nd 270, Sm 180, Eu 300, Gd 260, Ho 530, Er 690, Tm 1800, Yb 530, and Lu 450 [18]; based on a supply of material with a RE content corresponding to the North American-shale composite, the residence times are: La 210, Ce 48, Pr 180, Nd 180, Sm 180, Eu 160, Gd 280, Ho 440, Er 430, Tm 630, Yb 390, and Lu 570 [19]. More recently, the oceanic residence time of RE has been estimated to be on the order of a few hundred years or less [20], e.g., for Nd a very short residence time [21] of <100 years is suggested [22]; compare also other residence times for Nd below and on pp. 66/7. Due to the preferential enrichment in mineral structures, cerian RE have significantly lower partition coefficients ($K_y(sw)$) and shorter mean residence times ($\bar{t}_y$) in the oceans than yttrian RE. The logarithms of the partition coefficient and the residence time for individual RE are as follows [16]:

cation type	cation	$\log \bar{t}_y$ [1]	$\log K_y(sw)$ [2]
RE(Ce)	La	3.31	−5.69
	Ce	2.63	−6.48
	Eu	3.53	−5.63
RE(Y)	Gd	3.47	−5.52
	Y	—	−5.95
	Lu	3.83	−4.90

[1] Calculated from river input of dissolved material. Residence times an order of magnitude lower are obtained if the particulate loads in river water and in seawater are also taken into account. — [2] Recalculated from data given in [13].

Elements which are significantly depleted in the oceans relative to rivers (including RE) have a mean oceanic residence time (qualitatively describing the facility with which elements in seawater are made insoluble) less than the time of $\sim 10^3$ years required for a single stirring of the oceans. These elements are deposited very rapidly (in geological terms) on entering the oceans and therefore show a heterogenous oceanic distribution. In the following, calculated mean oceanic residence times ($\bar{t}_y$) of Y and RE are listed (predicted from the equation $\log \bar{t}_y = a_0 \log K_y(sw) + b_0$ with $K_y(sw) =$ seawater/rock partition coefficient and a_0, $b_0 =$ linear regression fitting parameters; note that subscript y denotes an arbitrary element). A well-stirred ocean at steady-state condition is assumed (for theoretical details, see original paper) [23]; observed $\bar{t}_y$ values are from data of [13], if not otherwise noted (calc. = calculated, obs. = observed):

				$\bar{t}_y$ in 10^2 yrs.			
	Y	Ce	Pr	Nd	Sm	Eu	Gd
calc.	5	3	8	10	8	10	10
obs.	75 [*]	61 [*] 4.3	20.8	25.7	2.14	33.9	29.5

Table [continued]

	Tb	Dy	Ho	$\bar{t}_y$ in 10^2 yrs. Er	Tm	Yb	Lu
calc.	10	20	10	10	10	10	20
obs.	33.9	—	67.6	67.6	67.6	67.6	67.6

*) Estimated from sedimentation rates.

In a reassessment, new linear regression fitting parameters for the calculation of $\bar{t}_y$ are introduced which only marginally alter the observed direct correlation between $\bar{t}_y$ and the electronegativity function Q_{YO} ($= (x_Y-x_O)^2$ where x is the electronegativity of the subscripted element) [24]. A residence time of RE in seawater of $\sim$2000 years is calculated, based on the transport of material via plankton to deep water in the Gulf of Aquaba and the southern Atlantic Ocean [25]. However, if the residence time is less than the time required for one stirring revolution of the oceans, as is shown, e.g., for La, then $\bar{t}_y$ cannot be interpreted strictly as a residence time [26].

The minimum residence time of $\sim$1 yr. for La relative to aeolian input (τ_{La}) in surface seawater from one station in the northern Atlantic Ocean is estimated from theoretical considerations (assuming a steady state and ignoring horizontal transport) if all RE are leached from the aeolian input; τ_{La} would be $\sim$6 yrs. if only 15% of particulate La dissolves. Another approach to estimate residence times is made by comparing the RE fractionation below and in the mixed layer of ocean water. As the Yb/La ratio decreases by a factor of 3.2, the upper limit of τ_{La} in the mixed layer (uppermost 100 m of the ocean) is about one-third (6.2 yrs.) of the residence time for the mixed-layer water ($\tau_{H_2O} \sim$20 yrs.). Corresponding residence times of Ce and Eu are shorter or longer, respectively, than their positions in the RE series might imply (see table below). Residence times with respect to river input alone are much too long, but a major atmospheric input will readdress the balance (see Chapter 9). Thus, overall RE may reside in the oceans for $\sim$500 yrs. before being scavenged, but are regenerated on average five times before finally being buried and thus have residence times with respect to river input of $\sim$2500 yrs. The residence times of the light RE are especially shorter. Residence times for some RE according to different methods of calculation (for details, see original paper) are as follows [27]:

part of ocean, basis of calculation	residence time in yrs. La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
surface ocean relative to aeolian input									
maximum	6.2	4.4	6.6	7.8	19	11	17	20	20
minimum	0.97	0.87	1.0	0.93	1.1	1.1	1.2	1.3	1.2
overall ocean relative to									
river input	1500	720	1100	1100	910	1200	1400	2000	2000
aeolian + river input	240	110	450	220	470	300	340	420	410
sediment output	690	400	620	600	460	720	810	980	970

Compare fairly long residence time of RE in the northwestern Atlantic surface water (depth 10 and 48 m) indicated by a heavy RE enrichment with Lu/La ratio about four times higher than in shales [28].

An actual residence time of Nd in seawater higher than the above estimates (see p. 65) is assumed if a part of the RE entering the oceans is isolated from chemical contact with seawater, as is indicated, e.g., by the ^{143}Nd/^{144}Nd ratios of western Pacific clays, providing

that cation exchange between pelagic clay and seawater is the controlling factor of the Nd isotopic composition in seawater. If the RE within particulates are isolated completely from seawater, the residence time of Nd may be as long as 3100 yrs. [29]. Approximate limits of the residence time of Nd (τ_{Nd}) in seawater can be calculated from variations of the Na/Nd ratio in crustal rocks (CR) and river water (RW) relative to the ratio in seawater (SW) and the residence time of Na in seawater (τ_{Na}). According to the equation $\tau_{Nd} = \tau_{Na}[(Na/Nd)_{CR}/(Na/Nd)_{SW}]$ (with $\tau_{Na} = 4.8 \times 10^7$ yrs., $(Na/Nd)_{CR} \sim 1000$, and $(Na/Nd)_{SW} = 3.5 \times 10^9$) a lower limit of ~ 15 yrs. is calculated. Compared with a τ_{Nd} range of 400 to 2000 yrs. (based on literature data assuming that only a small part of Nd eroded from the continents enters the oceans as dissolved components of river water) it is evident that more studies are needed to determine the fluxes of RE to the oceans to further define the residence time of Nd, which may be substantially greater than estimated previously. To maintain the clear distinctions of $\varepsilon_{Nd}(0)$ between individual oceans (see pp. 46/7), τ_{Nd} must be considerably shorter than the mixing time of the oceans [30].

According to their relative residence time R_0 in the ocean (ratio between the residence time of a given element (t_x) and the residence time of water (t_{H_2O})), RE have been subdivided into depleted elements with $R_0 < 0.1$ (La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb) and unchanged elements with $0.1 < R_0 < 10$ (Ho, Er, Tm, Yb, and Lu). Due to their mean oceanic residence times being less than the time required for a single circulation of the oceans (~ 1500 yrs.), the depleted elements are deposited, and their behavior in the estuarine zone is likely to be controlled by particulate removal which is usually due to a coagulation–flocculation process involving humic acids or hydrous Fe oxide colloids with which they may be associated. The rate of removal will depend in part on the affinity for inorganic ligands. The mean concentrations of the unchanged elements are not altered so strongly on transfer from river to oceans; however, they often are actively cycled by the biota and consequently will show marked spatial and temporal variations in concentrations [31].

For an influence of residence time on the Ce anomaly in seawater see pp. 191/2.

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7.3.2 Migration, Removal, and Precipitation in Seawater

7.3.2.1 Migration

The mobility of Y and RE in seawater varies laterally and vertically and is dependent on several factors such as the physico-chemical properties of the elements, and the amount and composition of suspended matter in water, as well as biological productivity. As is shown in the following, the forms of migration for Y and RE can be of inorganic or biogenous type (see pp. 70/1).

Rare earth elements pass through the oceans in adsorbed or insoluble forms rather than in true solution [1]. The active migration of RE in surface waters of continental and coastal marine basins is mainly determined by sorption processes [2], and migration of La, Ce, and Eu primarily in suspended form is indicated by comparing the elemental composition of bottom and suspended sediments from the Gulf of Riga, Baltic Sea [3]. On the average, 99.81% of RE migrates in suspended form and only 0.19% in solution from rivers into seawater (with a higher soluble amount for the heavy RE; for details see p. 11) [4]. The lithogenic clastic forms of the hydrolyzing elements (including Y) in suspended matter are supplemented by more mobile forms arising from biological absorption of the elements from seawater and also from sorption on small particles of suspensate [5]. Rare earth elements not associated with suspensions (particles $>0.7 \, \mu$) or organisms migrate in solution and account for the great mobility of the RE in the oceans, their transport being governed by hydrological and hydrochemical factors [6].

The particulate flux of RE to the oceans is governed by the sedimentary trap in the pericontinental zones. Since the concentration pattern of RE from river to sea shows no significant variation in the Gironde estuary, France, it is suggested that they are either lattice-held or quantitatively poorly reactive in the estuary [7]. A dominant continental com-

ponent is indicated for RE in seawater and sediments from the Pacific Ocean (offshore Monterey, California, and the Galapagos ridge crest) and from four locations in the Sargasso Sea, Atlantic Ocean, suggesting that at least some of these very insoluble elements are capable of breaching the estuarine environment and entering the oceans [8].

Dissolution of settling particles transports RE within the upper 500 m of the water column at one station in the northeastern Atlantic Ocean, as can be inferred from the approximately linear correlation between nutrient level (contents of PO_4^{3-}, NO_3^-, SiO_2) and Nd concentrations. A more rapid decrease of nutrients relative to RE in the particulate phase during dissolution of settling particles in deep waters is indicated by a marked change in the slope of the correlation due to a relatively greater rate of increase with depth in Nd concentrations as compared to PO_4^{3-} or NO_3^- [9]. Refer also to transport of RE to depth by particulate biological material which is supported by the slight similarity between the shale-normalized pattern of trivalent RE in deep-water ferromanganese nodules and foraminifera. A biogenic mechanism for the transport of RE to the sediments is supported by the higher concentrations of RE in the Pacific compared with the Atlantic Ocean and the similarity in both oceans of the RE distribution and the distribution of NO_3^- and PO_4^{3-}, two essential nutrients in the biological cycle, both increasing with depth. Sinking of organic matter may represent a significant flux of RE to the sea floor where they possibly may be incorporated into authigenic phases of pelagic sediments (see pp. 75/8) [10]. Since the RE profiles are dissimilar to the profiles both of phosphate (reflecting near-surface regeneration of soft tissues) and of silicate (reflecting deep-water regeneration of hard skeletal materials), except that all increase with depth (see pp. 39/40), a simple nutrient-like behavior of RE in seawater is considered to be unlikely for one station at 28°01′N, 25°59′W in the Cape Madeira abyssal plain, northern Atlantic Ocean. While for waters below the mixed layer (>100 m) the behavior is nutrient-like (i.e., light RE following Si and heavy RE following P), surface waters do not behave in a nutrient-like manner (unlike RE, both silicate and phosphate show near-zero concentrations). From the general depth trends of RE, P, and Si contents and of alkalinity, it follows that planktonic material cannot account for the deep-water enrichment of light RE (for heavy RE little data are available), that RE contents in foraminiferal carbonate only account for the heavy RE enrichment, and that diatom algae can readily account for both light and heavy RE enrichments. Large particles from sediment traps show a large excess of RE compared with the levels needed to satisfy the deep-water enrichments, as is suggested by the RE/P, RE/Si, and RE/Ca ratios of this material. Hence it is proposed that the RE are selectively removed from solution in surface waters by scavenging, with a more efficient removal of the light RE compared with the heavy RE (consistent with a heavy RE enrichment due to the increasing stability of complexes with seawater ligands or with a differential adsorption of RE on solid phases, see p. 32). While fractionation of the trivalent RE shows a maximum at the base of the mixed layer, indicating that the surface removal processes are restricted to this zone, the negative Ce anomaly develops at a depth of 500 m or more, pointing presumably to the oxidation of Ce^{3+} to the less soluble tetravalent state. In addition to surface removal, there is tentative evidence of deep-water removal below ~2 km, as is indicated by the negative curvatures in plots of RE vs. the conservative tracers temperature or salinity. However, the deep circulation of the Atlantic is complex, and deep-water scavenging is not necessarily implied [11]. Although the increasing trend of individual RE (except Ce) with depth slightly resembles the distribution of nutrients (especially silicate) at the station mentioned before and at one station in the Sargasso Sea, northwestern Atlantic Ocean, it is suggested that most of the processes governing the RE transport cycle are different from those controlling the nutrients, and any RE incorporation by biogenic phases does not seem essentially to control the vertical distributions. In the upper water column, RE and nutrient profiles diverge appreciably. While

the RE continue their linear increase up to the surface, the nutrients decrease to very low values. Removal of Lu is slow for depths below 1000 m compared with local renewal rates of the deeper water masses, since Lu shows a strong positively correlated linear relationship vs. silicate (an approximately conservative tracer in the deep northwestern Atlantic Ocean). Efficient scavenging for the lighter RE relative to Lu, however, is indicated by plots of the other RE vs. silicate showing increasingly negative curvatures with decreasing atomic number which, together with the heavy RE enrichment, is consistent with adsorptive scavenging over the entire water column combined with a release at or near the sea floor. Based on a modified version of a vertical scavenging model, preliminary calculations for deep water ($>$1000 m) suggest that the rate of removal for La and Pr is about twice that for Lu, but about four times that of Lu for Ce. Thus the change in oxidation state approximately doubles the removal efficiency for Ce in the Sargasso Sea. Oxidative scavenging removal in surface water also causes a decrease in extent of the observed positive Ce anomaly (see pp. 38/9) and Ce itself in the offshore direction [12].

A complex transport mechanism on a short time scale which does not depend on factors influencing local temperature and salinity variations is suggested for Nd (and Sm) in seawater from the Drake Passage, from the Bellinghausen Plain, and from the central Pacific Ocean, since Nd concentrations exhibit a regular increase with depth (see pp. 42/3). Removal of Nd from near-surface waters by settling particles (with continuous resolution during settling) coupled with vertical transport or circulations might provide a net effective local source of increased Nd concentrations at depth [13]. Refer also to complexities in the transport mechanisms of the RE into and out of seawater, indicated by enrichment factors $f_{Sm/Nd}$ (relative to a chondritic uniform reservoir; for details see original paper) in seawater and ferromanganese sediments from the Pacific Ocean which range for seawater between -0.39 and -0.421 (or -0.5 as based on data from [14] and [15]) and for ferromanganese sediments between -0.2 and -0.4. The ratios of seawater are typical of continental values, but the variation of $f_{Sm/Nd}$ in the sediments is not consistent with a steady-state model for the input vs. output of elements in seawater [16]. Some type of particle transport of Nd and Sm to deplete the surface and enrich the deep waters is required to account for the concentration gradients observed at one station in the northeastern Atlantic Ocean (see pp. 42/3) [9].

As shown in experiments with radionuclides added to seawater from the equatorial Pacific Ocean, the migration of [144]Ce and [91]Y in seawater depends on the state of the isotopes, specific adsorption laws, colloid formation, and other factors influencing their behavior in solution. Further, secondary dissolution, mineralization of suspended matter, and biological processes contribute to the migration of radionuclides in suspension (i.e., the amount retained by an ultrafilter). The quantities of [144]Ce and [91]Y extracted by suspension depend on the properties and granulometric composition of the suspension (see p. 28) [17].

Inorganic scavenging or biological uptake can also be responsible for the conveyance of RE from surface to deeper waters (see p. 43) [14]. Vertical biogenous transport by diatoms in Antarctic waters and by foraminiferal planktonic organisms north of the zone of the Antarctic convergence obviously produces a RE deficiency in surface seawater, e.g., in the Indian Ocean near the Princess Ragnhild Coast, Antarctica [18]. A significant influence on the vertical distribution of RE by biological action occurs only in areas of high productivity and high density of organisms, usually located near continents with upwelling water or addition of nutrients from continental runoff [19]. Refer also to the settling of faecal pellets and aggregates as the most important vertical transport mechanism of several elements (including Eu) from the surface to the depth of oceans, while direct settling of planktonic detrital materials and finely suspended particles is shown to be an unimportant transport

mechanism in the northern Atlantic Ocean for the biophile elements La, Ce, Sm, and Eu, which show in marine plankton enrichment factors $E^i_{Al} \gtrsim 10$ (E^i_{Al} = concentration ratio of element i to Al in the sample compared to this ratio in oceanic pelagic clay) [20]. Faecal pellet flux is a major contribution to the biogenic vertical transport of Ce, Eu, and other elements in Mediterranean surface seawater off Monaco, thus possibly being an important factor influencing their oceanic residence time. The degree to which faecal pellets and other biogenic debris transport their trace element load to depth will be a function of trace element regeneration time for these sinking materials [21]. Sorption and absorption of most of trace elements from seawater by organic matter can be factors keeping their contents ' constant in the ocean. The influence of sorption is ascertained by the corresponding coefficients of migration in water and coefficients of thalassophility (see p. 63) of most of the trace elements (including RE) [22].

Two biological transport mechanisms of RE from surface to deep waters are suggested: (1) the source in deep waters may be solid phases resulting from the death of organisms or from the formation of metabolic debris which fall through the water column and undergo oxidation; (2) dissolved species may be adsorbed onto the disorganized masses of organic matter resulting in a net transfer from the upper to the lower water layers [23]. A rather simplified model for the transport of metals (including RE) by plankton and pteropod tests (trapping some trace elements) into the deep ocean is as follows: During dissolution of the $CaCO_3$ of the tests below the carbonate compensation depth, small Fe-rich flocks, carrying the RE, will be released to the water column. Although the insolubility of these flocks at all depths of normal ocean environment will not return the metals into true solution, the extremely small size of the flocks (on the order of tenth of microns) will assure that they will behave as a "dissolved" phase. An authigenic component is strongly represented, if not actually dominant, in the pteropod tests, since their Ce/La ratios are lower than that ratio in any suitable detrital material and since extensive overlap exists between the ratios in pteropods and in seawater. The strong coupling of the elements Fe, Sc, La, Ce, and Th indicates that this authigenic component is carried by an Fe phase (hydrated oxide or phosphate) [24]. As a main product of nutrition, Fe probably plays a unique role as a carrier of fission products (including [144]Ce and [91]Y) and promotes their involvement in an active biological cycle [25]. Humic acids are significant in the transport of some trace elements (including Eu) in the marine food chain, as is shown in experiments with humic acids isolated from offshore sediments from the northern Adriatic Sea [26]. Due to flocculation of humic substances (mixtures of aromatic, phenolic, and carboxylic acids) comprising only a small part of the total dissolved organic matter, 50 to 80% of "dissolved" RE is removed over a salinity range of 0 to 10‰ (possibly with a fractionation of the RE) during estuarine mixing in the water of Luce Bay, Wigtownshire, western Scotland [27]. To the contrary, Er–Si relationships varying with location (as observed for seawater from the northern and southern Pacific and northern Atlantic oceans) and RE concentrations varying in waters with identical nutrient levels (as reported for Sm, Nd, Dy, and Er in the southern Pacific Ocean) contradict a simple cycling of RE with nutrients in seawater [28].

The major transport mechanism for Y and RE and some radionuclides, e.g., [144]Ce, from the mixed layer into the deeper waters of the ocean is affected through the influence of gravity on faecal pellets, moults, and carcasses with direct biological transport accounting for ≤10% of total movement toward the bottom of the sea. Where the transport by faecal pellets, moulds, and dead organisms constitutes ≥99% of total biological transport, the total RE content strongly increases with depth [19]. Associated with particles sinking at ~100 m/month or a little slower, [144]Ce is removed from seawater at various stations studied between 1956 and 1958 in the Atlantic Ocean (between approximately 40°N to 8°S and 7 to 78°W). Preferential retention of Ce in the water even at very efficient RE removal

is confirmed by high Ce/Pm ratios of two samples from Bimini Islands (Bahamas). Reduction of Ce^{4+} before adsorption may well occur near organic debris of lower density. Surfaces of large zooplankton (≥ 0.1 mm) are rarely significant in lanthanide sinking, for only <0.1% of ^{144}Ce is removed in this fraction [29]. Rapid sinking of ^{144}Ce at, possibly, a rate of 400 m/ month in deep layers of seawater collected during 1963 and 1964 around Japan is indicated by the uniform vertical distribution of the radionuclide through 500 to 6000 m thick layers [30].

Significant movement of fallout ^{144}Ce with particles between 1956 and 1960 is reported for surface water from 60 stations in the Atlantic Ocean [31]. A maximum of ^{144}Ce activity at ~700 m depth in the Caribbean Sea and in the Norwegian Sea outflow (at one station each) represents sinking populations of labelled particles (attributable to the spring 1959 delivery maximum) [32]. Refer also to ^{144}Ce peaks at 700 m (in the Atlantic at 15°32′N in 1960) and at 1000 m (in the Caribbean Sea at 0°13′S in 1961) suggesting a slow sinking rate of ~1000 m/2.5 yrs. Some of the observed secondary maxima of ^{144}Ce at various depth in the latitudinal hydrographic profiles are interpreted as local concentrations of sinking particles whereas others appear to represent retention in the bodies of plankton swarms. The very high RE concentration at 100 m in 1961 indicates that the RE, after introduction, can have had no significant vertical velocity other than due to water movement [33]. In contrast, biological or particulate settling of ^{144}Ce is considered to be an insignificant factor for three vertical profiles in the northern Atlantic Ocean, where <5 to 10% of the measured radioactivity is in the insoluble fraction (separated by 0.3 μm filters), and a constant ratio of soluble to insoluble forms occurs throughout the water column [34]; see also depth profiles sampled in 1968 and 1969 for the northern Pacific Ocean, where ^{144}Ce removal from the water column by particulate settling or biological activity seems to be insignificant, since the quantity associated with the particulate fraction is <10% of the total activity [35].

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7.3.2.2 Removal and Precipitation

Seawater

Scavenging of RE in seawater is very efficient, as the concentrations of RE in seawater are among the lowest observed for stable elements which is not due primarily to low crustal abundances [1]. Barite (see p. 78), the minerals of manganese nodules (see pp. 75/7), phosphorites, and ocean–ridge hydrothermal (metalliferous) sediments (see pp. 77/8) are the most important hydrogenous minerals removing RE from seawater [2, p. 358]; compare that assimilation by ferromanganese minerals at least partly causes undersaturation of RE in seawater [3]. Various complex and interrelated factors determine removal or precipitation of elements from the parent solution. Two simultaneous and often equally important factors contribute to the fractionation of RE between a precipitate and its solution: (1) crystallographic effects of cation substitution, and (2) solution effects of ion complexation [4]. Generally, the incorporation of the RE into hydrogenous minerals or biogenic phases and simple inorganic precipitation resulting from the concentration limits of the insoluble salts of the RE can remove RE from seawater and control their concentrations in water [2, p. 354]. However, their solution chemistry alone cannot be the reason for effective removal of the RE from seawater, since their concentrations in water are several orders of magnitude below the concentration limits set by their insoluble salts and their effective complexing should favor higher concentrations in sea– than in river water. The differences in behavior

within the RE series (enrichment relative to chondritic minerals of the cerian against the yttrian earths in most hydrogenous minerals [5]) confirm ion capture to be effective in removing lanthanides from solution; particularly where new minerals are formed in the oceans, lanthanides are enriched in various authigenic phases (e.g., ferromanganese nodules, phosphorite, glauconite) and in foraminiferal tests [1]. Compare also different RE patterns of seawater, both their deviation from those of river water and their fractionation from shales, caused by the RE distribution among authigenic phases (e.g., ferromanganese nodules, amorphous metal hydroxides, barite, phillipsite, montmorillonite) and biogenic phases of marine sediments (e.g., $CaCO_3$ tests of planktonic organisms, fish-bone apatite), i.e., phases that formed directly from seawater [6, pp. 292/3]. Since ion capture only becomes apparent when the elements are held in a reservoir with a long retention time (at least several thousand years), it is likely that oceans are depleted in lanthanides relative to the world's rivers. The preferential enrichment of light RE (La through Eu) in most hydrogenous minerals probably arises because the effect of the increasing polarizing power of the cation on going from La to Lu is outweighted by the higher coordination number which enables the larger, lighter cations to accomodate in oxide lattices, thus favoring their capture [1].

The **intensity of RE precipitation** with, or uptake by ferromanganese nodules or metalliferous sediments is **influenced** by the **sedimentation rate** prevailing at the special deep-sea area. Thus the entire mid-ocean ridge system is considered as a significant sink for RE, if the accumulation rate of Fe is as great as >30 mg/cm^3/1000 yrs. [7]. Coprecipitation of RE with Fe and Mn hydroxides and sorption on these hydroxides in seawater and at the sediment-water interface, being effective when sedimentation rate decreases, result in an accumulation of RE (especially of Ce due to its oxidation) in ferromanganese nodules and red clays from the Pacific Ocean with the RE first following Mn and then following Fe from the littoral (Uchina Bay, Japan) to the pelagic zone (northwestern basin) [8, p. 1185]. With long exposure on surfaces at great ocean depth (with very slow sediment accumulation rates), resorption of RE, released from the dissolving apatite of fish debris which incorporates RE from seawater (see pp. 78/9), causes addition of large amounts in the secondary layer of manganites to any RE already taken up in manganese nodules, while in pelagic clays and oozes with a higher rate of sedimentation the fish debris is largely preserved and micronodules are lower in RE [9]. Sorption of RE by slowly coagulating and precipitating gels of Fe and Mn hydroxides with a surface adsorption considerably higher than that of terrigenous suspended matter presumably occurs in ferromanganese and carbonate (mainly foraminiferal) oozes from four stations in the Bauer basin, East Pacific Rise, which show RE contents very similar to those of seawater. Extremely low sedimentation rates, indicated by the very low RE contents in seawater ($\sim 20 \times 10^{-6}$ g/t) in the presence of high RE accumulation in the ferromanganese and foraminiferal oozes (~ 1000 and 200 g/t, respectively) seem to favor the precipitation of dissolved RE. Moreover, the residence time of terrigenous suspended matter is insufficient for complete extraction of RE from seawater, and due to considerably higher surfaces, the sorption capacity of Fe and Mn gels is often higher than that of terrigenous suspension [10]. Compare also p. 77 for a higher adsorption of RE by metal-rich sediments from areas with slow sedimentation rates. Precipitation from the overlying waters during slow deposition, besides diagenetic changes in postdepositional stages, essentially causes the increased RE concentrations in red clays from the abyssal hill province of the northwestern Atlantic Ocean (depth >5000 m). These precipitations can be termed as the hydrogenous phase of the sediments (hydrogenous precipitation) [11].

As is only exemplified in the following, **removal** of Y and/or RE from seawater occurs mainly **via settling particles** comprising, e.g., inorganic suspensions (clay or mineral fragments, colloidal precipitates of oxides or hydroxides of Fe and Mn) or biogenous detritus;

direct removal from solution is minor. Compare direct precipitation from seawater as the source of RE (except of Ce) in sea-floor sediments (ferromanganese nodules and associated sediments) considered unlikely, since seawater is highly undersaturated with respect to trivalent RE salts, and rather association with settling particles is suggested as primary RE input (see p. 69) [12].

Bound to inorganic suspensions, RE fall down to sediments with two different groups of minerals: The larger part enters sediment with terrigenous clay particles; the second part of RE reaches the sediment with colloidal hydroxides of Fe or Mn and other compounds which are introduced partly from shore and partly formed in the water by oxidation, hydrolysis, and coagulation of dissolved elements. Due to leaching of Y and heavy RE from the clay particles during sedimentation (see p. 2), the solid phase of clay material falling down to the ocean floor is relatively enriched in elements of the cerian subgroup, and during sedimentation of the colloidal hydroxides, light RE (mainly Ce) are extracted from the water [13, p. 593]. Association with settling particles (Fe-oxyhydroxide coatings and flocks associated with biogenous debris) is supposed as the primary input of RE to the sea floor [12]. Rare earth elements adsorbed to large particulate matter will tend to sink to the bottom or to the appropriate density layer within the water column and, except for bottom feeding organisms, will be essentially removed from further distribution [14]. During horizontal and vertical migration, suspended matter assimilates the preferentially hydrolyzed Ce^{4+} and intermediate RE from shelf water by sorption and transports them to the bottom, as is found at one station from the Californian coast, Pacific Ocean [15]. As mineral fragments and as suspension, Y and Yb (and Ce?) are carried to the bottom sediments of the Black Sea [16].

Removal from seawater by calcite and possibly other biogenic phases followed by a subsequent transport to sediments is suggested for RE in ferromanganese nodules of the Pacific Ocean because their shale-normalized RE distribution patterns show a similarity in depth for the change between shallow- and deep-water nodule type at ~3500 m with the depth of ~3700 m for the lysocline (depth at which $CaCO_3$ is significantly soluble); the RE patterns are without extense fractionation for the shallow-water nodules above 3500 m and show strong fractionation for the deep-water nodules [17].

The removal of La and Ce from seawater, or their transfer from surface to deeper waters or to the sediments may be enhanced by the biological cycles in which phosphate is regenerated by decomposition of organic detritus descending through the water column. The solubility of phosphate appears to control their concentrations in seawater, keeping them at a remarkably low level [18]. Some unidentified solid, such as organic matter which later is dissolved and not necessarily the apatite itself, possibly carries RE to the sediment where they are sorbed to the surface of microcrystalline apatite of skeletal debris (see p. 74) [9]. During sedimentation of sapropelites in the Black Sea, organic matter extracts RE dissolved in water. Since Y forms the most stable complex compounds with organic and inorganic anions, suspended organic matter sinking down to the bottom for the most part combines with elements of the Y subgroup [19, pp. 154/5]. Ingestion by organisms, absorption to surfaces or ion exchange, and removal to deeper waters by processes of sedimentation occur for [144]Ce in the Gulf of Mexico [20]. Inspect further pp. 78/9 for RE introduction into sediments with biogenous matter.

Incorporation of RE in manganese nodules occurs **by direct precipitation** of the RE^{3+} hydroxides from seawater at an essentially constant rate. Since RE concentrations of nodules appear to be a function of the logarithm of the solubility product rather than the solubility product itself, and since trivalent RE are undersaturated in seawater with respect to their hydroxides by several orders of magnitude, it is suggested that this relationship is a kinetic

rather than a thermodynamic one and that the rate-determining step for RE incorporation is the adsorption of the trivalent RE ions on the surface of the nodule. The tendency of RE to precipitate may, however, be influenced by other factors such as the degree of complexation with organic ligands or carbonate species, since the thermodynamic properties of the RE depend on ionic radii. Variations in the absolute abundance of RE in seawater seem to have no effect on their abundance in manganese nodules, since only minor variations in absolute contents occur between different water masses [21]. Direct precipitation from seawater probably occurs for RE in one deep-water ferromanganese nodule from the Pacific Ocean (at 40°14'N, 155°52'W; depth 5000 m). A much higher abundance of Ce relative to La and Pr in the ferromanganese nodule than in seawater or phosphorite is explained by oxidation of Ce and its incorporation by the MnO_2 lattice [22]. Incorporation of RE present in seawater is reported for deep-sea manganese nodules and micronodules from the abyssal hill province, northwestern Atlantic Ocean (depth >5000 m) [11]. Precipitation from seawater supplies Eu into pore waters from the western manganese nodule belt between the Clarion and Clipperton fracture zones, central Pacific Ocean [23].

Introduction of RE together with colloidal Fe and Mn hydroxides is supposed for ferromanganese nodules from 23 stations at various parts of the Pacific and Indian oceans which show a dominant accumulation of Ce and Pr and a relative impoverishment of Y, owing to processes taking place in the ocean water (see also p. 75). While, depending on the conditions, Fe hydroxide acts as a coprecipitant for RE in solution to variable degrees, the relation of lanthanides to hydrated MnO_2 may be sorption and of a chemical nature. Lanthanides apparently may enter Mn minerals (chiefly polypermanganates) in nodules, replacing divalent elements such as Cu, Co, Ni, Ba, and others [13, pp. 592/3]. Compare also incorporation of RE in ferromanganese nodules by coprecipitation with Fe and Mn hydroxides after the RE having been released from inorganic particles, as is stated for two stations each from the Pacific and Indian oceans. During this development a RE fractionation occurs due to the increasing stability of RE to form complexes with increase of its atomic number. Thus the light RE show a greater tendency to coprecipitate with hydroxides and the heavy RE remain longer in solution. The preferential hydrolysis of Ce compounds, caused by oxidation of Ce to the tetravalent state, accelerates its passage into bottom deposits [24]. The differences in shale-normalized RE patterns for various shallow- and deep-water nodules from the Pacific Ocean (see p. 75) may be explained partly by coprecipitation of the RE with Fe and Mn phases; the positive Ce anomaly in nodules and the negative Ce anomaly in seawater are the main evidences for a precipitative origin of RE in nodules [17]. The suggestion that RE in nodules may be derived from terrigenous material settling onto nodules [25] rather than from seawater is not supported by shale-normalized RE distribution patterns for shallow-water nodules from both the Pacific and Atlantic oceans [6, p. 297].

A control of the RE balance in seawater by precipitation with manganese nodules is indicated to some extent by the RE abundance pattern for seawater with a negative Ce anomaly, while the nodules have a positive anomaly. However, steady-state considerations (assuming the enrichment factor $f_{Sm/Nd}$ of -0.390 for the North American shale composite as the correct value for $f_{Sm/Nd}$ in the dissolved component of RE runoff from the continents) indicate that ferromanganese sediments cannot be the only major sink for RE in the oceans. There must be other sedimentary deposits with $f_{Sm/Nd}$ values (and Ce abundances) which would balance the RE abundance in ferromanganese deposits with those in ocean water [27, pp. 133/4]. See also, ferromanganese deposits being of minor importance in the overall Nd budget of the oceans, while pelagic clays are considered as the largest repository of Nd. Although ferromanganese nodules possess a higher Nd concentration than pelagic clays, the ratio of the Nd accumulation rate in nodules relative to that in pelagic clays

is estimated to be ~0.05 and is further limited to be ≪0.05 by the more restricted occurrence of nodules. If the dissolved Nd concentration in seawater is at steady state, the excess Nd in river water (with the dissolved Nd concentration over one order of magnitude higher than in seawater) must be sequestered by particulate matter in the oceans and may constitute a portion of the Nd in the hydrogenous component of pelagic clays [28].

Enrichment of Ce by preferential adsorption or other mechanisms is evidenced by the lower La/Ce ratios (generally < 1) for ferromanganese crusts from the Juan de Fuca ridge, the East Pacific Rise, and the Mid–Atlantic Ridge [26].

While most ferromanganese nodules preferentially remove Ce from seawater, the chemically and mineralogically similar metalliferous sediments may preferentially reject Ce [29]; e.g., the different behavior of Ce with a positive anomaly in four samples of ferromanganese nodules from the northern Pacific Ocean and a negative anomaly in metalliferous sediments from the East Pacific Rise is a function of the mechanism of RE removal from seawater [30]. Coprecipitation or sorption from seawater probably incorporates RE into metal–rich sediments from the East Pacific Rise at 12° to 14°S, from the Bauer basin (~70 km east of the East Pacific Rise), and from the central northern Pacific Ocean. Slow sedimentation rates, indicated by the high percentage of fish debris, permit more adsorption of RE from seawater. The chondrite–normalized RE abundance patterns for six of the eight samples from the central northern Pacific and from the Bauer basin are similar to that of seawater; a Ce depletion is evident in all samples, which distinguishes these sediments from typical ferromanganese nodules. Due to the reported spread of Ce/Sm ratios in seawater (1.6 to 6.5 from [31]), it is uncertain whether these metalliferous sediments with low ratios actually have been depleted in Ce relative to seawater, but the data suggest some fractionation of Ce relative to the other RE during their coprecipitation with Fe hydroxides [29]. Incorporation of small amounts of La and Ce from seawater into (pseudo)hydrothermal*) Mn– and Fe–rich crusts (Mn–rich crusts from the Mid–Atlantic Ridge and from the Galapagos spreading center, Fe–rich deposits from the Dellwood seamount, northeastern Pacific Ocean, and from a seamount at 19°S near the East Pacific Rise) with only minor subsequent enrichment of Ce probably results in a Ce depletion in the shale–normalized RE patterns of these crusts with high La/Ce ratios approaching the seawater value of 2.8 (after [31]), and the rapid accumulation rate of these deposits may inhibit the subsequent Ce enrichment which occurs to most other ferromanganese deposits [26]. Introduction of RE by coprecipitation with amorphous Fe–Mn phases, precipitating near hydrothermal vents, without fractionation is reported for metalliferous sediments from the Bauer basin, coprecipitation of RE with Fe hydroxide being a well–known process for removing these elements from solution without fractionation [32]. Adsorption or coprecipitation with the Mn–Fe fraction of one sediment core from the East Pacific Rise at 17°S removes most of RE without fractionation from seawater [33]; refer also to incorporation of RE without significant fractionation in crestal sediments, East Pacific Rise, with the adsorption of RE from seawater onto hydrated ferric Fe phases (representing up to 15% of these sediments) possibly accounting for the greater fraction of RE. Within flank sediments, showing a covariance of Eu and Al_2O_3, the contribution of RE from seawater is significant [7]. Scavenging of light RE by oxidation products of Mn and Fe discharged with hydrothermal effluents causes fractionation of RE in seawater from the northern (Marianas Trench at 18°N and a mounds field some 60 km west of the main extrusion zone) and southern part of the Pacific Ocean (East Pacific Rise at 19°S), as is supported by normalizing the results from 2500 m depth at these vent sites to data from the northern Atlantic Ocean and by the following lines of evidence: (1) shale–normalized

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*) Being not of primary magmatic origin, but formed from seawater circulating along cracks through hot basaltic depositions.

RE patterns from the Marianas Trench become more light-RE depleted with increasing depth, and the Ce anomaly becomes increasingly negative with depth; (2) the trends of the East Pacific Rise depth profiles for Nd, Sm, Dy, and Er suggest anomalously low concentrations below 2 km at off-axis stations and no anomalously high concentrations at on-axis stations; (3) scavenging by hydrothermal products is plausible because Mn anomalies persist at depths below 2 km even at locations 800 to 1400 km away from the vent fields, establishing a link with hydrothermal activity on the rise crest, and, in addition, fine-grained Fe colloids can possibly be important scavengers at these remote locations; and (4) differences between on- and off-axis stations disappear above 2 km, and the variability below this depth decreases systematically with increasing atomic number, suggesting a greater degree of scavenging in the plume with the light RE being more reactive. Since precipitation of Mn and Fe oxides is ubiquitous in natural waters, fractionation of RE during the scavenging process may well fix the RE pattern of seawater [34].

Precipitation or fixation of RE from a seawater source is responsible for RE enrichment and the Ce depletion in phosphorites [38]. Direct precipitation from seawater is assumed for RE in one oceanic phosphorite sample (depth 100 m) off the continental shelf of Magdalena Bay, California [22], and introduction of RE from bottom water and sludge into a phosphorite nodule through an exchange mechanism (Ca $\rightleftharpoons$ RE) occurs at one station (No. 4214) at the California shelf, since shelf mud is in contact with seawater for a long period of time [15].

Precipitation of RE from seawater also occurs with microcrystalline barite deposition in deep-sea or shallow-marine sediments, and both formations subsequently (and not always clearly distinguished from, or distinguishable) may suffer diagenetic changes. In general, deep-sea barites have large RE concentrations (as do other authigenic deep-sea minerals) and display the chrondrite-normalized Eu minimum, but not the negative Ce anomaly of seawater; barites of shallow-marine origin display lower total RE contents. This RE distribution can be attributed both to crystallographic constraints of substitution, and to solution complexing of RE in the precipitating medium, for details see original paper [4]. See also diagenetic barite in "Rare Earth Elements" A6a, 1988, pp. 129/30.

Very low RE concentrations in salts (polyhalite and anhydrite) of the Salado formation, southeastern New Mexico, reflect the composition in the seawater during deposition. A negative Ce anomaly, though not nearly as pronounced as in seawater, and an enrichment of heavy relative to light RE probably are caused by ion exchange between the above minerals and the evaporite brine solution (which most probably exhibited a strong negative Ce anomaly). Light RE probably were leached from accompanying detrital clays or replaced by Ca^{2+} and Na^+ from the brine solution [40].

Rare earth elements can further be **introduced** into oceanic sediments **with** suspensions of **biogenous matter**, as is shown for various parts of the Pacific and Indian oceans [13, pp. 581, 593]. Growth of calcareous plankton tests is considered as the main way in which organisms remove RE from seawater, for Globigerina tests have higher RE contents than seawater. In addition, RE in Globigerina are fractionated mutually as in sediments in general, and not as in seawater, suggesting that the light RE preferentially are incorporated by these plankton tests [35]. In contrast, the shale-normalized RE pattern of biogenous calcite (foraminifera) from an eastern Pacific core sample does not show a depletion in heavy relative to intermediate RE and is indistinguishable from that of seawater, suggesting that planktonic carbonate does not preferentially incorporate any RE [12]. Since RE follows Fe concentrations in pteropod tests from the southern Atlantic Ocean and the Gulf of Aquaba and in bulk plankton samples from Long Island Sound, northern Atlantic Ocean, coprecipitation of RE by either hydrated ferric oxides or ferric phosphate is assumed [36]. Superficial

sorption of RE (? partly during diagenetic alteration, see "Rare Earth Elements" A6a, 1988, p. 135) from seawater is reported for microcrystalline apatite of skeletal fish debris which contains several percent of RE in the apatite phase [9] and for settled biogenous debris on the sea floor [12]. In view of the strong chemical affinity between P and RE, extraction by bone phosphate of the entire spectrum of RE characteristic for seawater occurs especially at the contact sediment–bottom water in red clays of the littoral (Uchima Bay, Japan) and pelagic zones of the northwestern Pacific Ocean. Sediments enriched in bone phosphate have a high total RE content with an enrichment of yttrian earths and especially of Y [8, pp. 1178, 1183]. In contrast to oceanic ferromanganese nodules with their RE associated with hydroxides of trivalent Fe and precipitation (especially of Ce and Pr) with polyperman- ganate at the bottom (see p. 76), in ferromanganese nodules at four stations of the Black Sea high concentrations of phosphate introduced into muddy and near–bottom waters during nodule formation lead to a bonding of total RE and, especially, of Y (since Y concentrations in water are higher than those of the other RE dissolved in water) [19, pp. 157/8]; see also accumulation of Y in Black Sea ferromanganese nodules which probably is due to processes taking place in the bottom layer of water (with a considerable concentration of soluble phosphates) which causes the RE (mainly the heavy yttrian earths) dissolved in water to become fixed. Subsequently, RE enter ferromanganese nodules together with Fe phosphate [37].

Besides the biogenous matter, biological processes cause environmental changes by which trace elements (including Y and La) are removed and precipitated in the Gulf of Sevastopol, Black Sea, USSR. The overall cycle depends on salinity of water, on pH of water and suspended matter, on the amount of heterotrophic bacteria in suspension, on content of organic phosphor, and on other factors [39].

Processes of sorption, precipitation, and coprecipitation may cause local **accumulations of radioisotopes** (e.g., of ^{144}Ce) in sediments, plankton, and other materials suspended in the marine environment. The diffusion of radionuclides into the sediments, expressed by the diffusion coefficient (for details see original paper and [41]), is influenced by nuclide concentration and granulometric composition of sediment and suspended matter in water, by salinity, and by the electric potential (describing the attraction of the radionuclides on the surface of sediments) [42]. See also, radionuclides of Ce in seawater are absorbed, coprecipitated, and involved in ion exchange processes [43], and particles of ^{144}Ce precipi- tate on the sea bottom and are difficult to dissolve [44]. Locally, deposition of ^{144}Ce and ^{91}Y on the sea floor (of the Black Sea?) occurs after the death and autolysis of marine benthonic organisms (red, green, and brown algae, mollusks, mussels, lobsters, and crabs) [45].

As follows from experiments using the most frequent silts from the Pacific and Indian oceans, the retention of ^{144}Ce and ^{91}Y from seawater by oceanic bottom sediments, depend- ing directly on the surface area and chemical composition of the sediment, is a complicated physical and chemical process including the mechanical retention of colloidal particles of the elements by silts and the sorption of the radionuclide fraction which is present in seawater in truely dissolved form. Almost complete retention of ^{144}Ce and ^{91}Y occurs with deep-sea silts containing >50% kaolinite in the finely dispersed fraction, ~85% is retained by tropical pelitic radiolarian ooze with >16% amorphous silica (radiolaria and diatoms), and 80% by low-calcareous argillaceous silts. Sediments with high Ca content and volcanic sands have the lowest retention of ~60 and ~75%, respectively [46]. The reaction of ^{144}Ce with sediments from 59 stations in open–ocean and coastal areas is probably connected with precipitation, since the half-time of sorption (10.5 ± 4.4 days) is relatively large, and later the ^{144}Ce is bound more strongly with another compound, resulting in more of the element being adsorbed on the sediment particles. The change in reaction on the sediment

particles may be related to aging (refer also to the next paragraph). Depending on sediment and radionuclide characteristics, [144]Ce shows highest affinity for the fraction 8 to 16 μm which is somewhat different from the general opinion that the affinity for a size fraction should be proportional to the surface of the particles [47]. For the influence of salinity on sorption and hydrolysis, see pp. 24/5. The degree of coprecipitation of fission product elements (including Y and Ce) also depends on the character of the solids, being colloidal or particulate [48], and, as is shown for microamounts of [91]Y added to prefiltered seawater, a change in the physicochemical properties of radioyttrium in seawater will be reflected by the values of its adsorption and by accumulation coefficients [49]. Artificially added [144]Ce is separated from [91]Y predominantly as a precipitate, as shown in experiments with prefiltered water from the Pacific Ocean [54] and coprecipitation of [144]Ce and [91]Y (added to seawater from the tropical Pacific Ocean) with ferric hydroxide occurs in the case of simultaneous penetration of Fe and the above radionuclides into water [55].

The association with a preformed solid phase rather than precipitation from solution as a simple solid phase is reported for [141]Ce added to pretreated natural seawater samples, since the fraction of the added Ce tracer that appears as particulate in filtration or centrifugation experiments depends on the source of the water, and this property may be altered by storage. Reaction of [141]Ce, added to precentrifuged seawater (to remove natural particles) may occur with the anions of seawater to produce insoluble compounds; Ce^{4+} reacts strongly with hydroxide and can form the extremely insoluble hydroxide. With added concentrations of 0.01 and 0.1 μg/L Ce^{3+}, 10 to 20% of Ce is removed by centrifugation; aging for 16 days does not increase the quantity removable, and with 10 to 50 μg/L, 80 to 90% of Ce is centrifugable, most of this would also settle out in five days as observed in replicates not centrifuged. Addition of Ce^{3+} produced centrifugable particles more readily than Ce^{4+} additions [50]. Compare that the equilibrium between natural and radioactive Ce introduced into seawater from Nakaminato City on the Pacific coast of Japan and into artificial seawater may be achieved after a fairly long time [51], since the residence time of natural Ce which precipitates as CeO_2 in the sea is $\sim$80 yrs. [22].

The precipitation percentage of trivalent [144]Ce from aged seawater increases with increasing pH value [52]. For ^{90}Y added to natural seawater, at low pH values a predominant extraction by $Zn(OH)_2$ is observed as against $Fe(OH)_3$ and $Al(OH)_3$, while with increasing pH the difference in the effectiveness of the collecting hydroxides is of the order Fe < Al < Zn, and is < 10% at pH 10 [53].

Differences in deposition rates of particles on the sea bottom are indicated by a wide variation for the ratios of mean concentration of [144]Ce in coastal sediments and seawater for the period 1964 to 1972 for samples from Tokyo Bay and Ibaraki, Fukushima, and Fukui prefectures, all Japan. Compared with other radionuclides (e.g., ^{90}Sr and ^{137}Cs), [144]Ce shows the highest degree of removal from seawater, although concentrations in seawater were nearly in the same order of magnitude during the period studied which is considered to be due to the different physico-chemical behavior of each nuclide in seawater. The ratios (range and mean) of the [144]Ce concentrations are as follows: 3700 to 22000, 13000 for the Tokyo Bay area; 500 to 70000, 19000 for the Ibaraki area; 2600 to 80000, 23000 for the Fukushima area; and 7500 to 110000, 41000 for the Fukui area [56]; refer also to the accumulation of [144]Ce in coastal sediments for Tokyo Bay in 1964 to 1965 with the [144]Ce/^{90}Sr ratio in the sediments being higher than that in seawater along Fukushima prefecture [57].

Estuaries

In estuaries precipitation on particulates usually affects elements with low dissolved transport index (ratio of dissolved transport to total transport) such as the lanthanides [58].

Coprecipitation with ferric hydroxide can explain the decrease of dissolved RE in estuaries [59]; see also pp. 21/2. Possibly, RE can be removed by adsorption onto particulate matter (including faecal pellets of marine organisms) along the traverse of a stream and in the estuarine zone before reaching the ocean and are carried to the sediments [27, p. 136]. In areas of mixing of fresh water and seawater, adsorption of several radionuclides due to inorganic and organic processes possibly occurs in places of extensive scouring and resuspension of bottom sediments by tidal currents. Simultaneously precipitated colloids of Fe and Al may act as scavengers for [144]Ce, which would be rapidly sedimented in estuarine regions by precipitation, coprecipitation, as well as biological activity [60]. The deposition of fine particles in suspension leads to an obvious accumulation of sparingly soluble active isotopes (including [144]Ce) in the area around lightship 'Elbe 1', North Sea. The concentration of [144]Ce in sediments reached twice that in solution, although the incomplete removal of solids by centrifugation may indicate a higher value of the concentration factor [61]. The coarseness of the sediment as well as salinity and pH of water influence the adsorption of [144]Ce and [91]Y on the bottom sediments of estuarine water of Osaka Bay, Japan, the highest adsorption occurring in the silt and clay fraction. Higher distribution coefficients in clay sediment occur at a chlorinity of 14 g Cl/L and a pH of 7.3 in the water. Distribution coefficients of [144]Ce in very fine sands being somewhat higher than in medium sands and the reverse observation for [91]Y are not explained [62].

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7.3.3 Migration, Removal, and Precipitation in Non-Marine Waters

7.3.3.1 Migration

In river water, RE migrate mainly in suspended form, while transport as colloids (mainly of the light and intermediate RE) and in dissolved form is of minor importance. The migration in suspended form is favored by a decrease in carbonate concentration of river water (by degassing or absorption during biological processes) and partial coagulation of the dissolved RE during dilution with meteoric water (accompanied by a breakdown of carbonate complexes, especially those containing the light RE). The highest migration ability in suspended form is reported for the light RE which are concentrated in feldspar, mica, and the pelitic fraction of clay material [1]; refer also to the important role of RE transport in suspended matter in rivers [2, p. 148]. Rare earth elements are carried to the oceans almost entirely by river-particulate matter (see also pp. 11/2), as is indicated by the dissolved transport index DTI (i.e., the ratio of dissolved transport to total transport) which is $<1\%$ for RE in several major world rivers and the Garonne River, France. Arranged in decreasing order, the percentage of dissolved transport for the individual RE is as follows: 0.7 for Tm; 0.5 for Lu; 0.4 for Gd; 0.3 each for Er, Ho, La, Nd, Sm, and Yb; and 0.2 each for Ce, Eu, and Pr. Related to an average Al content, the flux ratio $FR = \Phi_{theor.}/\Phi_{obs.}$ for the poorly soluble elements Ce, Eu, La, Nd, Sm, Tb, and Yb and their enrichment factor in suspended matter are near unity (since FR becomes the enrichment factor for elements with $DTI < 10\%$), i.e., the total amount carried by rivers is equivalent to the theoretical flux value. The fluxes are defined as $\Phi_{theor.} = [x]_{fr.}M_{pm.}[Al]_{pm.}/[Al]_{fr.}$ (with $[x]_{fr.}$ = average content of element x in the surficial fresh rock, $[Al]_{pm.}$ = average Al content in river-particulate matter, $[Al]_{fr.}$ = average Al content in the surficial fresh rock, and $M_{pm.}$ = annual river-particulate discharge to the ocean $\approx 15000 \times 10^6$ t/yr., $[Al]_{pm.}/[Al]_{fr.} = 1.36$) and $\Phi_{obs.} = [x]_{sol.}Q + [x]_{pm.}M_{pm.}$ (with $[x]_{sol.}$ = average dissolved content of element x in rivers, Q = annual river water discharge to the ocean $= 37400$ km^3/yr.) [3]. River-suspended matter carries between 99 and 99.9% of RE in the Gironde River, France, with the amount of RE in the solid phase possibly decreasing to 64% in the upper course of the river and decreasing even more in filtered water (e.g., ground water) [4]. At four stations of the rivers Thames and Kennet, Great Britain, La is transported mainly in particulate form [5]. The migration forms of La, Ce, and Sm, prevailing in surface waters of the Norwegian rivers Glomma (Fetsund) and Nitelva (Lillestrøm) (temperature $\sim 1\,°C$, pH ~ 6.9) and of the Lake Trehørningen

(Baerum) (temperature 13 °C, pH ~ 6.7), are colloidal or suspended particles which might consist of (hydr)oxides (particularly Al and ferric hydroxide) or basic salt micelles carrying the adsorbed or coprecipitated ions or molecules. Migration of Ce both as positively and negatively charged colloidal particles is found in electrophoresis experiments. Migration as free cations is minor (the observed high retention by ion exchange filtration of 64% is probably due to the filtration effect or to adsorption of colloids and molecules rather than to ion exchange of free cations) [6]. Migration with the clastic products is reported for Y in small rivers of the upper Vishera basin, northern Urals, USSR [7].

Due to self-purification of river water by sedimentary suspended matter and biological circulation, RE contents in river water of the upper Volga basin, USSR, are lower than in other natural waters (e.g., ground and subsurface waters). Moderate mobility is shown for La and Sm, weak mobility for Ce and Eu, and very weak mobility for Yb and Lu [8]. In contrast, negligible rates of radioisotope removal from water by self-purification are indicated by the distribution of [144]Ce and other radionuclides in sediment, water, and ice of an experimental water basin, depending on the physico-chemical state of individual isotopes in water [9].

The morphology of the source area can influence the relationship between RE transport in suspension and solution of rivers, transport in solution being more important in rivers flowing over plains (e.g., Volga River) than in mountain rivers (e.g., Ural River, both USSR), caused by a lower amount of suspended matter [10].

Among dissolved carbonate and hydrogencarbonate complex compounds in fresh water, maximum solubility occurs with the heavy RE, Y, and tetravalent Ce [2, p. 142]. Increasing stability from Ce to Yb is found for coordination compounds with fulvic acids (with a fixed molecular composition) in surface waters, leading to RE differentiation during precipitation (see p. 88) [11]. Compare a marked mobility of [144]Ce in surface waters indicated by the ability to form soluble undissociated complex compounds with oxalic and citric acids, e.g., $Ce[Ce(cit.)_2]^{3-}$ [12]. In surface waters of the humid zone, most of dissolved RE are transported in the form of carbonate complexes; organic compounds can also play a role, while migration as simple chlorides or sulfates (except possibly for La) hardly can be supposed, since such compounds hydrolyze in nearly neutral solutions [13]. Higher mean contents of La (7×10^{-6} g/L for 19 samples) than Y (1.5×10^{-6} g/L for 13 samples) in $HCO_3^- - Ca^{2+}$ surface waters (with an average mineralization of 80 mg/kg) from the Korosten granite, northwestern Ukrainian Shield, indicate that La in natural waters of this region is more mobile than Y. This is also corroberated by the coefficients of aqueous migration $K = m \cdot 100/a \cdot n$ (with m = content of the element in surface water, a = mineralization of the water, n = average content of the element in rocks in %) which are 2.9 for La and 0.4 for Y (erroneously given as 1.37 in the original paper) [14].

Migration of RE in ground waters is favored in acid sulfate waters and in alkaline waters enriched in F^- and CO_3^{2-} ions. The migration ability of RE in alkaline media corresponds to that in acid media which are both higher than migration ability in neutral media [15]. See also, lanthanides migrating as complex compounds mainly of the carbonate type $[Ln(CO_3)_nF_m]$ in alkaline natural waters (ground waters from agpaitic nepheline syenite massives, pegmatites, and sulfide-RE deposits, thermal waters from crystalline rocks, and saline soda lakes). Increased migration ability of Ce for alkaline waters, while Y shows higher migration in slightly acid and almost neutral solutions [16], and favorable to RE migration are hydrogeochemical media in the order alkaline > acid > neutral [17]. An alkaline pH favors migration of RE because complexes are formed which shift the pH of hydrolysis to the alkaline side and prevent hydrolysis. For example, in alkaline waters of the Kola Peninsula and Central Asia, both USSR, RE show an increased mobility and tendency towards accumu-

lation [18]. The probable forms of migration for RE in ground waters are RE^{3+}, REF_n^{3-n}, $RE(OH)_n^{3-n}$ in acid media, and $[RE(F,CO_3)_n]^{q-}$, $RE(CO_3)_n^{m-}$, $REPO_4^o$ [15], or $[RE(CO_3)_n$-$(F,OH)_m]^{q-}$ in alkaline media [17], and $[RE(CO_3)_n]^m$ and $[RE(CO_3)_nF_m]^q$ in alkaline subsurface waters. Since the coefficient of migration in these waters is in the order of 0.n to n, RE are highly mobile [19]. The migration capacity of RE is attributed to complex formation. An increasing amount of carbonate complexes of RE, due to an increase of carbonate in water, promotes higher stability of RE in solution, as is shown by a correlation between RE and $\Sigma(CO_3^{2-}$ and $HCO_3^-)$. The most favorable medium for migration of yttrian and cerian RE are Na^+ waters rich in carbonate ions. An increase of cerian RE mobility is indicated in alkaline subsurface waters of a weathering profile over agpaitic nepheline syenites of the Lovozero massif, Kola Peninsula, as the variable $(Ce+La)/(Y+Yb)$ ratio is higher in the waters than in rocks [20]. Migration solely as hydrogencarbonate is given for La in neutral $HCO_3^- - Ca^{2+} - Mg^{2+}$ stratal waters from the woodlands of the Ukrainian Shield, USSR, while Y, migrating in complex form, is most mobile in slightly acid HCO_3^- fissure waters [21]; see migration of Y in acid and weakly acid ground waters from the Ukrainian Shield [22]. Migration of the hydrolyzing elements (including RE) in subsurface waters can be accomplished as complex compounds with carbonate, phosphate, and oxide, as well as compounds with organic matter [23].

Migration as simple cations, compound ions, and (pseudo)colloids possibly occurs for Y, La, Sm, Dy, Er, and Yb in neutral or slightly alkaline ground waters (pH 6.5 to 8) from the Urals, from the Transuralian region, and from northern Kazakhstan, all USSR. Based on the coefficient of mobility K_x (concentration of element x in the mineral residue of water/ concentration of element x in rocks, i.e., the ratio of the regional background value of an element in the hydrosphere to its concentration in the specific water–bearing rocks), increasing with mobility, the following tentative hydrogeochemical classification can be given in an oxidizing and a reducing environment: Yb(?) is mobile with $0.1 \leq K_x < 1$; Dy, Er, and Sm(?) are slightly mobile with $0.01 \leq K_x < 0.1$; and Y and La are almost immobile with $K_x < 0.01$. Elements whose compounds are readily soluble in water (Y, La) belong to the class of almost immobile elements because most of the ions leached during weathering of the surrounding rocks are sorbed by clay minerals of the residue, and only small amounts are removed by water [24].

Moderate mobility in old (5000 to 10000 yrs.) ground and subsurface waters from the upper Volga basin, USSR, occurs for Sm, while La, Ce, and Eu have weak and Yb and Lu very weak mobility because they easily hydrolyze [8]. The mobility of Y and Yb in stratal waters below petroleum layers from the Dniepr–Donets basin, Ukraine, is dependent on the age of the surrounding rocks [25]. In well and spring waters from an area with small U and Cu–U occurrences near Monticello, New York, Ce and Y (with a low solubility in most natural waters) and some other elements belong to the immobile group as follows from R–mode factor analysis [26].

Besides in dissolved form, RE in subterranean mine waters of the $HCO_3^- - Na^+ - Ca^{2+}$ type from an undisclosed alkaline massif, USSR, migrate as mechanically suspended matter [27].

In mineralized subsurface waters (pH 2.0 to 7.8 and Eh +96 to -700 mV) from complex and chalcopyrite ore deposits of the Alaverdi region, Armenia, Y and Yb migrate as sulfate complexes or as trivalent free cations, the ratio between both forms being slightly influenced by pH and type of water [28].

A trend for migration in suspension is inferred for La, Ce, and Sm in Bulgarian hydro-therms (of various types and releasing N_2 or CO_2) from the distribution coefficients between

water and suspension. Based on an average saturation index, a transport ability of La (with respect to those of Cr and Ba) occurs with slightly soluble oxide, fluoride, and hydroxide. All hydrotherms studied are saturated with La with respect to $La(CO_3)_3$, and unsaturated with respect to LaF_3 and $La(OH)_3$, possibly reflecting a control of the elemental concentration by its presence in the mother rock. A lowered migrational ability of the studied RE (compared to the trend of other trace elements) is observed for reservoirs with higher temperatures [29]; see also, thermal waters from Plombières les Bains (e.g., the Sondage Neuf water), Vosges, France, with La concentration being controlled by its fluoride solubility (LaF_3 with a saturation index $\Omega\,0.5$, indicating saturation), while Ω for the other insoluble compounds ($La(OH)_3$ and $La_2(CO_3)_3$) is $10^{-4.3}$ and $10^{-3.2}$, respectively, indicating unsaturation [30].

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7.3.3.2 Removal and Precipitation

Removal of Y and RE from river and other waters occurs mainly by adsorption on and subsequent sedimentation with suspended matter, as can be seen from the following examples of investigations using radioisotopes.

Compared to values of the equilibrium concentration of ^{90}Y calculated from the ^{90}Sr content, the rate of ^{90}Y elimination from the water increases with decreasing depth in eutrophic lakes; other lakes (distrophic) show practically no ^{90}Y in the water. The ratio of actual concentration to equilibrium concentration in the water decreases from 0.795 to 0.382 when the water is in contact with silt from the bottom for three days (water:silt=5:1) [1]. Experiments with sediment and water from the River Var, near Nice, France, show a temporary loss of ^{144}Ce from the sediment after dilution of fresh water with seawater, followed by a shift to equilibrium systems [2]. The content of ^{144}Ce slowly settles down with suspension in lake water as shown experimentally with 10^{-5} Ci/L ^{144}Ce added to the water. Complete inactivation (100%) of the solution is attained for Ce with wood ashes while sorption is 84.2% for sand, 86.3% for soil, and 93.2% for silt [3]. Considerable portions of ^{144}Ce are insoluble in water of Japanese rivers (Agano, Edo, and Yodo) and, since it is sorbed onto suspensions and sediments, it is transported with these carriers to the river bottom. An average decontamination rate (DR $= [1-W_{CT}/W_{CR}] \cdot 100$; W_{CR} and W_{CT} are contents of radionuclide in resource (river) water and in treated (drinking) water, respectively) of 48% is calculated for three water works of the above rivers during 1962 to 1969. The greater the content of suspension, the higher the decontamination rate becomes [4]. From the total amount of ^{144}Ce supplied by atmospheric precipitation into suspension or sediment of several rivers of the Federal Republic of Germany, 0.47% is drained off via suspension. High mobility of the material deposited on the river bottom is indicated by the great differences in ^{144}Ce concentrations observed in suspension [5]. In contrast, the ^{144}Ce activity in suspended matter is about equal to that in solution for three tributary rivers of the Thames River, Great Britain [6].

In sedimentary suspended matter of river water from the upper Volga basin, USSR, Sm accumulates probably as the result of adsorption, coprecipitation, and other processes [7]. Contents of radionuclides in the sediments of various rivers of the Federal Republic of Germany reach the same values as those in the suspended matter within a few weeks

(e.g., [144]Ce in the relatively mobile suspension and immobile sediment layer of the Rhine River near Koblenz during <4 weeks), evidencing that equilibrium is attained rapidly between suspended phase and bottom sediment [5]. Precipitation or adsorption on particles is suppressed for La and Ce by the complexing effect of humus in water from Lake Trehørningen, Norway [8]. This is also corroberated by experiments using radioactive tracers added to surface water samples in the United States, comprising a wide range of hardness and geographical origin. So, lower extraction rates for radionuclides of La, Ce, and Nd in the Bayou Anacoco River, Louisiana (see table below), are due to the high content of organic matter in the water. In the Chattahoochee River, Georgia, representative of most of the waters containing an appreciable sediment load, the activities of La, Ce, and Nd are sorbed strongly on the sediments, and certain correlations in selective extraction to clay mineral type are indicated, which, however, are only indicative, the results depending on sediment concentrations and particle sizes. Calculation of the portions that were removed from solution by adsorption on suspended particles from the initial dissolved activities of [144]Ce and [140]La (using gamma-ray spectra) as well as simplified results of the portions of [144]Ce and [91]Y (counting only the resin and the sediment under conditions of similar geometry, using a scintillation detector and scaler) for the above mentioned and some other surface water samples are as follows; radioactive tracers have been added as mixtures, addition as individual isotopes is marked by an asterisk [9]:

water source, pH of water, and content of suspended and dissolved matter in ppm; sediment composition, see footnote	adsorption in % on sediments		
	[91]Y	[140]La	[144]Ce
Bayou Anacoco, Louisiana[1]; 6.2; 24 and 63	—	—	36.9
Lodgepole Creek, Nebraska[2]; 6.8; 965 and 200	—	30.5	96.9
Etowah River, Georgia; 6.9; 8 and 28	—	—	14.1*
Camp McCoy, Wisconsin[3]; 6.9; 12 and 60	—	—	44.6
Lake Allatoona, Georgia; 7.1; 3 and 20	—	—	70.3*
Oostanaula River, Georgia; 7.3; 10 and 82	67.0*	—	—
Tennessee River, Tennessee; 7.3; 15 and 80	62.8*	—	77.2*
Chattahoochee River, Georgia[4]; 7.3; 131 and 31	—	68.9	81.0
Colorado River, Utah[5]; 7.5; 299 and 350	—	—	72.0

[1] 30% quartz, 6% montmorillonite, and 2% kaolinite. — [2] 80% montmorillonite and 20% illite. — [3] 30% quartz, 24% illite, and 6% kaolinite. — [4] 44% kaolinite, 33% quartz, and 23% illite. — [5] 95% quartz and small amounts of calcite, feldspar, kaolinite, and illite.

Selective precipitation of individual RE is possible between pH 7.7 and 8.0 in fresh water (comprising the range of pH 5.5 to 8), since La possesses the highest pH of hydrolysis (pH~8) and is sharply distinguished from the other RE [10]. Since most natural waters have a pH >7, the trivalent cationic form of [144]Ce easily hydrolyzes to the practically insoluble $Ce(OH)_3$ which is sorbed by suspended matter and bottom sediments, possibly as a radiocolloid [11]. Dilution of alkaline river waters lower in their course by rivers which are not so alkaline leads to hydrolysis of RE carbonato-complexes and ultimately to a deposition of hydroxide gels. With increasing acidity, the RE precipitates redissolve and form aquo- and chloro-complexes [12]. Like solubility (see p. 84), the tendency to precipitate with fulvic acids (whose exact composition depends on pH and the metal–ligand ratio) from surface waters increases for trivalent Y, Ce, and Yb with the molecular mass, resulting in a RE differentiation with light RE, especially Ce, accumulating in bottom deposits [13].

Although F is one of the elements decomposing RE complexes and precipitating RE, in the alkaline subsurface waters of the Lovozero massif, Kola Peninsula, USSR, high concentrations of both RE and F occur, suggesting that special conditions prevail in these waters which prevent precipitation of RE [14].

Precipitation of RE from hot springs occurs with travertine or sinter formation. So, meteoric waters circulating deeply along a fault are heated and probably have been leaching elements from the country rocks and redepositing them in travertine mounds to form a low-grade mineral deposit of substantial volume at the Monroe hot springs, Utah. A representative sample of travertine taken in 1968 from the northern spring deposit contains 0.0030% Y [15]. A sulfurous sinter deposit from the Moto-yu hot spring, Nasu area, Japan, contains La 0.48, Sm 0.12, and Eu 0.02 ppm. The amount of Sm and Eu in the sinter deposit is somewhat lower than that in the contacting spring water (see p. 58); the abundance of La is almost unchanged. The anomalous behavior of Sm and Eu during the precipitation process possibly could be attributed to their presence in the divalent state in the H_2S-containing hot spring water [16], as is confirmed by distribution coefficients of RE between sinter deposit and hot spring water, which are lower for Eu and Sm by one order of magnitude than those of other RE at Moto-yu (caused by a reducing environment in the H_2S-containing acid spring), while for other hot springs of the Nasu area nearly the same distribution coefficients occur for all RE [17].

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8 Geochemistry. Atmosphere

8.1 Origin and Mode of Occurrence of Yttrium and/or Rare Earth Elements in the Atmosphere

8.1.1 General

Yttrium and/or RE are introduced to the atmosphere by both natural and anthropogenic processes. As shown in the following paragraph, both in aerosol (see pp. 93/101) and in rainwater (see pp. 102/3) they mostly originate from the earth's crust by aeolian resuspension of soil and deposited dust (both in the atmosphere over continents and over oceans), whereas the sea-surface (see pp. 101/2), volcanic activity (see p. 93), and the sun (see p. 93) are mentioned only as sources of minor importance. Also, anthropogenic activities play a minor role as local sources of RE in the atmosphere (see pp. 103/5). Artificial radionuclides of Y and/or RE in the atmosphere originate mainly from nuclear weapon tests, as is shown in only a few examples (see p. 103).

In the following, the various methods applied to identify an origin of an element and/or its type of occurrence are briefly summarized; for details see original papers:

Absolute trace element concentrations are difficult to use in identification of sources [1] (see also [2]), whereas cross correlations between absolute element contents [3], [4, p. 85], or for normalized concentrations [1] may be helpful. In addition, the value of the coefficient S of variation of an element in the atmosphere can give some indication regarding the source and is defined as $S = 1/x \left[\sum_{i=1}^{N} (x_i - \bar{x})^2/N \right]^{1/2}$ (with N = number of stations, x_i = content of element i at a particular station, $\bar{x}$ = arithmetic mean content). For instance, a small value for Lu suggests a more evenly distributed or natural source compared to La, Ce, and Sm in the atmosphere over Osaka district, Japan (August and September 1971), which have values of S intermediate between those for elements with small values and large coefficients of elements with important local sources [5].

Often used are enrichment factors, denoted EF or E_f, calculated as the ratio of the contents of an element X in air and in a reference medium, both normalized to a reference element as, e.g., Al, Fe, Sc, or Na (see examples below and pp. 93/102, 106/9, 113/5, 118, 127/8, 136). According to $EF_{crust} = (X/Al)_{air}/(X/Al)_{crust}$, or $EF_{sea} = (X/Na)_{air}/(X/Na)_{seawater}$ (subscripts denote the appropriate reference material), elements with EF_{crust} (or EF_{sea}) values <3 to 5 are considered to have approximately the same interelement concentration ratios in the atmosphere as in average crustal material (or in bulk seawater). This upper limit of enrichment factors frequently has been used for interpreting the crustal enrichment factors because the portions of trace elements in the actual crustal aerosol precursor may differ slightly from those in average crustal material [6]. Elements from other sources will have much higher enrichment factors (>10). For the calculation of crustal enrichment factors usually Si, Al, Fe, or Sc are used as reference elements. The crustal reference material usually is average rock or soil, although local rock or soil compositions are used frequently [7]. To determine the contribution of crustal weathering to any metal component of marine aerosol, Al (which comprises >8% of the average crustal material) is used as a reference element, and such factors, being near unity, suggest that crustal material is the probable source for the considered element in the atmosphere of remote areas. But there will be no characteristic difference between natural and man-made processes [8]; refer to [9] for the suitability of Al. For calculating aerosol-crust enrichment factors, bulk crustal rock [10] or (bulk) soil may be used as a reference material [11], but these factors are only a crude approximation, since the relative abundances of various rock types in the vicinity of the

sampling site may cause the ratio of crustal source elements in the atmosphere to differ somewhat from the mean crustal ratio. So the composition of crustal aerosol is somewhat dependent on the area's geology and weathering rate, crustal aerosol from different areas possibly having very different composition [12]; see also [8]. Although the concentration of Eu and other trace elements, which show relative amounts in remote aerosol particles similar to those in average crustal material, may be controlled by the long-term transport of crustal alumino-silicate particles (commonly named dust or mineral aerosol) from the continents, the crustal enrichment factors do not unequivocally demonstrate that their ultimate source is either crustal or natural, since quarrying operations and agricultural land clearing activities produce aerosol particles that are essentially crustal in composition, and also other anthropogenically generated particles (e.g., fly ash, road dust) are similar in composition to crustal material [6]. Refer to p. 104 for a somewhat inconsistent behavior of Eu and Ce in ground-level air filter samples from Chilton, Oxfordshire, Great Britain. As is shown in a compilation of world aerosol-rock enrichment factors $EF_{Fe}(X)$, elements with factors ≤ 5 are emitted primarily from natural sources and those with >5 are certainly from anthropogenic sources. Whereas Tb and Lu (with $EF_{Fe}(X)$ 0.8 and 0.9, respectively) could come from fossil fuel utilization, the elements La, Ce, Sm, Eu, Dy, and Yb (with 1.5, 1.4, 1.0, 2.2, 1.4, and 0.05, respectively) have various sources. For the calculation of $EF_{Fe}(X)$ by conversion of Al-referenced into Fe-referenced values distinguishing between two Fe fractions, see original paper [13].

More suitable than the above enrichment factor methods is a chemical mass balance approach because a quantitative estimate of each source contribution can be obtained. To calculate the mass of material derived from a source it is necessary to select a tracer element for each source (which ideally should contribute a large fraction of the total emission from this source, e.g., Pb for automobile emissions, Al for soil and fly ash) [14]. According to chemical mass balance, the observed elemental concentration pattern of aerosol is a linear combination of concentration patterns of particles from important types of sources. According to this method, the concentration of element i (c_i) in a particulate sample is given as $c_i = \sum_j m_j x_{ij}$ (with $m_j =$ fractional contribution to total suspended particulates of particles from source j, $x_{ij} =$ concentration of element i in particles from source j). A least-squares fit is usually performed with so-called marker elements to determine the value of m_j. The quality of fit can be tested by comparing predicted and observed concentrations of elements not used in fitting. Since most processes cause little fractionation among elements such as Al, Ti, Sc, Th, and RE, these elements should be fitted to within a factor of two by any resolution that predicts an approximate crustal abundance pattern for these elements (except under highly unusual conditions, e.g., RE affected by TV-tube manufacturing) [15]; see also [2]. Contents of RE are not predicted as well as for most other lithophile elements (although RE are chemically very similar to each other and usually behave as other lithophiles) for airborne particles collected in the Washington, D.C., area (see pp. 97/8), where the light RE have been slightly underpredicted and heavy RE considerably overpredicted, possibly due to an enrichment of light relative to heavy RE on suspended soil particles with respect to bulk soil [4, pp. 88/9]. Refer also to the ratio of heavy-to-light RE in atmospheric particles which is often lower than for soils or crustal abundance patterns, especially for urban particles [16]. If this were better understood, RE patterns would help to distinguish between otherwise similar components, e.g., between entrained soil and particles from coal combustion [4].

Particle size distributions are characterized by means of the mass median diameter (i.e., the diameter below which 50% of the total mass of an element is found) and can give some further indication regarding the source type of an aerosol, since condensation

and high-temperature processes are likely to produce small particles, whereas dispersion-type sources emit larger particles [9]; or, generally, particles of predominantly large size are released into the atmosphere by mechanical processes such as abrasion and wind erosion, whereas vaporization (followed by cooling and condensation) yields particles of very small size [17], and soil-derived elements are associated with larger particles having mass median diameters >1 µm [18]. Based on a compilation of Al-related enrichment factors of aerosol (from many areas of both hemispheres of the earth), it is shown that larger particles which appear to be of crustal origin (either directly or indirectly) are less enriched, and smaller ones which originate possibly from a gas phase are highly enriched. Thus, enrichment (of, e.g., La, Ce, Sm, Eu, and Dy) is related to greater mass median diameters (4 to 6 µm) [19]; note also that, the smaller the size of a particle, the higher is the enrichment factor of an element in urban aerosols (from Ankara, Turkey, and from Toronto, Canada), since larger and/or heavier particles (containing, e.g., La, Ce, and Sm) could settle down quickly due to gravitation [20]. Refer also to removal from the atmosphere on pp. 132/6.

Since only drastic geological changes can cause a fractionation of the original RE composition, crustal aerosol may be assumed to have the same relative RE concentrations as its parent crust. Thus, RE should be a suitable natural indicator to determine the origin, behavior, and fate of crustal aerosol in the atmosphere [12].

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8.1.2 Origin

Rare earth elements in the atmosphere are usually considered to have the earth's crust as their principal source [1]; e.g., crustal rocks or mostly soils, as can be seen from the examples given for aerosols over continental and marine areas (see pp. 93/9 and 99/100, respectively) or for rainwater (see p. 102). For an anthropogenic RE origin in the atmosphere, see pp. 103/5.

Based on literature data on the amount of terrigenous material entering the atmosphere (0.5 to 0.8, mean 0.65×10^9 t/yr.), a mass flux of La into the atmosphere of 6.0×10^4 t/yr. results [2].

Volcanic material generally is of minor importance as a source of RE in aerosol, as is shown, e.g., for La and Eu in two samples of atmospheric particulate matter from an active volcano on Heimaey, off the southern coast of Iceland. Both the enrichment factors of La and Eu relative to the earth's crust (normalized to Al) for lava-ash and fumarole deposits as well as for atmospheric particulate matter are near unity (the apparent depletion of La is due to the normalization to crustal abundances, while lava is typically basaltic and most basalts show concentrations of La lower than in the crust) [3]. Small enrichment with respect to volcanic ash occurs for the nonvolatile RE in suspended particles from the plume of the Augustine volcano, located ~290 km southwest of Anchorage in the lower Cook Inlet, Alaska, which show aerosol-ash enrichment factors (normalized to Al) close to unity. Samples were collected during a flight following the initial eruption on January 22, 1976, and during three flights following the second eruptive period later in February [4].

A formation in the sun is assumed for atmospheric particles collected at altitudes of 76 to 113.5 km during the night of July 31 to August 1, 1971 above Kiruna, Sweden, which contain La, Ce, Pr, Nd, Tb, Er, and Tm. The occurrence of elements with such a high atomic number at these altitudes is totally inconsistent with normal sources of cosmic dust [5].

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8.1.2.1 Aerosols of Continental Origin

In Continental Atmospheres

In "world" aerosol (the term applies to more than 100 aerosol samples analyzed by [1]), RE are indisputably of crustal origin, and no major pollution sources are known. World-aerosol enrichment factors (normalized to Al and relative to crustal material) are La 2.7, Ce 2.6, Sm 2.1, Eu 2.7, Tb 1.92, Dy 2.5, Yb 1.06, and Lu 1.95 [2]; for the corresponding Fe-referenced enrichment factors, see p. 99. A natural origin from weathered terrestrial material is inferred for La from the Sc-normalized concentration and the excess ratio $(La/Sc)_{aerosol}/(La/Sc)_{crustal\ average}$ as well as for Sm, Eu, and Tb in most of the ground-level aerosol samples collected in March 1972 at 14 sites ranging in latitude from Greenland to Santiago,

Chile. Based on the La/Sc ratio (ranging at 11 sites from 1.13 to 3.14) in most cases the local air concentrations of these elements can be represented by a mixture of ~90% basalt (La/Sc 0.9) and ~10% granite (La/Sc ~40), whereas the La/Sc ratios in aerosols over New York City (20.7), or Miami, Florida (5.83), and Chaltaya, Bolivia (3.87), indicate a higher granite component [3]; see also [4]. Of natural origin are Eu and Lu in aerosols collected in 1975 over coastal regions of the Black Sea; the average contents in aerosol coincide with those in the lithosphere [5]. An origin probably from crustal rocks is indicated by crustal enrichment factors (normalized to Al) near unity for La (3.48) and Sm (1.94) in ambient air filter samples collected for 12 consecutive days in July and August 1976 at the rural site High Point, northwestern New Jersey. In addition, the most highly correlated elements are those usually considered as crustal or soil-type material as, e.g., Sm and Ce [6]. Atmospheric enrichment factors relative to crustal material (normalized to Al) close to unity occur also for La, Ce, Sm, and Eu (2.0, 1.9, 1.8, and 1.6, respectively) in atmospheric particulates from the Boston area, Massachusetts [7].

The association with a source derived largely from crustal material is assumed for La, Ce, Sm, and Eu in atmospheric particles (collected 2800 m above sea level during a seven-week period beginning in October 1970) at a location ~400 m upwind of the Amundsen-Scott station, South Pole, Antarctica. The following air-crust enrichment factors (normalized to Al) are calculated: La 2.2, Ce 4.4, Sm 1.3, and Eu 1.9. A certain deviation from the mean crustal value of the ratio of crustal source elements in atmospheric particles may be caused by the weathering rates and relative abundances of various rock types in the vicinity of the sampling area [8]. Note also that, based on the above enrichment factors, crustal weathering is assumed as the main source of La, Sm, and Eu in aerosol (collected between October and December 1970) ~400 m upwind of the main South Pole station, Antarctica. The slight enrichment of Ce over that predicted from an average crustal source may be due to the use of an average crustal composition for normalizing rather than using a more basaltic source rock (generally richer in Ce) as it occurs in Antarctica [9]. An origin predominantly from the earth's crust is also assumed for La, Ce, Sm, and Lu in aerosol samples collected between December 1974 and February 1975 at a location 5 km upwind from the new Amundsen-Scott station, South Pole, which show aerosol-crust enrichment factors (normalized to Al) near unity [10].

A primarily crustal origin is indicated by a high correlation with total suspended particulate (TSP) and high cross correlations for La and Sm in 41 and 8 aerosol samples, respectively, collected between June 1971 and May 1978 from Beer-Sheva in a semiarid zone on the Negev desert border, Israel (see table). In addition, aerosol-crust enrichment factors (normalized to Fe) of <7 for La at low, normal, and high contents of total suspended matter confirm its crustal origin. The contents of La and Sm in aerosol with different amounts of TSP in the atmosphere of Beer-Sheva during normal meteorological conditions are given in the table on p. 95; exceptions are indicated [11]. Note also that La, Ce, Eu, and Sm are background elements due to dust that covers the area in aerosol samples collected simultaneously in the city of Beer-Sheva and 40 km away in a region called Shivta, Negev desert [12]. As is to be expected for elements of crustal origin, aerosol enrichment factors relative to crustal material or to the average local surface soil (both normalized to Sc) are close to unity for lithophilic elements such as La, Sm, Eu, and Tb in semiremote background aerosol collected between May and September 1975 (7 m above ground) at three sites near Colstrip (a large coal-fired power plant with a coal mining operation) in the semiarid rangeland area of southeastern Montana [13].

Crustal dispersion is presumed as the main common source of RE in atmospheric aerosol samples collected ~10 m above ground at three sites in the Osaka prefecture, Japan. The

TSP in $\mu g/m^3$	content in ng/m³ La	content in ng/m³ Sm	TSP in $\mu g/m^3$	content in ng/m³ La	content in ng/m³ Sm
104	5.6	—	556 [1), 2)]	19	—
196	6.9	—	124	3	—
169	11	—	541 [2)]	5.6	—
148	8.8	—	164	—	1.7
243	5.9	0.57	90	2.5	—
140	8.6	—	1600 [2)]	9.3	8
121	4.7	—	50 [3)]	—	0.5
160	6.6	0.8	680 [2)]	22	3.9
233	3.3	—	168	3.1	—
97	1.0	—	109	3.8	1.2
610 [2)]	5.5	—	412 [4)]	13	—
581 [2)]	4.5	—	5080 [4)]	143	26
154	3.5	—	—	—	—

[1)] Additionally, the sample contains 3.8 ng/m³ Yb and 2.8 ng/m³ Lu. — [2)] Sampling during dust storm. — [3)] Sampling during rain. — [4)] Sampling during Sharav conditions (very dry and hot winds).

spread of the La-normalized concentrations lies mostly between those for sandstone and granite (the predominant rocks in the vicinity of Osaka). Assuming that the relative atmospheric RE contents are linear combinations of their relative contents in sandstone and granite, it is predicted that aerosol produced at the air/land interface of the vicinity of Osaka metropolitan area and of an urban residential area is composed of crustal material with a composition similar to that of sandstone, while aerosol originating in the vicinity of the rural area studied probably consists of 49% sandstone-like and 51% granite-derived component [14].

A derivation from soil is confirmed for the elements belonging to the Fe cluster (calculated from linear correlation coefficients and containing elements with high intercorrelations among the group members), such as Ce and Sm and probably also La and Eu, for aerosol samples collected in July 1970 at nine stations from the San Francisco Bay area, California, because the ratios between the observed concentration in aerosol and the calculated concentration from known elemental abundances in soil (normalized to the observed Fe content, assuming essentially all the Fe to be soil-derived) are satisfactorily close to unity (see below). In the following are given the calculated soil-derived contents (based on the known relative elemental abundances in soil), the calculated and observed total average concentrations (from eight stations only; station No. 5 is deleted) as well as the ratios of observed to calculated concentrations; values in parentheses are based on crustal rock abundances [15]:

element	average content in ng/m³ calculated from soil	average content in ng/m³ total calculated	average content in ng/m³ total observed	ratio observed/ calculated content
La	1.8	1.8	1.4	0.8
Ce	2.2	2.2	2.5	1.1
Sm	(0.2)	(0.2)	0.22	(1.1)
Eu	(0.04)	(0.04)	0.05	(1.3)

A natural origin from soil is shown for La, Sm, Eu, and Tb by their aerosol–average soil enrichment factors (normalized to Fe) being close to unity in aerosol samples collected in July 1973 at one site in, and at three sites downwind of St. Louis, Missouri. The average enrichment factors for the four sites are La 1.4, Sm 1.8, Eu 1.3, and Tb 1.3 [16]. Small particles from the earth's surface, blown into the atmosphere by wind, are considered to be the main source of La, Ce, and Sm in ground–level aerosol (20 m altitude) collected during the period May to June 1971 at Heidelberg, Federal Republic of Germany, as follows from aerosol–crust enrichment factors (normalized to Na) of <3 (La 2.8, Ce 2.3, and Sm 2.5) [17], or is suggested by the arithmetic mean for relative contents which agree to within a factor of 5 with those in the earth's crust [18]. However, rather low linear correlation coefficients within the "earth's crust group" (including La, Ce, Sm, Eu, Mn, and Sc) seem to contradict a hypothesis of a common source (unless analytical errors are large). Using the data of [17] for some of the "earth's crust" elements (e.g., Ce and Sm) a good correlation with some of the "anomalous" elements such as In, Cs, and Cd becomes evident [19]. Soil dust is presumed to be the predominant natural source for Ce in air particulate samples collected monthly (starting January 1, 1976) at 1.5 m above ground in the savanna at Bagauda (11°36′ N latitude), northern Nigeria, as is inferred from correlations between element pairs (Ce–Fe and Ce–Sc show some of the highest correlations) as well as from the dry deposition velocity, indicating a very uniform aerosol with small particle size for all elements. This is also consistent with well–mixed material originating from the Sahara desert [20]. As follows from correlation coefficients calculated from a classification of elements into groups of common origin, a good correlation occurs for Fe, Al, and Sc (which show high contents in the lateritic soils at the investigated area) with Ce and Eu in five series of aerosol samples collected ~5 m above ground during the period 1970 to 1971 in the whole Ivory Coast [21, pp. 1104/5, 1108/9]. Derived from soil are La, Ce, and Eu in six aerosol samples each for northerly and southerly wind directions collected at a remote site of the Sudan (~150 km southwest of Khartoum) during October 1973 (when there is a distinct shift in direction of prevailing winds in the Gezira province each year). Enrichment factors relative to soil (normalized to Fe) for the north and south wind–aerosol, respectively, are: La 1.16 and <1.6, Ce 1.04 and 1.26, and Eu 0.75 and 0.85 [22]. An origin from soil (or rocks) for La and Ce in aerosols over Tashkent, USSR (collected at five sites for different times of the day in February 1980), follows from enrichment factors relative to soil (with Sc as reference element) between 1 and 10. In addition, the contents of La, Yb, and Lu change insignificantly (two–to–four times) which presumably is due to their origin in soil [23]. Dust from soil or rock weathering (silt particles) is the source of La, Ce, Sm, Nd, Eu, Tb, Yb, and Lu in aerosol samples collected at 25 m altitude in April 1980 (partly during a dust storm) over Beijing, China, which show air–crust enrichment factors (normalized to Sc) close to unity [24]. Note also that Ce is derived mainly from weathered rocks in the atmosphere above Moscow, USSR [25].

A probably terrestrial origin as soil dust (and no concentration by industrial processes, refer to p. 97) is indicated for Ce in air particulates collected continuously during 1974 (the majority of monthly samples has been bulked for quarterly analysis) at seven sites in the United Kingdom representing rural and more industrial, but no urban areas. Using the 1972 and 1973 factors for comparison, for the period 1972 to 1974 Ce shows air particulate–average soil enrichment factors (normalized to Sc) close to unity (0.4 to 1.3, mean 0.8) [26]. A terrestrial origin of Ce as soil dust also occurred in aerosol at these stations during the years 1976 [27, p. 5] and 1977 [28, p. 6] as well as at five non–urban sites during 1978 [29, pp. 1, 6]. Ranges and calculated mean values of the air particulate–average soil enrichment factors (normalized to Sc) of some RE at seven stations in 1976 [27, p. 13] and 1977 [28, p. 13] as well as at five of these stations in 1978 [29, p. 13] are as follows:

element	enrichment factors		
	1976	1977	1978
La	1.5 to 4.4; 2.6	1.2 to <3; ~1.7	<0.9 to 2.5; ~1.6
Ce	0.6 to 0.7; ~0.7	0.9 to 1.2; 1.0	0.9 to 1.3; 1.1
Sm	1.2 to <2; ~1.5	1.3 to 1.8; 1.5	1.1 to 2.0; 1.4
Eu	2.3 to 2.8; 2.6	2.2 to 2.8; 2.6	1.6 to 3.9; 2.3

Certain elements (e.g., Ce) have approximately the same concentrations relative to Sc in ground-level airborne dust (<100 μm, collected during 1970 and 1971) at Wraymires, near Lake Windermere, Great Britain, as in local soil (Grizedale series) and average soil from which aerosols are raised by passing winds [30]. And some natural contribution from soil is suggested for the lithophilic elements (included Ce and Eu) in some 5000 ground-level air filter samples from Chilton, Oxfordshire, central southern England (collected during the period 1957 to 1974 and bulked over three-month intervals) [31]; see also p. 126. Enrichment factors relative to the earth's crust (normalized to Al) and close to unity indicate the presence of La (2.1) and Sm (1.6) in soil-like ratios in aerosol samples (particulates with an aerodynamic diameter >100 μm have been screened) collected monthly in the period 1973 to 1975 at the Jungfraujoch, Bernese Alps, Switzerland [32].

Based on correlations between air enrichment factor E_f and dry deposition velocity V_g for element pairs, an origin from soil and/or industrial sources is proposed for Ce in ground-level (1.5 m above ground) airborne dust (of <150 μm diameter) collected continuously during 1972 and 1973 at seven rural to semirural stations throughout Great Britain (from 51 to 60° N latitude). Whereas Ce-Fe and Ce-Sc pairs, both with low E_f and high V_g (>0.5), indicate a direct terrestrial origin as soil or mining dust and an association with the same particle, Ce-Sc pairs, with both dissimilar E_f and V_g, indicate an industrial and terrestrial origin, each element in the pair probably is collected on different particles (but meteorological conditions similarly affect transport to sampling site, and sampling downwind of an industrial source could result in an element-pair dissimilarity of this nature) [33]; but refer to [34] which suggests a derivation from soil for Ce in ground-level airborne dust (collected monthly during 1972 on filters retaining particles of diameters up to ~150 μm) at the same seven sites in the United Kingdom.

It is inferred from chemical element balances that soil is the major source of La and Ce in ten ambient particulate samples collected on 0.4 μm pore filters during summer 1974 (including a broad range of meteorological conditions) at four sites in Washington, D.C. The predicted contributions from five sources (derived from weighted least-square fitting) and the predicted and observed total contents, in the aerosol samples are as follows [37]:

element	contribution in ng/m³ from					total content in ng/m³	
	soil	marine	coal	oil	refuse	predicted	observed*)
La	1.1	<0.001	0.44	0.036	0.004	1.6	1.9±1.7
Ce	1.4	<0.001	0.86	0.030	0.016	2.3	3.4±3.1

*) Uncertainty is standard deviation of a single observation.

Solely soil (for La and Ce) and soil together with coal (for Sm, Eu, Yb, and Lu) as major source is inferred from chemical element balances (with the components soil, sea salt, limestone, motor vehicle emissions, and particulates from combustion of coal, oil, and refuse) for RE in whole-filter samples collected at seven urban and three suburban sites

in the Washington, D.C., area during about one month in August and September 1976. The predicted and observed contents in mg/m^3, respectively, are: 1.0 and 1.5$\pm$0.1 for La, 1.5 and 2.0$\pm$0.2 for Ce, 0.12 and 0.20$\pm$0.02 for Sm, 0.028 and 0.029$\pm$0.003 for Eu, 0.065 and 0.034$\pm$0.003 for Yb, and 0.015 and 0.006$\pm$0.001 for Lu [35]. The chemical element balance of airborne particles collected on 18 days during summer 1976 (between August 10 and September 13) at ten sites in the Washington, D.C., area shows the following predicted contributions from seven sources. Additionally given are predicted and observed total contents as well as the ratio between larger and smaller content (derived from predicted/observed or observed/predicted content ratios, whichever is larger); number of samples = n [36]:

ele-ment	n	predicted contribution[1] in ng/m^3 from					total content in ng/m^3		ratio larger/smaller content
		soil	limestone	coal	oil	refuse	pre-dicted	observed	
La	130	0.75	0.014	0.31	0.016	0.0016	1.1	1.5$\pm$0.1	1.42
Ce	129	0.98	0.024	0.62	0.014	0.007	1.6	2.0$\pm$0.2	1.30
Sm	130	0.068	0.0027	0.057	0.0012	0.0003	0.13	0.20$\pm$0.02	1.59
Eu[2]	125	0.015	0.0004	0.014	0.0005	0.0002	0.030	0.030$\pm$0.003	1.32
Yb	111	0.037	0.0011	0.030	0.0004	0.0009	0.070	0.034$\pm$0.003	2.60
Lu	129	0.0067	0.0004	0.0080	0.0001	0.0004	0.016	0.0056$\pm$0.0006	3.34

[1] Predicted contribution from marine sources for all elements <0.0001 ng/m^3; contribution from motor vehicles not given, because contents in particles from motor vehicles are not known. — [2] Three observed values were eliminated from fits.

A major soil component with possibly additional contribution from local sources (as, e.g., coal combustion) is assumed for La and Sm in size-fractionated aerosol samples (equivalent aerodynamic diameter size ranges between <1 and >7 µm) collected during 1973 and 1974 at six sites (one urban, one expressway, and four industrial) in Toronto, Canada. Both elements are concentrated on larger particles according to their mass median diameters (see also pp. 107/8) and have relatively low atmosphere-crust enrichment factors (normalized to Al) of 2.0 for La and 1.9 for Sm [38]. Also a natural origin occurs for La, Eu, Tb, and Lu in aerosol collected in July 1974 at two weir sites at the Walker Brunch watershed, Oak Ridge, Tennessee, which show aerosol-soil enrichment factors (normalized to Ce) near unity in aerosol and fly ash emissions (data on fly ash from [39]); Ce is chosen as reference element because its content varies only slightly between soil samples and it is neither enriched nor depleted in fly ash. Source contributions calculated from chemical mass balance (for details see original paper) as well as observed average contents of La, Ce, and Eu are as follows [40]:

element	calculated contribution in %			observed content in %
	from soil	from coal	total	
La	0.002	0.000092	0.0021	0.0018
Ce	0.0036	0.00018	0.0038	0.002
Eu	0.000048	0.0000022	0.00005	0.00003

A good correspondence occurs between RE concentration ratios (Ce/La, Ce/Eu, Ce/Sm, La/Eu, La/Sm, and Eu/Sm) calculated from the geometric mean concentration in air particulates over 25 sites from northwestern Indiana (the Hammond-East Chicago-Gary-Whiting

metropolitan complex) and those in (1) the North American shale composite, (2) a glauconite-bearing sandstone, or (3) a limestone from Milwaukee, Wisconsin, which are believed to be reasonably representative of the minerals used in industry and for the soil contribution to the aerosol [41, pp. 140, 147, 164].

A widespread dispersion-type source (soil and/or dust generated by human activity) is suggested for elements associated with the larger particles (including La, Ce, Sm, and Eu) in aerosols collected during summer 1970 at seven Canadian stations from lower Michigan into northern Canada (varying in character from semiurban to remote) by their common aerosol-soil enrichment factors (normalized to Fe) near unity which are calculated from mean summer values, representative in most cases of eight weeks in July and August 1970, which are roughly equal to the enrichment factor of Fe, an element very likely to be mainly soil-derived [41, pp. 20/4, 26, 28/9, 42/7].

In Marine Atmospheres

In atmospheric particulates over marine areas, natural fluxes of continental and volcanic dust (32×10^8 and 9×10^8 g/yr., respectively) are the main source of Sm, since the Sm/Al ratio observed in clear air and in urban air particulates (for data see [42]) is close to the theoretical Sm/Al ratio (calculated by dividing the sum of the continental and volcanic dust fluxes for Sm by the sum of the dust fluxes for Al) assuming that continental and volcanic particulate fluxes are the most important natural fluxes and that they are well-mixed in the atmosphere [43]. A continental origin is assumed for marine aerosol as, e.g., for two samples (with a lower size limit of the dry particles of $\sim 1\,\mu m$) collected in March 1974, over the equatorial Pacific Ocean. They are without significant differences (at the 95% confidence level) for the contents of La, Ce, Sm, and Eu normalized to an unpolluted "standard" aerosol sample (collected in February 1970 over the northern Atlantic Ocean at 27°N, 30°W) which is very similar to the continental dust originating from North Africa; for one of the Pacific samples the continental dust originated in, or passed over Mexico [44]. Influx of terrigenous matter causes Ce (positively correlated with Fe) in aerosol collected near the water level in middle-latitudinal and tropical open-ocean regions of the southern Pacific and Atlantic oceans. La is also of crustal origin [45]. Using enrichment factors relative to the crust (normalized to Al), atmospheric Ce and Eu over the Bermuda Island, western Atlantic Ocean, appear to originate mainly from transported continental weathering products [46]. A crustal weathering source is assumed for La, with a mean crustal enrichment factor (relative to Fe) of 2.8, in atmospheric particulates collected over the northern Atlantic Ocean in the northeastern trade winds (or south of $\sim 30°N$) which often contain material from the African continent [47]. Similar in composition to continental soil or shale (included the contents of La, Ce, Sm, and Eu) are aerosol samples from the equatorial Atlantic Ocean (14°N, 21 to 34°W) which probably originate from the Sahara desert [48]. Related to the same source are RE in seven aerosol samples over the northern tropical Atlantic Ocean collected over a distance of ~ 2400 km during eight days in November and December 1978 in a large dust plume. The enrichment factors (relative to Fe) are near unity and are for La 1.78, Ce 1.85, Sm 1.68, Eu 1.73, Tb 2.02, Dy 1.06, Yb 0.91, and Lu 1.35 [2]. A uniquely terrestrial origin is assumed for certain elements (included Ce, Sm, and Eu) in nine aerosol samples collected in 1970 from 5 m above sea level along a north-south profile in the Gulf of Guinea (from 5°N to 3°S latitude). Especially indicative are the Ce/Fe ratios, varying in the aerosols from 2×10^{-4} to 45×10^{-4}, mean 18.2×10^{-4}, which are very close to that for earth crust materials (e.g., granite 44×10^{-4}, limestone 23×10^{-4}, clay 18×10^{-4}, and basalt 2×10^{-4}) and very different from that in seawater (3.5×10^{-4}) [21, pp. 1113/5].

Aerosol–crust enrichment factors (normalized to Al) at or near crustal values for Ce (EF_{crust}=0.69 to 1.6; see p. 127) occur in six size-separated fractions (between $\leq$0.49 and 7.2 µm) of aerosol particles collected in 1979 at 18 m altitude from the atmosphere over the Eniwetok Atoll (11°20′ N, 162°20′ E) in the Pacific northeastern trade wind regime during April and May (dry season, precipitation 4.3 cm) and June to August (wet season, precipitation 26.4 cm). The extremely low content of Eu in the size-separated fractions precludes detailed analysis of its mass–size distribution but the data available indicate that it resembles that of the crustal elements. Also for the bulk samples, the average atmospheric concentration ratios of Ce (1.3) and Eu (0.83) are similar to that in average crustal material [49].

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8.1.2.2 Aerosols of Marine Origin

Based on literature data on the amount of marine water (1 to 10^9, mean 5×10^9 t/yr.) and of terrigenous material entering the atmosphere (0.5 to 0.8×10^9, mean 0.65×10^9 t/yr.) and neglecting the possibility of trace-element leaching during migration of terrigenous material in the atmosphere, the amount of La originating from the sea surface is calculated at 16.1% in 15 aerosol samples collected between February and April 1976 over middle-latitudinal and tropical open-ocean regions of the southern Pacific and Atlantic oceans. The mass flux of La into the atmosphere from the sea-surface as a marine spray (with a La content of 1.0 to 6.1, mean 2.9 mg/L) is 1.2×10^4 t/yr. [1]. Assuming that all Ca measured in an aerosol originates from the sea, the upper limits for the portions of marine origin are 0.01 to 0.02% each for Sm and Eu, and <0.02% for Ce in aerosol samples collected

5 m above sea level along a north–south profile in the Gulf of Guinea (from 5°N to 3°S latitude) [2].

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8.1.2.3 Origin in Rainwater

A derivation from the earth's surface is assumed for La and Sm in rainwater collected 20 m above ground during the period April to June 1971 at Heidelberg, Federal Republic of Germany, based on the average concentrations relative to Na in rainwater residue and on washout factors of $\sim$1400 (i.e., concentration in rain/concentration in aerosol) [1]. And La and Sm in rainwater collected from April to June 1971 at ground-level in Heidelberg are blown by wind from the earth's surface into the atmosphere, since the arithmetic mean contents relative to Na are close to those in the earth's crust [2]. Highly calcareous rendzina, the local major soil type at Chilton, Berkshire, central southern England, may be responsible for the correlation between Ca and Ce in total rainwater collected monthly during 1972 and 1973 [3]; note also that, for samples continuously collected from 1972 through 1975 at Chilton and Styrrup, Nottinghamshire, the interelement ratios of Ce, Eu, and Sm (Ce/Eu 40 and 47; Ce/Sm 5.7 and 16; Eu/Sm 0.14 and 0.33, respectively) in the total atmospheric deposition (the annual total deposition is derived from rainfall $\times$ concentrations measured in rainwater, with both soluble and insoluble fractions included) are broadly comparable with those for average crustal rock (Ce/Eu 50, Ce/Sm 10, Eu/Sm 0.20) as a probable source [4]. For rainwater at Styrrup, a relatively heavy resuspension of local soil or mining waste is implied by a significant correlation between La and Ce in dry deposits [3]. Sedimentary rocks are the main source of RE in rainwater collected during the period 1972 to 1973 over the Black Sea and the Moscow region, USSR, as well as over the Atlantic, Pacific, and Indian oceans, as is indicated by analogous coefficients of fractionation for the trace elements in atmospheric precipitates and rocks [5].

A marine origin from sea-spray, driven by wind from the ocean's surface (maritime effect), is supposed, e.g., for the excess Ce in rainwater collected 25 m above sea level during the period June 1972 to May 1973 at a gas platform $\sim$55 km off the coast of Norfolk, Great Britain. The content of $<$4 µg/L is higher by about one order of magnitude than the contents for four sites at, or near the coast of Great Britain ($<$0.1 to 0.53 µg/L), at Arran, western Scotland (0.43 µg/L), and at Petten, northern Holland (0.55 µg/L) [6].

Compared to seawater, a more than tenfold enrichment of intermediate and heavy RE (starting with Eu) in rainwater over the Pacific, Indian, and Atlantic oceans can be caused by an absorption of volatile RE compounds which are metabolism products of plankton and evaporate at the ocean–atmosphere interface. Experiments with radioactive tracers on the physical evaporation of seawater show that it results in a loss of elements, included RE, into the atmosphere. However, the values obtained for La, Sm, Dy, Eu, and Lu are in the range of $(1.2 \text{ to } 1.9) \times 10^{-3}$ and, thus, cannot be used to explain the observed enrichment of intermediate and heavy RE. Possibly, the similar values are caused by a decomposition of organic matter during the storage of water samples [5]. Note also that evaporation of high-molecular weight organic compounds concentrated at the ocean–atmosphere interface is a probable mechanism for RE migration from the ocean into the atmosphere. A possible influence of organic compounds formed by plankton on the RE content in rainwater is evident by its enrichment in Eu, Gd, and Tb relative to seawater [7].

An origin from nuclear weapon tests is reported: in rainwater, e.g., for various RE radio-nuclides at Fayetteville, Arkansas [8]; for ^{144}Ce at Nice, France [9]; and for ^{144}Ce and ^{144}Pr at Tokyo, Japan [10]; in fallout (rain and dry deposition) for ^{141}Ce, ^{144}Ce, and ^{88}Y at Tokai, Ibaraki prefecture, Japan [11]; and in ice, snow, and meltwater for ^{141}Ce and ^{144}Ce at four stations in Antarctica [12]. But note that a natural origin is also assumed for ^{144}Ce in rainwater (of Japan?) [13]. Besides the fission products ^{144}Ce and ^{144}Pr, ^{155}Eu and ^{88}Y occur in very small quantities in dry deposition and atmospheric precipitation collected daily from January to December 1981 (in Romania?), and the latter isotope possibly originates from a nuclear reaction taking place between charge particle flux and fission products from thermonuclear explosions [14].

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8.1.2.4 Anthropogenic Origin

Specific RE elements may be enriched in atmospheric aerosol released during anthropogenic activity as, e.g., petroleum industry, glass manufacturing, or electrical industry [1]. Especially in chemical-metallurgical plants involved in the benefication and separation of RE metals, the plant atmospheres contain aerosols rich in RE [2]. Also mining and crushing of minerals as well as land cultivation, earth moving, and building operations can cause a rise in air concentration of Ce in regions of intense anthropogenic activity [3]. In addition, as a result of the combustion of fossil fuels, RE and Y can be introduced into the atmosphere in amounts less than, but comparable to their rates of flow through natural waters during the weathering cycle, as is shown, e.g., by the 1967 production figures in the table on p. 104 [4].

A relatively high content of Ce in aerosol collected at five stations in November and December in Paris [5] is assumed to be caused by the exhaust of automobiles [6]. Possibly, La is somewhat related to fuel in aerosol collected in the city of Beer-Sheva, Israel, since it correlates relatively strongly with S and Pb contents [7].

	amount mobilized into atmosphere in 10^9 g/yr.						
	Y	La	Ce	Pr	Nd	Sm	Eu
fossil fuel mobilization							
coal and lignite	1.4	1.4	1.6	0.31	0.65	0.22	0.1
oil	0.0002	0.0008	0.002	—	—	—	—
weathering mobilization							
river flow	25	7.2	2.2	1.1	7.2	1.1	0.25

	amount mobilized into atmosphere in 10^9 g/yr.						
	Gd	Tb	Ho	Er	Tm	Yb	Lu
fossil fuel mobilization							
coal and lignite	0.22	0.042	0.042	0.085	0.014	0.07	0.01
oil	—	—	—	0.0002	—	—	—
weathering mobilization							
river flow	1.4	0.29	0.36	1.8	0.32	1.8	0.29

The anthropogenic input of RE radionuclides into the atmosphere by nuclear weapon tests remains undiscussed in this handbook; for examples regarding rainwater, see p. 103.

Calculation of an interference factor, IF = (total anthropogenic emission/total natural emission) × 100, gives an assessment of the importance of the anthropogenic flux of any metal. Thus, the portions of anthropogenic fluxes of Sm into the atmosphere by industrial particulate emissions and by burning of fossil fuels are 7×10^8 and 5×10^8 g/yr., respectively. Furthermore, 0.1×10^8 g/yr. is introduced by the burning of woods and forests; i.e., 0.5% of the total (continental and volcanic) dust flux [8]. For a discussion of the intensity and extent of industrial pollution by the East Chicago industrial area causing La and Ce concentrations over northwestern Indiana, see [9 to 11]; or of coal combustion and some intense industrial sources causing concentrations of La, Ce, and Sm over Belgium, see [12]. Coal combustion is a major source of La and Eu in atmospheric particles collected in Poland during the late summer of 1979 and the subsequent winter at Katowice (located centrally in a large coal-mining and steel-producing area), since both elements have mean atmospheric enrichment factors relative to coal (calculated by averaging all samples from the same season) well inside the range of elements with coal as a predominant source. The RE, however, may as easily be attributed to other coal-related sources as, e.g., coal processing, coke production, or simply coal dust or coal tailings dust dispersal [13]. From a thorough investigation of trace element concentrations in particulate air samples (ground-level) collected from 1957 to 1974 on a daily basis in a high-volume air sampler at Chilton, Oxfordshire, Great Britain, the following statements concerning elements of the lithophilic group (Al, Ce, Eu, Fe, Sc, and Th) are given: These elements exhibit enrichment factors near unity. During the period investigated, four elements (Al, Eu, Fe, Sc) show significant downward trends consistent with combustion sources; the two other (Ce, Th), without significant trends, suggest a mainly natural origin. But both elements have high initial values and may at that time have had a more significant anthropogenic origin. In addition, a correlation between the decline in winter levels of black smoke (during a "period of grace" allowed by the Clear Air Act of 1956) with observed decreases in trace element contents (e.g., of Eu) indicate that fuel combustion is a major source. The residual summer levels may also stem from combustion sources together with contribution from natural ground surface disturbance [14].

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8.1.3 Mode of Occurrence

In the atmosphere, trace elements occur in aerosol and in the gas–vapor phase (condensate) [1, p. 62]. Atmospheric aerosol is defined as solid or liquid matter dispersed in the air [2], with the stable forms ranging in size from 0.01 to 100 μm in diameter. Particles <0.01 μm in diameter rapidly coagulate, those >100 μm are removed quickly by sedimentation (see p. 132) [3, p. 3]. The most used term to describe particles in air (other than water) is "total suspended particulates", which is defined as the mass per unit volume of those particles that are captured by pulling a large volume of air through a filter. Particulates have a large number of forms, chemical compositions, and sources [2]. Unequally distributed between the solid and liquid phases of atmospheric precipitation are trace elements (included La, Ce, and Sm); the distribution depends, e.g., on sampling location, on chemical composition of the precipitation, and on the properties and content of the element under consideration [1, pp. 61/2].

In **aerosol** the crustal–derived elements (included RE) usually have most of their mass associated with large particles [4], e.g., larger than 1 to 3 μm [5]. Rare earth elements belong to the so–called L–type elements (i.e., elements associated mostly with large particles of refractory compounds, especially oxides and silicates, in which they often are found in soil and minerals) in aerosol particles collected from surface–continental air at various stations in North America [3, pp. 1, 37/9, 58/9, 189, 191, 202/3]. Based on low aerosol–crust enrichment factors (for RE in the range of 0.5 to 3.0), fully one–half the elements in a typical aerosol appear to be associated with its mineral component (see, e.g., [6]); and a coincidence of the plateau region for particle size–related element contents with the aerosol size range implies that the composition of a mineral aerosol should not change markedly during long–range transport; this is borne out by observations for eleven desert soils from Africa and North America. And elements associated with highly resistive minerals such as zircon and rutile can sometimes become unusually enriched in the radius range 10 to 30 μm [7].

Mainly associated with irregular-shaped coarse particles ≥ 1.2 µm is Ce in aerosol samples collected daily in February 1980 at five sites over Tashkent, Usbekistan, USSR [8], and the larger size fractions (1.0 to 10 µ) of aerosols collected over Tashkent and Almalyk consist mainly of La and other elements of geochemical (natural) origin [9]. Most of La, Ce, Eu, Sm, Yb, and Lu occurs in particles with a radius >1 µm in five aerosol samples collected 3 m above ground between November 1975 and September 1976 around Moscow, USSR. Their content and percentage in three filter layers and the calculated aerosol-crust and aerosol-shale enrichment factors (normalized to Fe) are as follows [5]:

ele-ment	content and percentage in the						enrichment factor against	
	upper layer (r$>$1 µm)		middle layer (r$<$0.5 µm)		lower layer		av. earth's crust	av. shale
	ng	%	ng	%	ng	%		
La	64.8	90	10.9	10	1.2	—	1.0	0.3
Ce	1070	60	500	28	210	12	1.0	0.9
Sm	8.16	90	0.84	10	0.5	—	0.6	0.5
Eu	1.44	87	0.23	13	not found		0.6	0.6
Yb	1.15	92	0.09	8	not found		0.5	0.5
Lu	4.37	100	not found		not found		1.1	0.6

The coarse fraction (between 1.0 and 10 µm) contains the main part of La in the following aerosol samples from various environments (collected in the USSR?) [9]:

environmental area	La content in ng/m^3				
	11.5 µm	3.6 µm	1.8 µm	1.03 µm	$\leq$0.4 µm
industrial	1.1	6	$\leq$0.1	$\leq$0.1	4
municipal	$\leq$0.1	0.2	$\leq$0.1	$\leq$0.1	$\leq$0.1
rural	0.04	0.09	0.04	0.04	0.04
remote	$\leq$0.01	$\leq$0.01	$\leq$0.01	$\leq$0.01	$\leq$0.01

Only one maximum in the size distribution occurs at $\sim$3 µ for La, Ce, Sm, Yb, and Lu in two aerosol samples collected 3 m above ground at the Radiation Center, Osaka prefecture, Japan. The contents determined from sample A (June 1974) in the various size fractions are as follows [10]:

size fraction	content in ng/m^3				
	La	Ce	Sm	Yb	Lu
$>$11 µ	0.411	0.497	0.0537	0.0301	0.0050
7.0 to 11 µ	0.229	0.293	0.0294	0.0165	0.0032
4.7 to 7.0 µ	0.245	0.376	0.0415	0.0215	0.0041
3.3 to 4.7 µ	0.184	0.284	0.0329	0.0177	0.0029
2.1 to 3.3 µ	0.123	0.169	0.0216	0.0103	0.0019
1.1 to 2.1 µ	0.0579	0.0911	0.0084	0.0021	0.0006
0.65 to 1.1 µ	0.0472	0.0345	0.0065	—	—
0.43 to 0.65 µ	0.0560	0.0488	0.0091	—	—
$<$0.43 µ	0.0682	0.183	0.0091	—	—

A bimodal particle size distribution occurs for the nonvolatile lithophilic elements (included La, Sm, and Eu) in four semiremote background aerosols collected at three sites and 7 m above ground during July 1975 near the town of Colstrip in the semiarid rangeland area of southeastern Montana. The size distribution shows a peak at an estimated cutoff diameter of 1 to 3 µm which is undoubtedly the result of turbulent atmospheric processes which are capable of suspending soil particulates. The small particle size fraction is the result of the collection of all particles <0.3 µm by the backup filter and of particles created as the result of bounce-off. The La, Sm, and Eu contents (range and calculated mean) in the different size fractions of a cascade impactor are as follows [11]:

| ele-
ment | content in ng/m³ for the size fractions (D_{50} values) | | | | |
	10 µ	3 µ	1 µ	0.3 µ	<0.3 µ
La	0.019 to 0.080; 0.043	0.075 to 0.20; 0.122	0.050 to 0.12; 0.08	0.010 to 0.014; 0.012	0.020 to 0.040; 0.031
Sm	0.0023 to 0.014; 0.0069	0.013 to 0.036; 0.018	0.0080 to 0.020; 0.012	<0.0006 to 0.002; 0.0012	0.002 to 0.007; 0.004
Eu	0.002 to 0.003; 0.0023	0.0022 to 0.008; 0.0044	0.0017 to 0.008; 0.0039	0.0014 to 0.003; 0.002	0.0007 to 0.0019; 0.0012

Both small- and large-particle components are carriers for Ce as follows from size-distribution studies on aerosol collected during February and March 1970 at two in-town and at one suburban site of Boston, Massachusetts. This indicates an origin from two or more processes of comparable magnitude [12]. Preliminary results on size distribution for La, Ce, Sm, and Eu contents in three samples of airborne particulate material (collected with 0.8 µ pore-size filters) from Columbia, Missouri, are as follows; no cutoff diameters are given for the different impactor stages [13]:

| element | content in µg for the stage | | |
	1	4	7
La	6.04×10^{-2}	2.95×10^{-2}	5.81×10^{-2}
Ce	5.58×10^{-4}	3.93×10^{-4}	5.87×10^{-4}
Sm	2.74×10^{-2}	1.19×10^{-2}	1.81×10^{-2}
Eu	6.08×10^{-4}	—	1.74×10^{-4}

Most of the radioactivity (including ^{144}Ce) occurs in the size range of 0.02 to 0.15 µm radius in lower stratospheric aerosol (30000 to 100000 feet) over Minneapolis, Minnesota, and over Hyderabad, India, as well as between 15 and 21 km altitude over Minneapolis [14]. In particles with a mean maximum diameter of 4 µ, and with a ratio of the largest to the smallest diameter of 1.1, ^{141}Ce, ^{144}Ce, ^{147}Nd, and ^{140}Ba-^{140}La occur in air collected in autumn 1961 over Frankfurt, Federal Republic of Germany [15].

Concentrated on larger particles are La and Sm in size-separated aerosol samples collected during 1973 and 1974 at six sites (one urban, one expressway, and four industrial sites) in Toronto, Canada. The approximate mass median diameters (m.m.d., i.e., the diameter below which 50% of the total mass of an element occurs) for typical summer aerosol (samples influenced by local sources excluded) are 4.7 µm for La and 6.5 µm for Sm, with 15 and 21%, respectively, occurring in particles <1.1 µm in diameter [38]. A predominance of large particles, or almost flat size distribution curves occur (despite analytical uncertainties) for Yb and Lu in ground-level aerosol (up to 100 m altitude) from two in-town and one suburban site in the Boston area, Massachusetts, collected during February and March

1970 [12]. Mainly associated with >1 μm particles (mass median diameter) are La, Ce, and Sm in eight aerosol samples from three sites in the industrial area north of Ghent, Belgium (collected over a period of two years, between September 1971 and November 1973, under varying weather conditions). Almost the same size distribution is given by literature data for aerosols collected from various other locations, as is shown in the following [16]:

locality	m.m.d. in μm for particles containing		
	La	Ce	Sm
Belgium			
Ghent (industrial)	2.3	2.8	2.7
Ghent (residential)	2.1	1.6	2.8
Liège	—	5	5
Mechelen	2.1	2.5	2.7
Niles, Michigan	2.1	2.8	3.0
Jungfraujoch, Switzerland	2.9	5.9	2.9
Lakselv, Norway	2.1	1.0	—

The occurrence of Ce in particles with m.m.d. >3 μm is given for ground-level airborne dust collected at Chilton, Berkshire, and at Trebanos near Swansea, Glamorganshire, both Great Britain [17, pp. 15/6].

From a plot of the enrichment factor (normalized to Sc) vs. dry deposition velocity V_g (rate of dry deposition [μg/cm^2 sec]/concentration in air [μg/cm^3]) of trace elements in the atmosphere at Chilton during 1972, it follows that the soil-derived elements, such as Ce, are associated with particles with a m.m.d. >1 μm (since at this station a deposition velocity of 0.5 cm/sec corresponds to a m.m.d. of ~1 μm) [18]. It should also be noted that elements with low enrichment factors (normalized to Sc) <2, such as Ce, are associated with particles having a V_g > ~0.8 cm/sec at Chilton and other locations of Great Britain [17, pp. 15/6, 44/5]; and, based on its high V_g, Ce associated with large particle size is found in airborne dust (<100 μm) collected 1.5 m above ground during 1970 and 1971 at Wraymires, Westmorland, Great Britain [19]; see also [20]. Concentrated in larger particles are La, Ce, and Eu (with m.m.d. of 3.5, 4.1, and 4.2 μ, respectively) in atmospheric particulate matter collected monthly from September 1976 to February 1977 in Ankara, Turkey [21].

An occurrence with dust, composed mainly of $CaCO_3$, SiO_2, and other minerals derived from two components (dust from the Negev desert, from Saudi-Arabia and North Africa and a polluting component from industrial and transportation sources) is given for Sm and probably La in aerosol collected in the city of Beer-Sheva, Israel. Both elements show a relatively high correlation with total suspended matter (i.e., the total weight of aerosol collected on the filter). However, according to size distribution, La is not part of, but is almost completely adsorbed by, the dust [22]. Also, La, Ce, and Eu occur as impurities in KCl, and NaCl and in other compounds (SiO_2, $CaCO_3$, Al_2O_3, etc.) in air samples collected simultaneously in the city of Beer-Sheva and at Shivta, 40 km away in the Negev desert. Elements which are not typically urban are part of the dust and hence are found everywhere in the area. According to the element ratios derived from city-to-desert and from day-to-night data, the following groups of elements are given that might form certain dust combinations: K-La-Pa, Ce-Fe-Sc, and Eu-Na-Cr [23].

In contrast to the suspensate (aerosol) over continents, in marine aerosols (central Pacific and Atlantic oceans, Japan Sea) elements are present preferentially in water-soluble (or-

ganic?) or exchangeable and weakly-bound forms. The ranges and mean values of the amount of La in water-soluble or organic phases of suspensate, collected between February and April 1976 in the middle-latitudinal and tropical regions of the southern Atlantic and Pacific oceans, are 2 to 75%, 31% and 2 to 25%, 15%, respectively, with enrichment factors relative to seawater (normalized to Na) of 1.8×10^5 and 7.9×10^6, respectively [24]. As follows from R-mode factor analysis of data from [25], in 16 samples of marine aerosol from the northern Atlantic Ocean (18° to 32°N latitude, 18° to 29°W longitude) the RE belong to the alumino-silicate detritus phase [26].

For most elements, in particular for the hydrolyzing ones (e.g., La, Ce, Sm, Eu, Yb, and Lu), the main mode of occurrence in atmospheric water is dusty aerosol which enters **rainwater** mainly from soil. These elements have enrichment factors relative to sedimentary rocks (normalized to Fe) in the order of 0.1 to 10 [27]. Ranges and mean concentrations of La, Ce, and Sm in the particulate fraction (i.e., the insoluble fraction retained on a filter with $0.4 \mu m$ pore size) and in the soluble fraction (i.e., the fraction passing through the filter) of 37 rainwater samples collected during May 1980 across Canada are as follows [28]:

element	content for	
	particulate phase in µg/g	soluble phase in µg/L
La	< 6.9 to 1750; 274	—
Ce	<19.2 to 105; 21.0	<0.30 to 3.39; 1.34
Sm	<0.61 to 14.1; 5.69	<2.92*) to 0.010; 6.87*)

*) Expressed in ng/L.

The annual mean total and dissolved Ce contents in rainwater collected between June 1972 and May 1973 at five sites in Great Britain and one site each in northern Holland (Petten) and in the North Sea are, respectively: 0.53 and <0.2 mg/L at Leiston, Suffolk; 0.53 and <0.08 mg/L at Gresham, Norfolk; <0.1 and <0.018 mg/L at Collafirth, Shetland Isles; <0.47 and <0.10 mg/L at Lerwick, Shetland Isles; 0.43 and <0.08 mg/L at Arran, Bute; 0.55 and 0.078 mg/L at Petten (collected from February to May 1973 only); and <4 and <2 mg/L at a gas platform [29].

Associated with large particles of sea spray is Ce in rainwater (wet plus dry deposition) collected monthly at Lerwick Observatory, Shetland Isles, as is inferred from the association of a higher washout factor $W_{sol.}$ (soluble concentration in rainwater [µg/kg]/concentration in air [µg/kg]) with a greater dry deposition velocity V_g (for definition, see p. 108) compared with other sites studied [17, p. 44].

Present in water-soluble (as ions, molecules, colloids, pseudocolloids, and finely-dispersed suspensions in the 0.1- to 1 µ-size range) and in water-insoluble form (as suspended particles of organic and inorganic origin ranging in size between 1 µ and 1 mm) are the radioisotopes [91]Y, [144]Ce, [141]Ce, and [155]Eu in 57 atmospheric precipitation samples collected during the years 1961 to 1972 in the Leningrad area, USSR [30]; note too that [144]Ce is uniformly distributed between the liquid and solid phases of atmospheric precipitation. In the liquid phase, most probably [144]Ce occurs as hydrocomplexes with a different degree of polymerization as well as in complex units with organic and inorganic ligands [31]. Mostly in cationic form (59%) occurs [144]Ce in atmospheric precipitation collected in the Moscow region, USSR, and 41% occurs in anionic and in neutral forms. On average, 12% of the [144]Ce is in water-soluble form [32].

In the solid phase (>0.7 µm) of **snow**, trace elements occur in exchangeable, mobile, acid–soluble, or difficultly soluble form, their proportions determined by the chemical properties of the elements and by the composition of the solid phase [1, p. 55]. For La in snow water collected at Tashkent and Almalyk, both Uzbekistan, USSR, the following modes of occurrence are given [9]:

| location | La content in ng/L | | | |
	suspended	neutral and colloidal	anionic	cationic
Tashkent	230	<10	41	150
Almalyk	380	64	<10	36

In contrast to snow from Antarctica, where both La and Ce occur at ~50% with the difficultly soluble (insoluble) form, in snow of the Moscow region, USSR, these elements occur mainly (73 to 93%) with the insoluble form. There are differences in the percentage of insoluble mode of occurrences for La, Ce, and Sm: Snow collected in March 1975 shows, respectively, 63.7, 91.1, and 92.9%, whereas snow collected in November 1975 shows 40.6% Ce and 30.8% Sm as insoluble. With increasing dust content (i.e., increasing age) of snow, contents of trace elements also increase, e.g., the content of Ce from 0.5 g/L in freshly fallen snow (November 1975) to 4.2 g/L in "aged" snow (January 1976). The contents of Ce in aerosol and snow collected in the Moscow region are in the same order of magnitude as in rocks and soils [1, pp. 54/7, 60/1].

The geographic location of Antarctica leads to special features in the distribution of nuclides between the soluble and insoluble fractions in atmospheric fallout. Except for ^{141}Ce, all other radionuclides (including ^{144}Ce) are present nearly completely in soluble or colloidal form, as follows from a comparison of concentrations in snow– and in meltwater from a puddle on the snow (the water samples did not contain visible suspended matter and consisted mainly of true and colloidal solutions of the substances contained in the snow), collected in 1969 at 250 m above sea level during the summer (beginning of December) from a snow dome of Bellingshausen station. The average concentrations (of samples taken in four pits) of ^{141}Ce and ^{144}Ce in snow– and meltwater are as follows [33]:

| radio-nuclide | content in 10^{-12} Ci/L | | |
	meltwater	upper snow layer, 56 cm thick	annual snow layer, 110 cm thick
^{141}Ce	0.15	0.3	0.47
^{144}Ce	4.6	3.9	5.6

Bound to different organic compounds, Ce, Sm, and Yb occur partly in the solid and liquid phases of freshly fallen snow collected in November 1978 at Moscow, USSR. In the solid matter of the snow, 6.0% of Ce, 3.3% of Sm, and 13.2% of Yb are extractable by an alcohol–benzene mixture, but the discrepancy between parallel determinations is 20 to 50%. In the liquid phase, <12% of Ce occurs in anionic form in freshly fallen snow (collected in November 1975 under trees) from outside the city of Moscow, confirming the formation of complexes with humic acids, low–molecular weight carbonic and phenol acids, and other organic compounds [1, p. 58].

Primarily associated with the nonvolatile matrix material are RE in the larger size fractions of **fly ash** collected from the precipitator of a coal–fired steam plant in the western United States, since the contents for RE together with that of Fe show a maximum at 25 µm

(whether this maximum is real or results from a sampling artifact is not entirely clear). The contents of Y and RE (possibly contained in apatite) in relation to particle size (mass median diameter) are as follows; results are from instrumental neutron activation analysis, and, in parentheses, from X-ray fluorescence [34]:

particle size in µm	Y	La	Ce	content in ppm Nd	Sm	Eu	Tb	Dy	Yb
0.5	(48)	70.3 (53)	180 (115)	83	8.68	1.95	1.15	7.3	4.26
2	(54)	73.7 (74)	170 (115)	80	10.50	2.14	1.28	8.7	4.69
4	(61)	76.7 (81)	180 (132)	83	10.50	2.29	1.40	9.6	4.79
5	(55)	72.8 (64)	145 (115)	50	10.1	2.17	1.36	8.8	4.96
8.5	(49)	69.6 (64)	135 (121)	55	9.4	1.97	1.45	7.8	5.00
12.5	(37)	53.4 (30)	110 (78)	45	6.92	1.49	0.92	6.6	3.47
15.5	(35)	55.7 (45)	100 (86)	50	7.23	1.56	1.00	7.1	3.49
25	(32)	41.9 (36)	80 (75)	30	6.00	1.16	0.86	4.7	3.33
50	(28)	− (29)	− (43)	76	−	−	−	−	−

Predominantly matrix-associated (apatite?) are the RE in aerodynamically-sized stack fly ash from a large coal-fired power plant in the western United States. Except for Sm and Nd, no dependence on particle size occurs [35]. Mainly concentrated in the glass phase (represented as $(SiO_2)_x \cdot (R_2O_3)_y$ with R = Al or Fe) are RE in the 100 to 200 µm fraction of fly ash from the Bull Run coal-buring power plant, as well as in fly ash from other plants of Tennessee. In the magnetic phase of the fly ash, La and Ce probably are incorporated as substituted spinel (ferrite with an approximate composition of $Fe_{2.3}Al_{0.7}O_4$) [36]. As dust deposits of intermediate products or separated chemicals rather than as monazite ore, RE occur in 14 air filter samples collected in 1967 and 1970 from a Th- and RE-processing refinery of Illinois [37].

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8.2 Transport, Regional Differences, and Temporal Variations of Yttrium and/or Rare Earth Element Concentrations in the Atmosphere

8.2.1 Transport

Smaller particles of terrestrial aerosol, raised from the surface of continents and oceans by winds (causing suspension of soil and dust), by the eruption of volcanoes, or by industrial activities may diffuse vertically upwards to higher altitudes, against competition from sedi-

mentation and washout by rain, by updraughts and turbulence, so that disposal is more widespread. Those particles capable of reaching the stratosphere would eventually be distributed on a world-wide scale, whereas particles that remain in the troposphere will be transported in the zonal circulation (westerly airstreams in the middle and upper troposphere) before returning to the earth's surface [1]; note also that probably enough atmospheric particulate material below $\sim 10\ \mu m$ in size will diffuse vertically upwards and join the westerly airstreams in the middle and upper troposphere at altitudes up to $\sim 15\ km$. There will be a continuous exchange by vertical diffusion throughout the troposphere [2].

Evidently, transport over more than 1000 km occurs for dust-storm aerosols (collected in April 1980 at 25 m altitude) over Beijing, China, which are formed by silt particles from the area where these strong winds originated (Siberia) and from areas in the path of the winds, as is inferred from the Sc-normalized enrichment factors of some elements (including RE) relative to the earth's crust in the aerosols [3]. Integrating the results of mass size distribution and enrichment factors (assuming that the content of Al in the aerosol particles reflects the dust loading in the atmosphere), it is shown that the Ce content in aerosol particles is controlled virtually always by transport of crustal weathering products from the continents, as occurs for aerosol particles from the lower atmosphere (in the Pacific northeast trade wind regime) over the Eniwetok Atoll, Marshall Islands, collected at 18 m height from April 15 to May 18, 1979 (dry season, precipitation 4.3 cm) and from June 26 to August 7, 1979 (wet season, precipitation 26.4 cm). When the dust content changes in the atmosphere over Eniwetok, the amount of Ce in the bulk and size-separated aerosol particles changes correspondingly [4]. In seven samples collected during November and December 1973 over a distance of $\sim 2400\ km$ (ranging from ~ 600 to $\sim 1300\ km$ distance from the western coast of Africa), and over an elapsed time of eight days, the majority of elements (including La, Ce, Sm, Eu, and Lu) in the tropical northern Atlantic Ocean shows variations of the concentration ratio X/Fe for the various elements X which are just about the same as their analytical uncertainties. This constancy can be explained by a constant amount within the Sahara sand (mean mineral content 75.6 $\mu g/m^3 \pm 30\%$) and/or by extensive mixing of the aerosol before it moves out over the Atlantic Ocean [5]. Also, after a long-range transport from the Sahara, the relative contents of clay-associated hydrolysate elements (such as Y and La) are only slightly increased in Caribbean dust [6]. For a relatively constant composition of mineral aerosol after transport over >1000 km, see p. 105.

The vertical transport of contamination (e.g., by ^{144}Ce) both within the lower stratosphere and across the troposphere is influenced only relatively slightly by sedimentation, as is shown by particle-size measurements on stratospheric aerosol collected between 30000 and 100000 feet altitude over Minneapolis, Minnesota (from June 1960 to June 1961) and over Hyderabad, India (from February to April 1961). The finely-divided radioactive aerosol (see also p. 107) mixes down from higher stratospheric levels and either seeds the formation of, or becomes attached to, sulfate aerosol particles; the nature and details of this mechanism are not known [7]. ^{141}Ce with a large part of explosion products from the Chinese nuclear test of September 29, 1969 has been transported during three months in the troposphere from middle latitudes of the northern hemisphere to the south pole region. During transport in the upper troposphere of the southern hemisphere, the radionuclides react with marine salt particles, thereby forming marine aerosols with the formation of soluble compounds (primarily chlorides), which is a lengthy process, as is indicated by the relatively low value for the meltwater/snow ratios in both the annual and the upper snow layer at Bellingshausen station for the short-lived ^{141}Ce (0.32 and 0.5, respectively) compared to the long-lived ^{144}Ce (0.82 and 1.2, respectively) [8]. Tropospheric transport may account for the appreciable amount of radioactive fallout (e.g., for ^{144}Ce of $6.2 \times 10^{-14}\ Ci/m^3$) in

dust collected between November 30 and December 21, 1958 over the southern Atlantic Ocean (at 15° S latitude) [9]. Diffusion of radioactive debris within the troposphere after the 26th Chinese nuclear test explosion brought about one peak of deposition at Tokai, Ibaraki prefecture, Japan, during November and December 1980. And the debris injected up to the stratosphere remained there temporarily and was spread down into the troposphere by upper-tropospheric turbulent air movement, leading to a second, so-called spring maximum between February and July 1981 with maximum fallout values for all radionuclides (including ^{141}Ce, ^{144}Ce, and ^{88}Y) except ^{140}Ba-^{140}La [10]; see also pp. 126/8 for seasonal variations in content of RE elements or radionuclides.

The weaker the vegetation cover of soil, the stronger is the removal of dust from soil by winds and, therefore, an influence of vegetation may play an important role in the increase in contents of Eu and Ce in aerosol collected ~5 m above ground in October and December 1970 from a north-south profile over the Ivory Coast [11].

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8.2.2 Regional Differences (Spatial and/or Environmental)

In the following paragraphs are given examples comparing especially differences between aerosol or rainwater over oceans and continents, over different oceans, and over open-ocean regions and inland seas, as well as between different environments (industrial, urban or municipal, rural, and remote areas) and between different localities of the same environment (which may point to differences in the origin of RE; refer also to pp. 93/103). Only a few examples are given for regional differences in the RE nuclide distribution.

Generally, the contents in the marine atmosphere of terrigenous elements are lower by a factor of 10 to 20 than in the earth's crust [1]. Contents of RE elements in air from marine regions are nearly equal (2.26×10^{-6} g/m^3 for the Atlantic Ocean and 2.56×10^{-6} g/m^3 for the Indian Ocean, in the original paper erroneously given as g/cm^3) but are considerably lower (13 times) than for the continental Moscow region [2, p. 253]. Recalculated to the mineral residue content (1.0 to 2.0×10^{-2}%), the RE content in air suspensions collected over the northern Indian Ocean equals the concentration in suspended matter of surface seawater and in average sedimentary rocks [3]. Compared to ocean regions, higher RE

contents occur in air above inland seas (e.g., 4.5 to 6.0×10^{-9} g/m^3 for the Black Sea against 0.93 to 1.7×10^{-9} g/m^3 for the Arabian Sea) and may be explained by a stronger continental influence on the air composition above the Black Sea [4]. Also, mean annual contents of Eu and Lu (calculated from monthly contents) are higher in the inorganic fraction of aerosol collected during 1975 over coastal regions of the Black Sea (Eu 1.6 and Lu 0.35 mkg/g) than in aerosol collected over oceans [5]. In air over the Atlantic Ocean (collected from March to July 1961) contents of ^{144}Ce are at least twice as high (7.8×10^{-18} Ci/L) as over seas surrounded by large land masses (Black Sea 3.0×10^{-18}, North and Baltic seas 3.4×10^{-18} Ci/L) [6].

Less than 24 hours after the major eruption of Mount St. Helens, Washington, contents of some RE in the highest (17.7 km) and lowest altitude samples (13.1 km) collected on May 19, 1980 in the stratosphere over Oregon, Idaho, Montana, and Wyoming are as follows; additionally, the enrichment factors (normalized to Al) of the plume material relative to the volcanic ash (ash data are from a composite sample collected at Pullman, Washington, after the May 18 eruption) are given [7]:

element	content in μg/m^3		enrichment factor relative to ash	
	17.7 km	13.1 km	17.7 km	13.1 km
La	0.046	0.040	—	—
Ce	0.11	0.079	0.99	0.87
Sm	0.012	0.0080	1.32	1.04
Eu	0.0039	0.0024	0.91	1.17
Gd	0.014	0.0074	1.73	1.08
Tb	0.0019	0.0013	1.32	1.57
Yb	0.0038	0.0033	0.84	0.87
Lu	0.00087	0.00049	—	—

In **aerosol** over oceans the relative RE contents depend on their relative contents in the terrigenous fraction [8, p. 942]. Possibly due to a more basaltic nature of the Pacific dust compared to the shale-like elemental abundances of the Atlantic aerosol, some RE are depleted in two equatorial Pacific aerosol samples relative to an unpolluted dust sample of Atlantic aerosol (taken as standard). The ratios of the element contents are 0.78 ± 0.10 and 0.68 ± 0.18 for La, 0.71 ± 0.4 and 0.61 ± 0.14 for Ce, 0.69 ± 0.08 and 0.65 ± 0.20 for Sm, and 0.61 ± 0.06 and 0.63 ± 0.12 for Eu [9]. The contribution from a marine component to the suspensate appreciably affects content and form of certain minor elements in marine aerosol. Thus, the least contribution from sea-salt occurs in the tropical open-ocean regions of the northern Atlantic Ocean, which show a considerable contribution from terrigenous material of central Africa compared to the Pacific Ocean. With increasing portion of sea-salt, the RE distribution in aerosol reproduces that in seawater (i.e., the shale-normalized RE pattern shows a Ce deficiency and a relative enrichment of heavy RE). The mean calculated summary contents of light (La, Ce, Nd to Eu) and heavy RE (Tb to Er, Yb, Lu) for 15 aerosol samples collected between February and April 1976 above the open middle-latitudinal and tropical Atlantic and Pacific oceans are as follows [10]:

location	content in ng/m^3	
	Σ light RE	Σ heavy RE
Atlantic Ocean	1.063	0.029 *)
Pacific Ocean	0.663	0.112

*) Without Ho and Er.

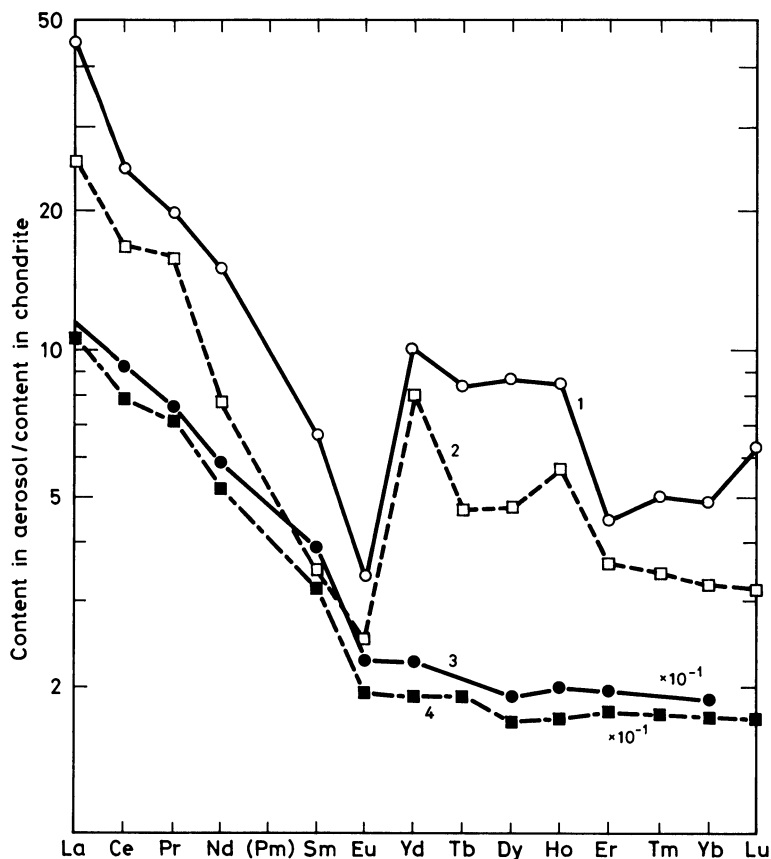Fig. 1a. Chondrite-normalized RE distribution patterns for aerosols from above the Atlantic (1) and Indian oceans (2), the Moscow area (3), and in sedimentary rocks (4) from [2, p. 257].
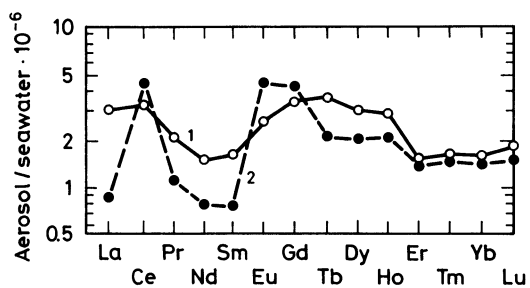

Fig. 1b. Distribution pattern for RE in aerosols in relation to seawater from the surficial parts of the Atlantic (1) and Indian oceans (2) from [8, p. 940]. Given on the ordinate is the ratio of the corresponding absolute contents in g/g.

The calculated summary contents of light (La to Eu) and heavy RE (Gd to Lu) in other aerosol samples collected over the Atlantic and Indian oceans are as follows; contents of Pr, Dy, and Tm are not analyzed but calculated [8, p. 937]:

location	content in 10^{-6} g/t	
	Σ light RE	Σ heavy RE
Atlantic Ocean; 48°37′ N, 19°00′ W	45.34	8.26
Indian Ocean; 07°52′ S, 65°58′ E	30.18	5.37

The contents of Ce, Sm, and Eu at various distances from the African continent are as follows for nine aerosol samples collected 5 m above sea level during November 1970 over the Gulf of Guinea (5° N to 3° S); distance from shore increases from sample No. 1 to 9 [1]:

	content in ng/m^3 for sample								
	No. 1	2	3	4	5	6	7	8	9
Ce	0.55	0.27	0.21	0.42	0.02	0.17	0.16	0.16	0.08
Eu	0.0096	0.0061	0.0079	0.0051	—	0.0048	0.0072	0.0036	—
Sm	0.0343	0.0151	0.0102	0.0038	0.0088	0.0079	0.0018	0.040	0.0143

Contents of RE elements in aerosols from the northern Atlantic Ocean are 1.5 times those from the Indian Ocean, but are on average 4 times lower than in aerosols from the continental Moscow region [2, p. 253]. The calculated summary contents of light (La to Eu) and heavy RE (Gd to Lu) in marine aerosol (average for the Atlantic and Indian oceans) and in continental aerosol from the Moscow region, USSR, are as follows:

location	content in 10^{-6} g/t		Ref.
	Σ light RE	Σ heavy RE	
marine [1]	37.71	6.82	[8, p. 937]
continental	495.5	20.8 [2]	[11]

[1] Contents of Pr, Dy, and Tm are calculated. — [2] Without Tb, Tm, and Lu.

Equal to the concentration in suspended matter of surface seawater and in average sedimentary rocks is the RE content, recalculated to the mineral residue (1.0 to $2.0 \times 10^{-2}\%$) in air suspension collected over the northern Indian Ocean [3]. Relative contents of light RE (La to Gd) are identical in aerosols collected over the Atlantic and Indian oceans and in platform–type clays (which are used for comparison since terrigenous dust over oceans contains ~80% clay minerals), although the absolute contents in clay are considerably higher than in aerosol. Such a discrepancy is quite possible because clay minerals in aerosol can dilute sea salts almost tenfold. Compared with RE in clays, elements in the range Gd to Ho have a small variance in distribution in aerosol collected over both the Atlantic and Indian oceans. Apparently, during the formation of marine aerosol a fractionation of RE takes place, as can be seen from **Fig. 1b** [8, pp. 939/40]. Compared with seawater, an enrichment of Ce and intermediate RE (Eu to Ho) occurs in aerosols collected during 1972 and 1973 over the Atlantic and Indian oceans [12]. Compared to aerosol from the continental Moscow region and to sedimentary rocks, aerosol collected over the Atlantic and Indian oceans is enriched in heavy RE (see **Fig. 1a**) which can be due either to a

different mineralogical composition or to a fractionation of RE during the process of transfer from seawater into the atmosphere [2, pp. 255, 257].

Comparing RE contents in aerosols from various environments, a stronger pollution in industrial or urban than in rural or remote areas is obvious; see, e.g., [13] and [14] for differences between Heidelberg, Federal Republic of Germany, and the rural site Niles, Michigan, and the industrial region of East Chicago, Indiana; or [15, pp. 11, 25] for differences between the rural sites Wraymires, Windermere, Great Britain, and Canadian stations and the industrial sites of Osaka, Japan, and Chicago; or [16] for differences between the city of Beer-Sheva and a nearby desert area (Shivta), Israel. For quantitative data refer also to Table 3 (pp. 120/1).

For a 12-months period (June 1972 to May 1973), lower average Ce contents are found in air over the clean and rural sites Lerwick and Collafirth, both Shetland Isles (0.054 and 0.077 ng/kg, respectively) than in air over five more industrial, although non-urban, sites (0.30 ng/kg at Leiston, Suffolk; 0.29 ng/kg at Gresham, Norfolk; 0.175 ng/kg at Petten, northern Holland; 0.195 ng/kg at Arran, Bute, western Scotland; and 0.20 ng/kg at a gas platform, North Sea) [17]. Compared to industrial and municipal regions, for La in rural and remote (background) regions a relative increase in the coarse fraction of aerosol occurs, probably due to the large contribution of lithogenous aerosol; for the contents in different size fractions, see p. 106, [18].

An overall resemblance in the elemental composition of aerosol samples collected at the Jungfraujoch, Bernese Alps, Switzerland, with literature data for aerosols collected at other remote sites (Lakselv, North Cape, Norway, from [21]; Amundsen-Scott station, South Pole, Antarctica, from [23]) or at 14 urban, industrial, and rural locations in Belgium (from [45]) and, especially, with those from Twin Gorges, Northwestern Territories, Canada (from [19]) becomes evident by normalizing the aerosol-rock enrichment factors to those of the mean Jungfraujoch aerosol. With aerosol-rock enrichment factors (normalized to Al) of 2.1 for La and 1.6 for Sm both elements at the Jungfraujoch are not significantly more enriched than at the other locations [26]. A constancy of atmospheric trace element contents in atmospheric particulate samples collected during two austral summers (1970/71 and 1974/75) near the new Amundsen-Scott station, Antarctica (see p. 125), is not surprising since the south pole is far from potential aerosol sources so that an aged, well-mixed aerosol of nearly constant composition is sampled. In addition, meteorological conditions over the polar plateau do not change significantly [25]. Note also that for rural sites at some distance from specific sources, as, e.g., at Chilton, Oxfordshire, Great Britain, mixing due to diffusion and deposition and resuspension would tend to provide a chemically uniform aerosol [46]. No substantial differences occur between the contents of La and Sm in aerosol samples (collected ~1 m above ground during 1973 and 1974) at one urban (No. 1), express-way (No. 4), and four industrial sites (Nos. 2, 5 to 7) in Toronto, Canada. The mean and range of contents are as follows; average of 20 to 40 samples for La at each site, number of determinations >5 for Sm [47]:

| element | content in ng/m^3 at site | | | |
	No. 1	No. 4	No. 2	Nos. 5 to 7
La	2.9; 0.6 to 6.5	2.3; 0.5 to 5.6	2.3; 0.6 to 4.1	1.9; 0.3 to 4.0
Sm	0.38; 0.16 to 1.0	0.32; 0.06 to 0.81	0.35; 0.08 to 0.88	0.27; 0.05 to 0.52

For a spatial variation in [144]Ce peaks related to meteorological conditions, see p. 130.

When comparing trace element contents in **rainwater** it is necessary to mention that meteorological and local conditions may influence their concentrations much more than in aerosol. Therefore, not too much account should be taken of the relative contents in rainwater at different places [14]; note too that there is no reason for an agreement in trace element contents of rainwater because of different air pollution and meteorological conditions [48, pp. 837, 839]. Different absolute RE contents in atmospheric precipitations can lead to a change of their relative distribution. The fractionation of RE in atmospheric precipitations depends on the different mobility of individual elements during processes of entrance into the atmosphere and during their transfer over considerable distances from their source area [2, pp. 253/4].

Since the RE are strictly lithophile elements, an identical relative distribution in rainwater and in sedimentary rocks is expected. However, only light RE show such an identity in rainwater samples from the Moscow area, the Black Sea, and the Atlantic Ocean. For rainwater collected over the Indian and Pacific oceans, a Ce minimum (as in seawater) is typical which is not observed in aerosol [2, pp. 254/5]. Furthermore, the Ce minimum is the main difference between the RE distribution in rainwater and that in aerosol and clays [8, p. 940].

Obviously due to a decrease in dust content in the atmosphere, the RE content in rainwater over oceans is 100 to 1000 times lower than in rainwater over continental or inland-sea regions, which both have contents of the same order of magnitude [12] as can be seen from the calculated summary contents of light (La to Eu) and heavy RE (Gd to Lu) in rainwater collected over marine and continental areas in 1972 (marked with an asterisk) and 1973:

location	content in 10^{-6} g/t		Ref.
	Σ light RE	Σ heavy RE	
Atlantic Ocean; 48°37′ N, 19°00′ W	6.79[1]	3.64[1]	
Pacific Ocean; 19°32′ N, 138°16′ E	10.25[1]	4.19[1]	
Indian Ocean; 07°52′ S, 65°58′ E	8.07[1]	4.13[1]	[8, p. 937]
Black Sea; 42°16.5′ N, 40°26′ E	1269[1]	437.5[1]	[2, p. 254]
Black Sea; Sevastopol*)	1452	456	
Black Sea; Batumi*)	1106	420	[4]
Moscow region, USSR	1751[1]	519[1],[2]	[2, p. 254]

[1] Contents of Pr, Dy, and Tm are calculated. — [2] Refer to 529×10^{-6} g/t for a sample taken September 1972 in [4].

In contrast to rainwater collected from the Moscow area, a maximum for the relative contents of heavy RE (Tb to Lu) occurs in rainwater over the three oceans (possibly due to sorption of volatile RE compounds on solid aerosol particles near the ocean surface [12]; refer

Fußnote to Table 3 on pp. 120/1:

[1] Given in pg/m^3. — [2] Average contents of La <0.5 and Ce 0.30 ng/m^3 are given for the period January to December 1971 in [43]. — [3] Additionally, Pr 0.0060, Nd 0.017, Dy 0.0026, Gd 0.0028, Tb 0.00027, Ho 0.00032, Er 0.00087, Tm 0.00011, Yb 0.00069, and Lu 0.00017 are given. — [4] Additionally, for the period December 16, 1974 to February 1, 1975 is given Yb <0.05 pg/m^3 (average of 5 sampling periods) in [44]. — [5] Given in ng/kg. — [6] n=12. — [7] n=2. — [8] n=3. — [9] Additionally, Y 3.2 ng/m^3 is given. — [10] Additionally, Lu 0.009 to 0.035, 0.021 ng/m^3 is given. — [11] Additionally, Yb 0.084 ng/m^3 (one sample) and Lu 0.018 to 0.051, 0.030 ng/m^3 are given. — [12] Given in ng/L; additionally Pr 32 to 328 and Nd 25 to 76 ng/L are given. — [13] Additionally, Lu 0.037 and 0.033 ng/m^3 are given.

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Table 3. Range and/or Mean Content of Some Rare Earth Elements in Aerosol from Various Environments. Number of analyses = n. Footnotes see p. 119.

Type of environment; location and sampling date	content in ng/m^3 La
remote	
Twin Gorges	0.091
Mackinac Island, Michigan	0.23 ± 0.04
Lakselv, Norway	0.042
Lerwick, Shetland Isles, Great Britain; 1972	<0.3
Lerwick, Shetland Isles, Great Britain; 1973	<0.06
Plynlimon, Montgomerys, Great Britain; 1972	<0.2
Plynlimon, Montgomerys, Great Britain; 1973	<0.2
South Pole, Antarctica; austral summer 1970; n = 10 [1]	0.21 to 1.4; 0.51 ± 0.37
South Pole, Antarctica; austral summer 1974/75 [1,4]	0.45 ± 0.15
Jungfraujoch, Bernese Alps, Switzerland; August 1973 to August 1975; n = 20	<0.005 to 0.200; 0.040
semiremote	
Colstrip, southeastern Montana; May to September 1975	0.50 ± 0.46
rural	
High Point, New Jersey; July 21 to August 1, 1976; n = 12	0.325
Canada; summer 1970; n = 7	0.091 to 0.76; 0.25
Niles, Michigan; June 11, 1969; n = 4	1.0 to 1.7; 1.3
Wraymires, Westmorland, Great Britain; January 1971 to April 1972; n = 14 [2,5]	0.02 to 0.71; ~0.44 [6]
Osaka prefecture, Japan [3]	0.027
semirural	
Northwestern Indiana; n = 12	1.9
urban	
San Francisco, California; July 23, 1970	1.2 ± 0.13
East Chicago; June 11, 1969; n = 4	5.6 to 6.5; 5.9
Chicago; April 4, 1968; n = 22	0.9 to 4.8; 2.1
Boston, Massachusetts	1.75
Boston, Massachusetts; March 25 to April 27, 1970; n = 5	0.56 to 2.4; 1.45 ± 1.26
Paris, France; November and December 1970; n = 36	0 to 10.4; 3.42
Heidelberg, Federal Republic of Germany; April to June 1971; n = 14	0.35 to 0.92; 0.62
Ankara, Turkey; n = 4 [9]	2.0
Ankara, Turkey; September 1976 to February 1977; n = 6	2.08 to 3.95; 2.86
Osaka, Japan; August to September 1971; n = 30 [10]	0.40 to 3.76; 1.57
Osaka, Japan; February to July 1972; n = 6 [11]	1.3 to 4.7; 3.1
industrial	
Northwestern Indiana; n = 10	3.4
Northwestern Indiana; June 11 to 12, 1969; n = 24	0.9 to 5.9; 2.8
Illinois (RE-processing refinery); 1967 and 1970; n = 14 [12]	44 to 340
Marietta region, Ohio; n = 4	0.66 to 2.2; 1.57
Osaka, Japan; February to July 1972; n = 2 [13]	9.1 and 8.9

Ce	content in ng/m^3 Sm	Eu	Ref.
—	0.013	—	[19]
0.36 ± 0.10	0.013 ± 0.004	0.006 ± 0.004	[20]
—	0.0057	—	[21]
0.07	—	—	
0.03	—	—	
0.14	—	—	
0.15	—	—	[22, pp. 15/6, 66]
0.8 to 4.9; 2.3 ± 1.6	0.028 to 0.089; 0.055 ± 0.023	0.004 to 0.024; 0.017 ± 0.004	[23, 24]
<4.1	0.088 ± 0.040	0.020 ± 0.007	[25]
—	<0.002 to 0.025; 0.006	—	[26]
0.17 ± 0.13	0.073 ± 0.064	0.016 ± 0.012	[27]
—	0.036	—	[28]
0.24 to 1.6; 0.55	0.013 to 0.11; 0.039	0.0017 to 0.019; 0.0076	[29, p. 65]
0.77 to 0.86; 0.82	0.20 to 0.30; 0.24	0.045 to 0.065; 0.055	[30]
0.13 to 0.54; 0.29	—	—	[15, pp. 17/9]
0.043	0.0025	0.0051	[31]
2.5	0.33	0.085	[29, p. 163]
1.5 ± 0.2	0.16 ± 0.05	0.015 ± 0.005	[32]
8.6 to 15.2; 13.0[8)]	0.35 to 0.53; 0.41	0.10 to 0.17; 0.135	[30]
2 to 20; 7	—	0.02 to 0.23; 0.12	[33]
3.0	0.24	0.046	[34]
0.91 to 3.4; 2.2 ± 1.8	0.080 to 0.33; 0.20 ± 0.17	0.0133 to 0.059; 0.035 ± 0.030	[35]
0 to 49.5; 14	0 to 1.04; 0.416	—	[36]
0.41 to 6.1; 1.01	0.07 to 1.9; 0.27	—	[13]
9	0.1	0.1	[37]
3.36 to 53.17; 18.34	—	0.038 to 0.186; 0.083	[38]
0.8 to 7.7; 3.1	0.09 to 0.84; 0.33	—	[39]
3.3 to 8.7; 5.7	0.25 to 0.66; 0.43	0.049 to 0.12; 0.078	[40]
6.1	0.34	0.10	[29, p. 163]
1.4 to 13; 4.7	0.17 to 0.65; 0.36	0.06 to 0.17; 0.096	[41]
25 to 680	—	—	[42]
1.3 to 14; 5.95	0.12 to 0.71; 0.37	0.022 to 0.17; 0.081	[20]
16 and 18	0.73 and 1.4	0.093 and 0.10	[40]

also to p. 102); rainwater collected over the Black Sea takes an intermediate position [2, pp. 255/8].

A possible influence of organic compounds in plankton on the RE content in rainwater is indicated by the relative enrichment of Eu, Gd, and Tb in diagrams for the relative contents in rainwater compared to contents in plankton or in seawater (see original paper). The contents of RE in organic compounds in rainwater over the Pacific Ocean correspond to the RE distribution in plankton, while over the Atlantic and Indian oceans rainwater is depleted in La, Ce, and Pr [8, pp. 941/2]. The RE distribution between plankton and seawater is given in **Fig. 2**.

Contents of RE in rainwater collected during 1972 and 1973 over the northern Atlantic, northwestern Indian, and southwestern Pacific oceans are approximately equal to those in seawater (on average 12×10^{-6} g/t) [2, pp. 252/3]. Compared to aerosol contents, rainwater over the Atlantic Ocean is impoverished by a factor of 15 in Ce, 6 in Gd, and 3 in Ho; in rainwater over the Indian Ocean a depletion occurs only for Ce. Such a divergence can be explained by a higher marine influence on RE composition in the atmosphere over the Atlantic than over the Indian Ocean [8, p. 940].

Some examples of La and Ce contents in rainwater in relation to the annual rainfall for various locations of Great Britain are given in the table on p. 123. In ten rainwater samples collected by airplane between March 18 and July 1, 1971 over Heidelberg, Federal Republic of Germany, the La concentration (soluble and insoluble fraction) varies between 0.13 and 1.9, mean 0.65 g/cm^3; and 11 rainwater samples contain Sm between 0.04 and 0.41, mean 0.16 g/cm^3 [48, p. 838]. A comparison of cloud and rainwater concentrations in samples taken June 28, 1971 for the Heidelberg area shows that between 3.5 and 2.5 km altitude the relative concentrations of most elements are constant, except for Ce and Sm, which could not yet be explained. Between the lowest cloud level (1.5 km) and earth's surface, constant or increasing concentrations occur for all elements not originating in the ocean. With respect to Na, it is possible to estimate the distance between cloud and ground level for a doubling in the cloud-base concentration, by approaching the earth's surface. For elements related to the earth surface or anthropogenic production as their main source, these distances are, e.g., 500 m for La, 430 m for Sm, 250 m for Sc, and 100 m for Fe [48, pp. 835, 840/3].
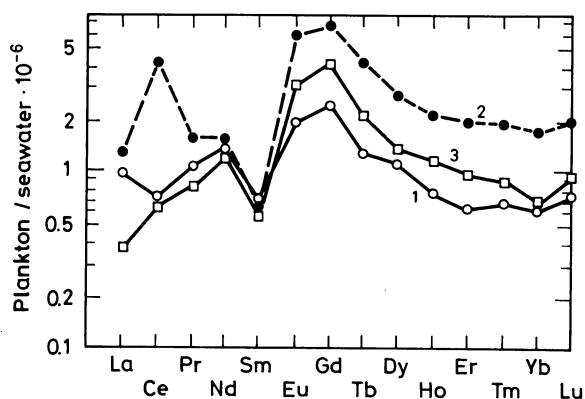

Fig. 2. Distribution pattern for RE in plankton in relation to seawater of the Atlantic (1), Indian (2), and Pacific oceans (3) from [8, p. 941]. Given on the ordinate is the ratio of the corresponding absolute contents in g/g.

| location and date of sampling | | content in µg/L | | rainfall | Ref. |
		La	Ce	in mm/yr.	
Wraymires, Westmorland	1971	<0.3	0.42		[43]
	1971/72[1]	~0.27[2]	~0.39[2]	1866	[15, p. 20]
	1972	<0.2	0.13	1797	
	1973	<0.2	0.10	1482	
Chilton, Berkshire	1972	<0.7	0.85	626	
	1973	<0.4	0.49	574	
Leiston, Suffolk	1972	<0.3	0.64	404	
	1973	<0.2	0.4	478	
Lerwick, Shetland Isles	1972	<1	0.79	1065	
	1973	<2	<0.3	1437	
Plynlimon, Montgomerys	1972	<0.4	<0.2	2151	
	1973	<0.1	<0.05	2754	
Styrrup, Nottinghshire	1972	<5	2.7	545	
	1973	<1	1.1	586	
Trebanos, Glamorganshire	1972	<0.4	<0.4	1538	
	1973	<0.4	<0.6	1012	[22, p. 69]

[1] February 1971 to March 1972. — [2] Mean for 13 samples with a variance of <0.25 to 0.52 for La and <0.05 to 1.8 µ/L for Ce.

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8.2.3 Temporal Variations (Seasonal and/or Meteorological)

During a 24-hour period very large variations (up to a factor of ten) occur within a few hours in the contents of several elements (e.g., Sm, Eu, La) in aerosol samples collected on August 21 and 22, 1969 at a rural site 5 km off Niles, Michigan ($\sim$45 km east of Lake Michigan and $\sim$100 km northeast of the heavily industrialized northwest Indiana area). Elements showing those large variations share two characteristics, namely relatively deep morning minima and masses concentrated on larger particles. The ranges of contents in aerosol during a 48-hour period are as follows: La 0.3 ± 0.3 to 3.8 ± 0.4 ng/m^3; Sm 0.055 ± 0.025 to 0.39 ± 0.4 ng/m^3; and Eu <0.02 to 0.09 ± 0.02 ng/m^3 [1, pp. 189, 191, 193, 195, 198/202].

An increase in the content of La and a $<20\%$ decrease or no change of Ce and Eu contents occur during 1976 in air at five or more sites out of seven in Great Britain [2, p. 6]. No seasonal influence is apparent on trends for the contents of La, Ce, Eu, and Sm in air particulate samples collected in 1978 at five non-urban sites in Great Britain; only small differences between winter and summer contents occur for Ce which are attributed to more limited resuspension of soil dust into the atmosphere by agricultural cultivation and civil engineering in winter [3, pp. 1, 6/7]. Similar particle concentration and composition in austral summer seasons of different years (as well as fairly constant atmospheric trace element contents within a single austral summer) are indicated for the new Amundsen–Scott station, Antarctica, by comparing the average contents of trace elements (including La, Ce, Sm, Eu, and Lu) in atmospheric particulate samples collected between December 1974 and February 1975 (during six sampling periods) and the contents (data from [4]) in samples collected from the 1970/71 austral summer. The arithmetic mean contents of some RE are as follows [5]; see also [6]:

austral summer	mean content in pg/m^3				
	La	Ce	Sm	Eu	Lu
1970/71	0.51 ± 0.37	2.3 ± 1.6	0.055 ± 0.023	0.017 ± 0.004	—
1974/75 *)	0.45 ± 0.15	<4.1	0.088 ± 0.040	0.020 ± 0.007	0.0067 ± 0.0018

*) Additionally, a content of <0.05 pg/m^3 for Yb is given in [6].

With time, three distinct types of variation in the atmospheric concentration of elements and ions occur: (1) Long-term trends over the period of a survey (see p. 126); (2) medium-term fluctuations (often covering several years) which may be enhancements or reductions about the general level; and (3) a regular seasonal variation between summer and winter months (see pp. 126/8) [7, p. 178]. Medium-term fluctuations of trace elements in some 5000 air filter samples collected during the period 1957 to 1974 at Chilton, Oxfordshire, Great Britain, have no obvious cause and show obscure general trends in trace element behavior. Major fluctuations, as, e.g., troughs in 1961 and 1967, are common to most components (including Ce and Eu) and are thought to be dependent on meteorological conditions [7, pp. 165/6, 172/3, 179]; refer also to pp. 128/31.

Overall (long-term) trends in element content may be expected to demonstrate possible changes in anthropogenic emissions and in climatic patterns. The overall fluctuations in the major lithophilic group of elements (including Ce and Eu) are greater than those observed for other constituents occurring in small forms in some 5000 samples of air-particulate material collected between 1957 and 1974 at Chilton, Oxfordshire, Great Britain, which possibly is due to differences of the chemical behavior at the source, to differing diffusion rates of large compared to small particles, or simply to the occurrence of wind-blown soil at times of high winds [7, p. 193]. A decreasing long-term trend of Ce (examined by fitting simple regression lines to quarterly results) with a slope of 25%/yr. occurs in samples of total deposition collected continuously from 1971 to 1975 at Wraymires and from 1972 to 1975 at six other sites, all Great Britain. The annual total deposition is derived from contents in rainwater × rainfall; both soluble and insoluble fractions of rainwater are included [8].

Time-dependent variations in the ^{141}Ce/^{144}Ce ratio, which give information on the transfer of radioactivity in the atmosphere, are observed in ground-level air samples collected between December 1973 and July 1980 at Nagoya, Japan. The ratio decreases with an expected half-time of 36.7 days and is attributable to individual Chinese nuclear test explosions. After a world-wide circulation, the ratio increased again and thus yields mean tropospheric residence times of 20 days for the debris from the 22nd, and of 7 days each for the 23rd and 24th nuclear explosions [9].

Regular **seasonal variations** between summer and winter months occur, e.g., for contents of large-particle elements (including RE) in aerosol particles from surface continental air collected at Twin Gorges, at Algonquin, and at Mackinac Island, all Canada. Both the number and content of large-particle elements tend to decrease in winter compared to summer (possibly due to the presence of a local snow cover). At Mackinac Island, nearly all soil-derived elements are more abundant in summer (in keeping with the effect of exposed soil vs. snow cover) with summer/winter concentration ratios (S/W) usually between 1 and 2 (see table below); for the two other sites, data are more dispersed and do not show easily interpretable trends. The contents of some RE are as follows for the three locations [1, pp. 28/9, 53/4, 71]:

	Twin Gorges content in ng/m³		ratio S/W	Algonquin content in ng/m³		ratio S/W	Mackinac Island content in ng/m³		ratio S/W
	summer	winter		summer	winter		summer	winter	
La	0.20	0.10	2.0	0.33	0.065	5.1	0.29	0.17	1.7
Ce	0.45	0.11	4.1	0.58	0.16	3.6	0.35	0.38	0.92
Sm	0.024	0.020	1.2	0.050	0.012	4.2	0.035	0.021	1.7
Eu	0.0039	0.0064	0.61	0.0086	0.0040	2.1	0.0058	0.0047	1.2

Lowest average ratios of winter-to-summer contents (e.g., for Ce 1.21 and for Eu 1.14) appear to be associated with elements occurring with particles of large size in some 5000 air filter samples collected during the period 1957 to 1974 at Chilton, Oxfordshire, Great Britain [7, pp. 162/3, 166, 178, 187/8]. A 25%-difference in slope between winter (October to March) and summer (April to September) occurs in samples of total deposition collected continuously from air between 1971 and 1975 at Wraymires, Lancashire, and between 1972 and 1975 at six other sites, all Great Britain; i.e., the deposition of Ce in winter declines more than in summer. A winter-to-summer comparison of enrichment factors relative to average soil (normalized to Sc) for the total deposition shows a ratio of 0.7 for Ce. The ratio of total deposition of Ce in winter compared with summer months based on the five-

years results at Wraymires is in the range of 0.9 to 1.1 [8]. Average summer and winter contents of some RE for aerosol samples collected in 1979 at Katowice, Poland, are as follows; number of samples is given in parentheses [10]:

sampling season	average content in ng/m^3				
	La	Ce	Sm	Eu	Lu
summer	3.3 ± 1.4 (27)	11 ± 9 (36)	0.6 ± 0.2 (30)	0.18 ± 0.11 (18)	0.05 ± 0.03 (21)
winter	6 ± 3 (34)	14 ± 10 (34)	1.4 ± 0.6 (21)	0.53 ± 0.32 (7)	0.10 ± 0.04 (20)

Changes in contents and/or enrichment factors of RE occur during the transition from dry to wet season in 55 samples of aerosol particles from the lower atmosphere (18 m altitude) above Eniwetok Atoll, Marshall Islands, tropical northern Pacific Ocean. The contents of Ce and Eu in bulk samples are 89 ± 1.6 and 1.0 ± 1.6 pg/m^3, respectively, during the dry season (April 15 to May 18, 1979; precipitation 4.3 cm; dust concentration in the atmosphere ~2.3 µg/m^3 at the beginning of the dry season) and 4.8 ± 2.4 and 0.09 ± 2.0 pg/m^3, respectively, during the wet season (June 26 to August 7, 1979; precipitation 26.4 cm; dust concentration in the atmosphere ~0.02 µg/m^3 at the end of the wet season). The corresponding crustal enrichment factors EF_{crust} (normalized to Al) in the bulk samples are 1.6 and 0.95 (dry season) and 1.0 and 0.54 (wet season). Enrichment factors EF_{sea} relative to seawater (normalized to Na) for all crustal elements decrease by >80% from the dry (Ce 33000, Eu 26000) to the wet season (Ce 3000, Eu 3100), since contents of crustal elements decrease faster than that of Na, the representative sea-salt element. The size-separated aerosol samples have the following enrichment factors for Ce (extremely low contents preclude the detailed analysis of the mass-size distribution of Eu) [11]:

sampling season	enrichment factors for Ce in different size fractions of aerosol					
	7.2 µm		3.0 µm		1.5 µm	
	EF_{crust}	EF_{sea}	EF_{crust}	EF_{sea}	EF_{crust}	EF_{sea}
dry	0.97	3000	1.6	2000	1.4	72000
wet	0.92	260	0.99	4500	1.6	20000

sampling season	enrichment factors for Ce in different size fractions of aerosol					
	0.95 µm		0.49 µm		≤0.49 µm	
	EF_{crust}	EF_{sea}	EF_{crust}	EF_{sea}	EF_{crust}	EF_{sea}
dry	1.4	110000	1.4	170000	1.4	53000
wet	0.99	27000	1.5	65000	0.69	71000

Over the Ivory Coast, contents of terrigenous elements (including Eu) are two to four times higher in two series of ground-level aerosol (20 samples collected from a north-south profile) during the dry season (October to December 1970) than their contents in aerosol samples (three series taken at five sites with distances between 5 and 400 km from shore) collected in the rainy season (May to June 1971). In the dry season, the winds of the northeast sector carry large quantities of dust from the Sahara and washing-out by precipitation is very weak. The average Eu contents at 100 and 400 km distance from shore, respectively, are 0.66×10^{-4} and 1.20×10^{-4} (dry season) and 0.20×10^{-4} and 0.33×10^{-4} µg/m^3 (wet season) [12]. Lowest contents of La occur in the rainy season (in April) in airborne particulate matter collected between March and August 1978 at three sites each in the Taipei and Kaoshiung regions, Formosa (except one site in the latter region), whereas La content

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gradually increases to highest values in June or July [13]. In accordance with the mechanism of radioactive transfer from the atmosphere, seasonal variations are observed for [141]Ce and [144]Ce in the atmosphere over Bratislava-Koliba, Czechoslovakia, with highest levels occurring in August and September 1977 of [141]Ce and in June 1977 of [144]Ce [14]. Comparatively high levels during late winter and early spring of each year occur for [144]Ce in ground-level air collected at Bombay, India, between November 1961 and June 1965, which are attributed to seasonal effects in the mixing between the stratosphere and the troposphere [15].

A seasonal variation of [144]Ce ascribed to the influx of stratospheric air into the troposphere during spring occurs in surface air collected between January 1960 and September 1961 at Sutton, Surrey, Great Britain [16]. Caused by stratospheric exchange during the spring, a maximum [144]Ce/[141]Ce ratio occurs in 1974 in ground-level air at Brunswick, Federal Republic of Germany, and at Tromsö, northern Norway [17], and in ground-level aerosol collected between 1963 and 1970 at Brunswick; most of the fission products (e.g., [141]Ce, [144]Ce) have been injected into the stratosphere and reach the surface air during the spring peak [18]. A spring peak is also observed for RE radionuclides in rainwater; e.g., for [141]Ce and [144]Ce in samples collected in 1960 and 1961 at Fayetteville, Arkansas [19]. Spring-summer maxima occur also for [141]Ce, [144]Ce, and [155]Eu in fallout samples collected monthly during the period 1977 to 1980 at Parma, Italy [20]; for [141]Ce and [144]Ce in deposition and precipitation samples during 1979 and 1980 in Cluj-Napoca, Iasi, Craiova, Pitesti, and Constanta, all Romania [21]; and for [141]Ce and [144]Ce in fallout collected during 1980 and 1981 at five stations covering the whole territory of Romania. The maximum of the [144]Ce activity is shifted towards summer months compared with [141]Ce [22].

Apart from initial source strength, **meteorological factors** such as speed and direction of wind, temperature, and rainfall are expected to influence air contents of elements [23, p. 5]. According to wind direction, Al-normalized crustal enrichment factors for Sm in ambient air samples collected between July 21 and August 1, 1976 at High Point, northwestern New Jersey, vary as follows: 1.77 for southwesterly, 1.35 for westerly, 2.33 for northwesterly, 1.60 for northerly, 2.1 for easterly, and 1.8 for southerly winds [24]. Direction and velocity of wind (besides location of sampling site) may cause a high variability of some RE in semiremote background aerosols collected 60 m above ground in 1975 at three sites in the semiarid rangeland area of southeastern Montana near the town of Colstrip. The contents (variance and mean) are as follows and given in ng/m^3: 0.10 to 2.6, 0.50 ± 0.46 for La; 0.024 to 0.60, 0.17 ± 0.13 for Ce; 0.003 to 0.34, 0.073 ± 0.064 for Sm; 0.0019 to 0.070, 0.016 ± 0.012 for Eu; and 0.0010 to 0.19, 0.02 ± 0.04 for Tb [25]. The contents of some RE before (sample Nos. 1 to 8, collected on April 16 and 17, 1980) and during a dust storm (sample Nos. 9 to 12, collected on April 18, 1980) over Beijing, China, vary as follows; the aerosol concentration is usually between 4×10^{-5} and $\sim 2.5 \times 10^{-4}$ g/m^3, the highest value during the dust storm is 6.13×10^{-3} g/m^3 [26]:

	No. 1	2	3	4	5	6	7	8	9	10	11	12
La	6.1	9.0	4.2	4.2	3.8	10	7.9	5.4	87	150	26	5.6
Ce	11	16	8.0	7.2	8.5	18	17	13	180	410	57	9.4
Nd	—	—	—	—	—	—	—	—	120	210	—	27
Sm	0.84	1.3	0.59	0.61	0.52	1.6	1.2	0.81	14	33	4.4	0.87
Eu	—	—	—	—	—	—	—	—	3.1	8.2	—	—
Tb	—	—	—	—	0.25	0.48	0.26	0.18	2.6	6.5	0.87	—
Yb	—	—	—	—	—	—	0.45	0.56	5.3	11	1.8	0.60
Lu	0.058	0.094	0.044	0.069	0.11	0.11	0.13	0.10	1.0	2.4	0.35	0.14

content in ng/m^3 in sample

Reflecting the dustiness of winds from the Sahara, higher contents occur on October 12, 1973 for La, Ce, and Eu in aerosol collected ~15 km west of Wad Medani, Gezira province, Sudan, during dry north to northeasterly trade winds than in aerosol collected from humid southerly winds on October 14 and 15, 1973. The content (range and mean) besides enrichment factors relative to average local soil (normalized to Fe) for three aerosol samples each and for both wind directions are as follows [27]:

| | content in ng/m³ for aerosol from | | enrichment factor | |
	northerly wind	southerly wind	northerly wind	southerly wind
La	1.5 to 2.6; 2.23	<1	1.16	<1.6
Ce	2.5 to 2.7; 2.57	0.79 to 1.38; 1.01	1.04	1.26
Eu	0.031 to 0.090; 0.065	0.025 to 0.036; 0.031	0.75	0.85

The annual average contents of some RE in airborne dust for various rural to semirural sites of Great Britain are as follows:

location and date of sampling		content in airborne dust in ng/kg				Ref.
		La	Ce	Sm	Eu	
Wraymires, Lancashire	1971/72[1]	<0.3	0.25	—	—	[28]
	1972	<0.7	0.15	—	—	
	1973	<0.2	0.19	—	—	[29]
	1974	<0.2	0.24	—	—	[23, p. 9]
	1976	0.69	0.30	0.024	0.008	[2, p. 11]
	1977	0.28	0.30	0.017	0.006	[30]
	1978	0.16	0.21	0.008	0.003	[3, p. 11]
Chilton, Berkshire	1972[3]	<0.3	0.40	—	—	[28]
	1972	<0.3	0.36	—	—	
	1973	<0.3	0.29	—	—	[29]
	1974	<0.2	0.31	—	—	[23, p. 9]
	1976	0.63	0.41	0.026	0.012	[2, p. 11]
	1977	0.25	0.36	0.020	0.007	[30]
	1978	<0.4	0.43	0.026	0.010	[3, p. 11]
Leiston, Suffolk	1972[5]	<0.3	0.39	—	—	[28]
	1972[2]	<0.1	0.32	—	—	
	1973	<0.3	0.28	—	—	[29]
	1974	<0.2	0.31	—	—	[23, p. 9]
	1976	0.70	0.36	0.028	0.010	[2, p. 11]
	1977	0.29	0.42	0.024	0.007	[30]
	1978	<0.2	0.36	0.021	0.005	[3, p. 11]
Lerwick, Shetland Isles	1972[3]	<0.3	0.11	—	—	[28]
	1972	<0.3	0.07	—	—	
	1973	<0.06	0.03	—	—	[29]
Collafirth, Shetland Isles	1974	<0.2	0.11	—	—	[23, p. 9]
	1976	0.20	0.046	0.005	0.001	[2, p. 11]
	1977	<0.14	0.079	0.003	0.001	[30]

Table [continued]

location and date of sampling		content in airborne dust in ng/kg				Ref.
		La	Ce	Sm	Eu	
Plynlimon, Montgomerys	1972[3]	<0.3	0.16	—	—	[28]
	1972	<0.2	0.14	—	—	
	1973	<0.2	0.15	—	—	[29]
	1974	<0.3	0.39	—	—	[23, p. 9]
	1976	0.30	0.23	0.016	0.006	[2, p. 11]
	1977	0.34	0.39	0.024	0.008	[30]
Styrrup, Nottinghamshire	1972[4]	<0.3	0.54	—	—	[28]
	1972	<0.6	0.70	—	—	
	1973	<0.6	0.49	—	—	[29]
	1974	<0.4	0.69	—	—	[23, p. 9]
	1976	0.89	0.54	0.039	0.017	[2, p. 11]
	1977	0.57	0.70	0.040	0.018	[30]
	1978	0.47	0.50	0.023	0.009	[3, p. 11]
Trebanos, Glamorganshire	1972[4]	<1	0.31	—	—	[28]
	1972	<0.7	0.50	—	—	
	1973	<0.3	0.39	—	—	[29]
	1974	<0.3	<0.5	—	—	[23, p. 9]
	1976	0.94	<0.3	<0.03	0.009	[2, p. 11]
	1977	0.53	0.45	0.025	0.007	[30]
	1978	0.50	0.37	0.017	0.004	[3, p. 11]

[1] January 1971 to April 1972. — [2] February to December 1972. — [3] January to March 1972. — [4] January and February 1972. — [5] February and March 1972.

Two concentration peaks of ^{144}Ce (at 30° N along the southern periphery of the Azores atmospheric-pressure peak and at 15° S along the northern periphery of the southern Atlantic atmospheric-pressure peak) separated by an equatorial trough occur in samples of radioactive dust collected at eight sampling points between November 30 and December 21, 1958 over the Atlantic Ocean (between 46° N to 34° S and 18° W to 61° E). Apparently, the equatorial concentration minimum can be accounted for by a rise in heated air masses offsetting the fallout activity from the stratosphere. Assuming equal yields of ^{144}Ce and ^{106}Ru in all 1958 nuclear weapon tests, comparatively fresher activity would be observed at latitudes north of 40° N, whereas at latitudes south of 34° S relatively older fragments would occur. Between 33° N and 34° S, the ^{144}Ce/^{106}Ru ratio remains constant within limits of precision [31]. Concentration maxima of ^{144}Ce are also observed between March 8 and July 2, 1961 at about 20 to 30° N and 25 to 30° S latitude over the Atlantic Ocean; a minimum $(0.8 \times 10^{-18}$ Ci/L) occurs in the region of the equator. For equatorial discharges the period of existence of ^{144}Ce in the atmosphere is ~1 yr. Moving toward the Azores anticyclone (high atmospheric pressure) at about the same latitudes and under similar meteorological conditions, a monotonic increase in contamination level occurs which is five times higher near Gibraltar than in the Black Sea. Concentrations of ^{144}Ce in air are 3.0×10^{-18} Ci/L over the Black Sea; 3.4×10^{-18} Ci/L over the North and Baltic seas; and 8.4×10^{-18} Ci/L (moving south) and 6.8×10^{-18} Ci/L (moving north) over the Atlantic Ocean [32].

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8.3 Removal of Yttrium and/or Rare Earth Elements from the Atmosphere

Removal of particles and their associated trace elements from the atmosphere to the earth's surface occurs by dry deposition and (predominantly) by rain [1, p. 23] or wet removal (see below); furthermore, the removal of stable and radioactive isotopes from the atmosphere occurs by sedimentation of aerosol and washing-out from very high layers of air by atmospheric precipitation [2, p. 252].

Dry fallout (or sedimentation) is determined by particle size, shape, and density. For radii $>10\,\mu m$ sedimentation may be the dominant removal mechanism in quiet near-surface air [3]. Material raised from the earth's surface either by wind or by industrial processes will probably lose by gravitation particles of $>10\,\mu m$ size [4] which return to the surface by sedimentation [5, p. 41], [1, p. 23]. For smaller particles, dry deposition rapidly becomes insignificant with decreasing particle size, and for radii $<10\,\mu m$ dry impaction may be an effective removal mechanism [3]. The dry deposition of elements can be described by the dry deposition velocity Vg in [cm/sec] ($=$ rate of dry deposition in [$\mu g/cm^2$ sec]/concentration in ground-level air in [$\mu g/cm^3$]) [6, p. 44], [7, p. 7].

The average annual dry deposition of some RE from the atmosphere over Great Britain for the years 1971 to 1978 is given in the table on p. 133. For the annual dry deposition of light and heavy RE over the Atlantic and Indian oceans and over total world ocean, see p. 134.

Wet removal of particles from the atmosphere may proceed by cloud droplet nucleation (rainout) or by washout beneath the cloud. Rainout is particularly effective for soluble particles and those with diameters greater than a few tenths of a micron, while washout is a purely physical process effective for particles with diameters $>1\,\mu m$ [3]. Rainout relates to removal mechanisms that occur within the cloud by particulate matter acting as condensation nucleus or being captured by cloud particles. Washout (or below-cloud-scavenging) is the removal of air particulates by raindrops, but the inertial capture of particles by impaction with rain is important only for particles with diameters $>5\,\mu m$ [1, p. 23]. The effectiveness of wet removal of trace elements from the atmosphere is determined by their mode of occurrence in the atmosphere [12] and can be quantified by the ratio of their contents in equal masses of rain and air (washout factor). In principal, this factor relates to the efficiency of removal of particulate material by rain. In practice, the collection of dry deposition in rain will enhance the apparent washout of the larger soil-derived particles [5, p. 47]. It should also be borne in mind that the calculation of washout factors from the soluble rather than from the total content in rainwater would provide a more realistic parameter because the collection of insoluble deposit gives values (e.g., for Ce) that are frequently an order of magnitude greater than those calculated from soluble contents, especially at dusty locations [6, p. 44]. It is suggested (by their washout factors) that trace elements in the atmosphere of natural origin (as, e.g., La and Sm), on a whole, are washed out more efficiently by rain than most of the trace elements of anthropogenic origin [13].

The deposition profiles of many relatively non-volatile metals (including La and Ce) follow the profile of pH in rain collected downwind from the industrial zone of Charleroi, Belgium, i.e., their deposition shows a maximum at a short distance from the industrial center and decreases rapidly to attain (after ~20 km) the deposition rates observed in purely rural, remote areas (Ardennes) which are $\sim20\%$ of the maximum deposition [14].

A different effectiveness of removal of RE from the atmosphere by aerosol and by rain can lead to a different RE composition in aerosol and atmospheric precipitation. The relative

location and year of sampling		dry deposition in µg/cm yr.				Ref.
		La	Ce	Sm	Eu	
Wraymires, Lancashire	1971/72[1]	~0.55[2]	0.44	—	—	[7, p. 23]
	1972	<0.02	0.004	—	—	
	1973	<0.003	0.002	—	—	[6, p. 71]
	1974	<0.005	0.003	—	—	[8]
	1976	0.004	0.006	0.002	0.0002	[9]
	1977	0.008	0.007	0.00045	0.00015	[10]
	1978	<0.003	0.005	0.0006	0.0001	[11]
Chilton, Berkshire	1972	0.018	0.014	—	—	
	1973	0.014	0.011	—	—	[6, p. 71]
	1974	<0.01	0.012	—	—	[8]
	1976	0.021	0.024	0.003	0.0007	[9]
	1978	0.025	0.026	0.002	<0.0005	[11]
Leiston, Suffolk	1972	<0.005	0.002	—	—	
	1973	<0.005	0.003	—	—	[6, p. 71]
	1974	<0.002	0.006	—	—	[8]
	1976	0.014	0.014	0.001	0.0004	[9]
	1978	0.006	0.012	0.0009	0.0002	[11]
Lerwick, Shetland Isles	1972	<0.02	0.003	—	—	
	1973	<0.006	0.004	—	—	[6, p. 71]
Collafirth, Shetland Isles	1974	<0.01	<0.003	—	—	[8]
	1976	0.028	<0.002	<0.0009	<0.0001	[9]
Plynlimon, Montgomerys	1972	<0.007	<0.005	—	—	
	1973	<0.004	<0.003	—	—	[6, p. 71]
	1974	<0.007	0.012	—	—	[8]
	1976	0.009	0.008	0.0008	0.0002	[9]
Styrrup, Nottinghamshire	1972	<0.02	0.029	—	—	
	1973	0.029	0.028	—	—	[6, p. 71]
	1974	0.015	0.030	—	—	[8]
	1976	0.04	0.038	0.003	0.001	[9]
	1978	0.003	0.030	0.039	0.005	[11]
Trebanos, Glamorganshire	1972	<0.01	0.015	—	—	
	1973	0.016	<0.02	—	—	[6, p. 71]
	1974	0.015	<0.03	—	—	[8]
	1976	0.082	0.028	0.002	0.0006	[9]

[1] February 1971 to March 1972. — [2] April 1971 to March 1972.

distribution of RE in atmospheric depositions is controlled by (1) the relation of terrigenous and marine sources in the atmosphere (see p. 115) and (2) by the entrance of gaseous RE compounds from the oceans into the atmosphere and their subsequent association with solid aerosol (see p. 102) [2, pp. 254, 259]. The input of terrigenous material from the atmosphere into the oceans is caused by sedimentation of aeolian dust and material washed out by rainwater from the bottom-layer of air. Washing-out of RE is determined not only by the latitudinal distribution of aerosol (with two maxima between 10 and 15° N and between

10 and 15°S, i.e., within the zone of trade winds, and one maximum on the northern hemisphere at 50°N originating from anthropogenic activities), but also by the amount of rainfall, the height of the bottom-layer of air, and other factors. A different degree of migration of RE and a different amount of aerosol in the atmosphere over the oceans possibly are indicated by higher washout factors for total RE and individual elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) in samples from the Indian compared to those from the Atlantic Ocean. Washed-out RE are sinking to a higher degree over the Indian than the Atlantic Ocean (see below). Washing-out of aerosol by rainwater leads to an enrichment of atmospheric depositions in Ce and intermediate RE (Eu to Tb) relative to seawater. In the following are given the calculated annual summary densities of dry deposition (by sedimentation of the inorganic fraction of aerosol) and the annual deposition by rain for light (La to Eu) and heavy RE (Gd to Lu) for the oceans; contents of Pr, Dy, and Tm are only calculated [15]:

element	density of dry deposition in 10^{-9} g/m^2 yr.[1]			annual deposition by rain in 10^{-6} g/m^2 [2]			
	Atlantic Ocean	Indian Ocean	world ocean	Atlantic Ocean	Indian Ocean	Pacific Ocean	world ocean
Σ light RE	965.7	730.3	1025.7	6.12	7.19	9.2	7.5
Σ heavy RE	176.0	130.4	185.5	3.28	3.72	3.78	3.56

[1] The density of aerosol deposition is 21.3 mg/m^2 yr. for the Atlantic, 24.2 mg/m^2 yr. for the Indian, and 27.2 mg/m^2 yr. for the world ocean. — [2] Average amount of precipitation over oceans is assumed as 90 cm/yr.

The average annual total deposition (dry plus wet) of some RE from the atmosphere over Great Britain reported for the years 1972 to 1978 is given as follows:

location and year of sampling		total deposition (dry and wet) in µg/cm^2 yr.				Ref.
		La	Ce	Sm	Eu	
Chilton, Berkshire	1972	<0.04	0.053	—	—	
	1973	<0.03	0.028	—	—	[6, p. 73]
	1974	<0.04	<0.03	—	—	[8]
	1976	0.045	0.037	0.004	0.001	[9]
	1978	<0.03	0.041	0.003	0.0007	[11]
Leiston, Suffolk	1972	<0.01	0.026	—	—	
	1973	<0.01	<0.02	—	—	[6, p. 73]
	1974	<0.02	<0.03	—	—	[8]
	1976	0.023	<0.02	<0.001	<0.0005	[9]
	1978	<0.02	0.045	0.003	0.0009	[11]
Lerwick, Shetland Isles	1972	<0.02	0.084	—	—	
	1973	<0.03	0.048	—	—	[6, p. 73]
Collafirth, Shetland Isles	1974	<0.01	0.024	—	—	[8]
	1976	0.14	<0.02	<0.008	0.0008	[9]
Plynlimon, Montgomerys	1972	<0.08	<0.03	—	—	
	1973	<0.04	<0.01	—	—	[6, p. 73]
	1974	<0.07	<0.05	—	—	[8]
	1976	<0.05	<0.02	<0.005	<0.0008	[9]

Table [continued]

location and year of sampling		total deposition (dry and wet) in µg/cm² yr.				Ref.
		La	Ce	Sm	Eu	
Styrrup, Nottinghamshire	1972	<0.3	<0.1	—	—	
	1973	0.15	0.07	—	—	[6, p. 73]
	1974	<0.06	0.079	—	—	[8]
	1976	0.053	0.057	0.004	0.002	[9]
	1978	0.043	0.080	0.005	0.001	[11]
Trebanos, Glamorganshire	1972	<0.06	<0.04	—	—	
	1973	<0.07	<0.06	—	—	[6, p. 73]
	1974	<0.09	<0.1	—	—	[8]
	1976	0.072	<0.06	0.003	<0.002	[9]
Wraymires, Lancashire	1972	<0.04	<0.03	—	—	
	1973	0.024	0.015	—	—	[6, p. 73]
	1974	<0.06	<0.03	—	—	[8]
	1976	0.12	<0.03	<0.004	0.0008	[9]
	1977	<0.07	<0.03	<0.005	<0.0006	[10]
	1978	<0.03	0.023	<0.003	<0.0004	[11]

The average annual total deposition (wet and dry) of the same elements and summarized for the period 1972 to 1975 at seven sites in Great Britain is as follows; for comparison insoluble deposition and annual rainfall are given [1, pp. 28/9]:

location	total deposition in g/ha · yr.*)				insoluble deposition in kg/ha · yr.	annual rainfall in mm
	La	Ce	Sm	Eu		
Chilton, Oxfordshire	<4	4.0	0.7	0.1	62	643
Leiston, Suffolk	<2	<2	<0.3	<0.03	21	534
Collafirth, Shetland Isles	<10	<2	<1	<0.07	39	1520
Plynlimon, Montgomerys	<6	<3	<0.4	0.09	38	2521
Styrrup, Nottinghamshire	<10	9.3	0.6	0.2	180	532
Trebanos, Glamorganshire	<7	<10	<0.8	<0.2	93	1269
Wraymires, Lancashire	<5	<2	<0.3	0.09	30	1717

*) Sm and Eu analyzed only in 1975.

Capture of trace elements by falling snow flakes may possibly account for a value of 1.7 for the ratio of enrichment factors for Ce in freshly fallen snow and in aerosol collected in the Moscow region, USSR [16, pp. 54, 60/1]. Comparing the chemical composition of freshly fallen snow with that of the condensate of atmospheric moisture, it is shown that the contents of RE differ by factors of 2 to 4 from those in the condensate [12]. With time (as snow becomes dusty) contents of trace elements increase in snow collected in Moscow and its suburb during November 1975 and January 1976, indicating that snow cover is a natural accumulator of chemical impurities precipitated from the atmosphere. About one-and-a half month after snowfall, the content of trace elements in the snow increased by factors from 2 to 92, e.g., the content increased from 0.5 g/L in freshly fallen snow (dust content 30 mg/L) to 4.2 g/L (dust content 87 mg/L) [16, pp. 55/6]. According to the ease of

extraction of elements from the solid phase (sum of exchangeable and mobile forms) elements can be arranged in the order $Cu > Hg > Cr > Sc > Au > Ba > La > Ce > Co > Sb > Fe$ in the Moscow snow sample [16, p. 58]. Note further that Ce, connected with terrigenous matter (clay minerals), in deposited with snow at the central region of East Antarctica [19].

A special kind of removal of Y and/or RE from the atmosphere is their direct uptake through vegetation or animals, as is shown in the following. Even if trace elements are deposited on the earth's surface as water-insoluble compounds, they can migrate in the soil-plant systems [16, p. 58]. Root or leaf uptake of Ce from the atmosphere is indicated by increased Ce/Sc ratios relative to soil or total deposition in grass collected at Chilton, Oxfordshire, and in alga from the bark of larch at Rogate, Surrey, both Great Britain (Sc is used for element ratio comparisons rather than Al or Fe because plants show virtually no uptake and translocation of Sc). It seems most probable that total deposition from the atmosphere exerts a major influence on composition of the plants studied. However, La/Sc and Ce/Sc ratios show little variation between media (total deposition, soil, grass, alga, coal, and fly ash) and cannot be concentrated preferentially by any mechanism associated with plant uptake [1, pp. 38/40]. Experiments with rye grass indicate that practically all of the ^{144}Ce present in two samples of rainwater is taken up directly on the aerial parts of the plants by ad- or absorption. Compared with the other fission products studied, the uptake is in the order $^{144}Ce > {}^{95}Zr > {}^{90}Sr > {}^{137}Cs$ [17]. An example for uptake of ^{144}Ce and ^{141}Ce from nuclear weapon tests through animals (jack rabbits) is given by [18].

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9 Cosmo– and Geochemical Cycles and Balance For the Contents of Yttrium and/or Rare Earth Elements

Complete cosmo– and geochemical cycles for the behavior of RE and/or Y alone cannot be given without regard to their relation to other elements, or even to the behavior of major rock–forming elements. Some statements in the literature for RE and/or Y may have been obtained merely from analogy in view of its crystalchemical (diadochic) behavior and without direct investigation. To avoid a vast amount of information relevant only peripherically to these elements, the sections and paragraphs of this chapter will contain only data clearly derived for, or belonging to, the RE elements and/or Y. Especially the principal processes influencing their behavior in the natural cycles will be outlined. Further, there will be given preference to a discussion of information regarding the lithosphere (or mantle and crust) of the earth, for it is the main medium producing geochemical variation.

Values for mean contents of RE and/or Y in individual geospheres, or in parts of it, are given in the last paragraph dealing with the balance; see pp. 194/205.

9.1 Source, Distribution, and Behavior of Yttrium and/or Rare Earth Elements in Extraterrestrial Environments. Balance

There are no special papers in the literature dealing with the cosmochemical cycles or balances of the contents for Y and/or RE. To derive such a topic, as a first approximation the statements and data given in "Seltenerdelemente"A3, 1980, and described briefly in the following can be used. Note that the page numbers given in parentheses for the present chapter only relate to the above volume of the handbook! Additionally, some more recent papers will be given.

Origin of Y and RE elements in the cosmos by nuclear processes, and their quantitative distribution in individual stellar spectra, including the sun (see pp. 1/2 and 2/24, respectively).

Distribution and fractionation of Y and RE between minerals of individual meteorite types (see pp. 26/32 and 47/54). A preliminary study of RE element distribution in the Kirin meteorite, China, and its chondrules is given in [1]. Fractionation of Y and RE (including normalized RE distribution patterns) in individual meteorite types and its components (see pp. 57/68). Inspect also the following papers for Sm–Nd isotopic evolution of chondrites [2]; for Lu–Hf total–rock isochron of eucritic meteorites [3, 4]; and for Al–Sm–Eu–Sr systematics of eucrites [5]. Genetical discussions based on data for Y and/or RE for the different meteorite classes and groups (see pp. 68/74) and for tectites and impact glasses (see pp. 81/2). For RE abundances in chondritic phosphates and their implications for early stage chronologies, see [6]. Distribution of RE elements in the Melrose–b howardite and an indication for a pre-terrestrial negative Ce anomaly are given in [7].

Distribution and fractionation of Y and/or RE in minerals of moon rocks (see pp. 83/91) and genetical discussions based on RE distribution patterns and abundances in relation to the individual landing sites of the moon (see pp. 133/68). Implications for petrogenesis of aluminous mare basalts as derived from isotope and RE element studies of the lunar basalt No. 12038, see [8]. Behavior of Y and/or RE during the accretion from solar nebula and formation of moon crust by a fractional crystallization process (see pp. 169/77). For a thorough, general compilation of the stages of growth of the moon, and for an interpretative summary of lunar rock formation, see [9]. Time and duration of lunar highlands' crust formation as derived from Sm–Nd systematics is given in [10], and implications for the processes involved in lunar crustal formation as follows from Sm–Nd age of lherzolite No. 67667, see [11].

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To derive balances for special cosmochemical sections, the following data may be used: Mean contents (related to 10^6 atoms of Si) of Y and the individual RE elements in the cosmos, in carbonaceous chondrites, and in the solar system (see pp. 24/6). Total abundances of Y and individual RE elements in iron meteorites (Lu only), chondrites, achondrites, and tektites (see pp. 32/3, 33/41, 41/7, and 75/81, respectively). Implications for planetary bulk compositions may be derived from Al-Sm-Eu-Sr systematics of eucrites and moon rocks [5]. Average contents of Y and/or RE elements in crystalline rocks, breccias, and soils of the moon (see pp. 120/7), and for the whole moon (see p. 125, as is derived from a model composition, and p. 170, as is derived from analytical data). Hints to papers containing data for contents of Y and/or RE elements (see pp. 91/120).

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9.2 Source, Distribution, and Behavior of Yttrium and/or Rare Earth Elements in Terrestrial Environments. General

The geochemical cycle of RE±Y is intimately connected with the questions of earth formation and its subsequent differentiation into geospheres (especially the mantle and crust), but also with problems of magma generation or alteration and of geological evolution (e.g., of rock series and complexes, of regional parts of the lithosphere, etc.). Therefore, from the numerous, detailed discussions given in the literature, in the following sections and paragraphs only the general trends made evident by the RE data will be mentioned; for a detailed discussion (often in relation to the behavior of other elements) refer to the cited references which, in most cases, contain extensive bibliographies. Arrangement of topics will follow predominantly the ideas developed by the plate tectonic (or new global tectonic) model. Besides the RE distribution patterns, especially the Sm-Nd (ε_{Nd}, $^{143}Nd/^{144}Nd$, etc.) and both the Sr-Nd or Sm isotopic systems (systematics) have been used in discussing plate tectonics. Also widely used are characteristic element ratios as, e.g., La/Nb, Ce/Y, Y/Tb, or Lu/Hf.

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Abbreviations used in the following sections and paragraphs are:

LIL(E)	large-ionic lithophile (elements)
MORB	mid-ocean ridge basalt
OIB	ocean-island basalt
CFB	continental flood basalt
[La/Sm]$_N$	chondrite-normalized element ratio

9.2.1 Accretion of the Earth, Core-Mantle-Crust Differentiation, and Geochemical Variation in the Geospheres Related to Geodynamical Processes

9.2.1.1 Accretion of the Earth

A strong enrichment of RE together with Ca and Al occurs in outer parts of the earth during accretion of planetesimals and during the development of the protocrust, where the enrichment is about 2 to 3 times that of the source material due to a partial melting of 40 to 50% [1]. Both Sm and Nd probably condensed from the solar nebula at the same time, and neither would have entered the core, so there was no fractionation of Sm from Nd at those times. However, substantial fractionation does occur essentially only in magmatic processes. Thus the Sm-Nd system provides an excellent means at studying the magmatic differentiation of the planet [2]; refer also to pp. 147/60. No interaction between core and lower mantle, which would destroy the Nd-Sr correlation, is observed [3].

Isotope data for Nd (^{143}Nd/^{144}Nd) and Sr indicate that the earth is made of thoroughly mixed achondrites and chondrites. The present-day isotopic heterogeneity of the earth's mantle (see pp. 165/6) is unrelated to an accretional heterogeneity [4], or may have been produced by previous single- or multi-stage fractionation events earlier in the earth's history (see also pp. 166/7) [5]. On a graph ε_{Nd} vs. time, the values of initial ^{143}Nd/^{144}Nd ratios for Precambrian igneous rocks cluster tightly near the $\varepsilon_{Nd}(T) = 0$ line, suggesting that the earth was relatively undifferentiated 2.7 Gyr ago and that the Sm/Nd ratio of the earth is

close to the average chondrite value [6]. But it might be more correct to consider the achondrite isotope ratios for Sr and Nd as the primordial values for the earth [7]. Terrestrial Sm–Nd data suggest that during the first two aeons (10^9 yrs.), the earth did not undergo an early differentiation which greatly fractionated the RE, or if it did, a mixing process operated during the subsequent aeons to erase the Sm–Nd variations produced in this event [8].

The systematics of isotopic evolution in a differentiation planet show that correlated isotopic variations of Nd and Sr result only under restricted circumstances. The functional relationship between ε_{Nd} and ε_{Sr} is an indication of the differentiation process involved [9].

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9.2.1.2 Core–Mantle–Crust Differentiation

As is justified by the observation that the refractory elements (RE included) occur in roughly constant proportions in the various meteorite classes, it is commonly assumed that the earth should have an unfractionated chondritic pattern of these elements. Once they are in a planet, the refractories become fractionated by a variety of processes. The refractory siderophiles enter the core, the compatible refractories are retained in mantle silicates, and the incompatible refractories (as, e.g., Rb, U, Th, and RE [1]) preferentially enter melts and the crust. But the crust, of course, is just one repository of the incompatible elements and is less than 0.6% of the mass of the mantle [2] which has the key position in the geochemical cycle of RE; refer to pp. 161/74. A self-consistent earth model can be constructed from the primordial abundances of non–volatile (or incompatible) trace elements (e.g., RE) requiring a strong enrichment of these elements in the upper mantle and the crust. And all, or most of the mantle had been subjected to partial or complete melting at some stage. Partial melting commences at the core–mantle boundary, the liquid thus formed moves upwards, solid phases dissolve at the top and precipitate at the bottom while incompatible elements are strongly concentrated in the liquid. Thus, two explanations appear possible for the strong fractionation of incompatible trace elements (while major elements have negligible degrees of fractionation): Complete mantle melting with a small quantity of residual liquid squeezed upward, and zone melting causing extreme fractionation [3]. Note too that a complex picture of element distribution beneath the oceanic and continental segments of the earth is obtained from trace element distribution (including RE) in various basalts and peridotites of rift zones. Whereas in the lower parts a primary concentration as in chondrites occurs, a zone of enrichment in lithophile elements is localized in the upper parts; both zones are separated by a zone of depletion. For the continental segment, the trace element distribution may be connected with zone melting of the mantle which

preceded sialic crust formation. In the upper mantle zone (represented by undifferentiated pyrolite) beneath the oceanic segment, the melting process becomes more difficult and in the highest part it is quite impossible. The high concentration of lithophilic elements in the upper zone of the mantle may be explained in two ways: (1) The process of transportation of trace elements was similar for both segments, and preceded the formation of the earth's crust. Later, after the formation of the continents, the lithophilic trace elements concentrated in the sialic layer and after the formation of oceanic crust they were preserved in peridotite (which represents the less differentiated upper mantle of oceanic type). (2) The enrichment in ultrabasic rocks beneath ocean ridges is possible owing to the hydrothermal process which may be realized by the mantle degassing. This process may be supported by the high permeability of zones characterized by tectonic activity, and which commonly are used by hydrothermal solutions. Both the above processes may occur jointly, and are useful for hypotheses about independent development of the oceanic and continental parts of the earth [31].

For a general sketch (partly based on Sm/Nd systematics) illustrating the relationship between the geodynamic cycles and chemical fractionation of the mantle–crust system, refer to [28, pp. 121/9] and [29]; inspect also pp. 154/63.

Successive solidification of molten chondrite-like material resulted in the formation of the earth's mantle and crust. However, it is not always necessary to assume that the earth melted all at once, but the earth's primordial oxide phases fused completely after several events of different epochs. It is assumed that most of this melting occurs during a short time compared with the whole geological age. Accordingly, the protocrust formed as the result of freezing or solidification of the last-stage liquid [4]. The mantle crystallized progressively upwards during the pre-Archean era by convective and radiative cooling, concentrating lithophile elements such as U, Th, K, Rb, and RE into a near-surface layer of basaltic composition [5, pp. 35, 50]. The composition of the primary crust (e.g., for La, Ce, Eu, Yb) can be derived according to two different hypotheses: The crust had a composition of the present continental crust (model R), or had most probably a fractionation model composition (model S). Model R is more strongly supported by data of other elements and radioactivity. Since formation, two thirds of the continental crust must have been recycled during geological time (see also pp. 177/8) [5, pp. 42/4, 50]. The existence of an early basaltic crust seems to be necessary for the Archean silicic volcanics and granitoids of the Pilbara Block, Western Australia. As follows from RE geochemistry and isotope data, the silicic rocks are not direct partial melts of the upper mantle; rather they are derived from basaltic layers which were transformed to amphibolites or eclogites. Possibly, most of the Pilbara rocks had a multistage history, best explained by a partial melting of amphibolitic sources followed by some fractional crystallization. The fractionated phases should have had a combined bulk distribution coefficient of ~ 1 for heavy RE and <1 for light RE, caused by a combination of clinopyroxene, orthopyroxene, and biotite [6]. The source region of the early crust, and by inference the earth as a whole, had a Sm/Nd ratio indistinguishable from the cosmic abundance ratio. The separation of the continental crust leaves the residual mantle with a higher-than-whole-earth Sm/Nd ratio; hence the average initial $^{143}Nd/^{144}Nd$ ratio of the present mantle (in a plot of this ratio vs. time) cannot lie on the extrapolated portion of the correlation line but must lie above it [7, pp. 128/9]. In contrast to relatively uniform ε_{Nd} values for Precambrian igneous rocks, a large range of ε_{Nd} for younger basaltic rocks (<2.7 Gyr) indicates the existence of distinct reservoirs at present. Most of young oceanic basalts have positive ε_{Nd} values representative of mantle reservoirs which may be complementary to continental crustal reservoirs with negative ε_{Nd} values today [8].

The mantle and the crust are considered to be a closed system, and "bulk earth" refers only to it excluding the core. But identification of a third mantle component (subducted

oceanic crust) no longer allows one to consider continental crust as the sole complement to depleted mantle [9]. Mantle differentiation and crustal growth can be described simply by a two-reservoir model with time-varying transport of materials between the reservoirs. The abundances of Sm and Nd in the continental crust and the estimated Nd isotopic composition of crust and mantle are reproduced by involving transport between the crust and only one half of the mantle [10]. The Nd isotopic data can be discussed in terms of two reservoirs, mantle and continental crust. The movement of certain elements from the mantle to the crust has influenced the subsequent isotopic evolution of the mantle. Thus, the $^{143}Nd/^{144}Nd$ ratios of recent MORB seem to be entirely consistent with the hypothesis that components with an Sm/Nd ratio lower than that of the bulk earth have been removed and now reside in the continents. It is not possible to specify unequivocally, however, whether the depletion of the mantle has been a continuous or an episodic process. Nevertheless, it is clear that the ocean floor created at mid-oceanic ridges is derived from a previously LILE-depleted mantle which comprises no more than half, and possibly as little as a third of the total mantle [7, pp. 130/1, 133]. Neodymium isotope data (for rocks of the Sierra Nevada and Peninsular Range batholiths) would be consistent with a model that a limited volume of the mantle ($\sim$20 to 30%) has been repeatedly tapped throughout the earth history to produce new continental crust. And the extraction of crustal material has caused this part of the mantle to become substantially depleted in those elements (Nd and Sm included) that show marked enrichment in the crust. This suggests that the average chemical composition of new crustal additions today may differ from the composition of average Archean crust, which would have been derived from a mantle which at that time was much less depleted than the present-day upper mantle. The model of a depleting mantle source appears to apply both for silicic rocks of the continental crust and the oceanic and continental basalts [11]. There is also good fit of Lu-Hf and Nd isotopic data indicating that only 25 to 50% of the mantle volume has been depleted during formation of continental crust. The present-day depleted mantle with a long history of raised Lu/Hf and Sm/Nd ratios is widely accepted to be the residue from the extraction of continental crust over geological time. The continental crust has low Lu/Hf and Sm/Nd ratios and is compositionally complementary to the depleted mantle [12]. Derived from Nd and Sr isotopic data for anhydrous and hydrous ultramafic nodules from the Dreiser Weiher area, Eifel, Federal Republic of Germany, a model for the evolution of this lithospheric mantle comprises the following episodes: (1) A first depletion event $\geq 2 \times 10^9$ yrs. ago starting from chondritic mantle and indicating involvement in the formation of old crust; (2) a second partial melting event $\sim$560 m.yrs. ago resulting in the depletion of basaltic components in the spinel lherzolites found today; and (3) a partial metasomatism by a fluid or liquid resulting in incompatible-element-enrichment and hydration of originally anhydrous spinel peridotites [13], see also [14].

For crust formation, two simple transport models are given for trace elements: (1) melts are derived over the age of the earth by equilibrium partial melting from undepleted mantle; and (2) melts are derived from a mantle reservoir that is continuously depleted through time. Model 1 indicates a larger degree of melting (1.7%) than model 2 (0.5%), and both models require the depleted mantle complementary to the continental crust to make up about $^1/_3$ of the mantle ($\sim$ upper 650 km of the mantle). The major difference in the results for the two models is in the composition (ε_{Nd} and ε_{Sr}) of new additions to continental crust. Model 1 best describes the mantle-crust evolution [15, pp. 7411/2, 7455]. As follows from Sm-Nd and Rb-Sr data combined with the mean age of mantle and crustal reservoirs in the above two models of continent formation, early crust was destroyed by rapid fluxing into the mantle from 4.5 to 3.6×10^9 yrs. ago, or very little early crust ever formed. Both models show that the continents were only formed from $\sim$30% of the total mantle [16]. As follows from Sm-Nd isotope studies of Archean metasediments and metavolcanics, west-

ern Greenland, there is no evidence for the former existence of older pre–3.8 Gyr continental crust. One possibility therefore is that the mantle sources (with Sm/Nd ratio >CHUR) for these and other Archean crustal segments might have been a relatively minor proportion of the mantle and considerably less than that supplying mid–ocean ridge basalts at the present day [30]. The mean age of the crust is 1.8×10^9 yrs. for model 1 and 1.5×10^9 yrs. for model 2, so a young mean age of the crust is confirmed by both models. Since both models indicate that the growth rate over the last 0.5×10^9 yrs. is much less than the average growth rate, most of the crust probably formed in the time interval from ~ 0.5 to 3×10^9 yrs. ago [15, p. 425].

Volcanic arc magmatism is the main mechanism for the creation of continental crust, as can be shown by a multicomponent melting–mixing system, and accounting for chemical differences in alkali, alkaline earth, and RE content between arc basalts and a wide range of oceanic and intraplate basalt types [17]. But the fact that lower as well as upper crust appears to have fractionated RE distribution patterns casts doubt on the validity of the andesite model of crustal generation (see [18]), at least in the Precambrian [19, pp. 165]. Based on Nd–Sr isotope correlations, Archean crust, represented by both Lewisian granulites (~lower crustal level) and amphibolite–facies gneisses (~intermediate crustal level) of northwest Scotland, may to a first approximation complement the lithophile element depletion observed in modern MORB mantle sources. Crustal compositions based on the andesite model for crustal growth may be less compatible with the isotopic constraints for the present upper mantle reservoir. The Precambrian crust, particularly its lower part, must have significantly higher Nd/Sm ratios (and hence higher $[Ce/Yb]_N$, see [19, p. 158]) than is suggested by the andesite model. This requirement is not compatible with a lower crust dominated by the residues of partial melting, or the cumulates from fractional crystallization. The higher $[Ce/Yb]_N$ ratios implied for (and heavy RE depletion observed in) many Archean crustal rocks suggest a role for eclogite in Archean crustal generation processes. Because the residues of crustal extraction need to be recycled into the mantle to generate the Sr–Nd isotope correlation, some form of subduction in the Archean is suggested [20]. During subduction of oceanic crust, calc–alkaline magmas (comparable to modern Cordillerian types) are generated by partial melting, but obviously the more differentiated fraction of oceanic crust (with a negative Eu anomaly) would melt preferentially and contribute to crustal growth; the refractory cumulates (with a positive Eu anomaly) are carried into the deep mantle [19, pp. 158, 165/8]. Archean granulites cannot necessarily represent the modern lower continental crust, since there is a fundamental difference between the Archean and post–Archean in the upper crust composition which is related to an essentially episodic intrusive event at the end of the Archean (see [21]). A major crustal event is also supported by the Sm–Nd systematics (see [22]). It is unclear whether this event is related to a period of crustal growth (as appears from Sm–Nd evidence) or simply to a chemical redistribution within the crust. In any case, it must have had a profound influence on the crust composition, including the lower crust. The heavy RE–depleted patterns of Archean granulites (see above) are secondary features (due to hydrothermal complexing) [23]. Note too that heavy RE depletion in Archean granulites is not due to hydrothermal complexing, but these rocks have been generated in equilibrium with eclogite (residual garnet retains the heavy RE) [24].

Isotopic data for Nd show that growth of Precambrian continental crust by irreversible differentiation of upper mantle predominates over recycling and reworking of older sialic crust. If extraction of continental crust occurred very early in the earth's history, Nd isotopic evolution in light RE–depleted mantle should have accelerated and diverged from the chondritic growth line from the early Archean onwards. Almost all $(^{143}Nd/^{144}Nd)_i$ ratios (i = initial) so far (1981) obtained from Sm–Nd isochrons or model calculations (see [25, 26]) on Archean

rocks lie on the chondritic growth curve for the bulk–earth mantle reservoir (Sm/Nd ratio of 0.308, equivalent to a $^{147}Sm/^{144}Nd$ ratio of 0.1936), and indicate that departures of mantle source regions from chondritic Nd evolution are very small until at least back to Proterozoic times. Extraction of a light RE–enriched continental crust from a bulk earth with a chondritic RE pattern necessarily leaves a light RE–depleted mantle residuum. Progressive development of continental crust must have increased the Sm/Nd ratio of the residual mantle, so that the latter should have a $^{143}Nd/^{144}Nd$ ratio greater than the bulk earth value (~ 0.51262, see [26]; refer also to "Seltenerdelemente" A5, 1981, p, 9). The actual range of measured $^{143}Nd/^{144}Nd$ ratios (0.5125 to 0.5133) indicates that different segments of the mantle have at different times suffered varying degrees of RE fractionation as a result of magma generation [27].

For an overview, based on Sr–Nd isotope geochemistry, discussing the growth curve for the continental mantle and the initial isotopic ratios of continental crust and the recycling process, see [28].

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9.2.1.3   Geochemical Variations for Yttrium and/or Rare Earth Elements in the Geospheres. General

The following paragraphs deal only with the more general statements related to: (1) the geochemical behavior of RE and/or Y in the geospheres (for examples relevant to special geospheres or locations, see pp. 161/74 for the mantle, pp. 174/82 for the crust, pp. 182/94 for the lithosphere, and pp. 1/89 and 90/136 for the hydrosphere and atmosphere, respectively); (2) the models and/or RE data-based constraints for melt formation processes in the lithosphere (see pp. 147/54; refer also to an influence of crystallizing rock-forming and accessory minerals on the RE composition of residual melts in "Seltenerdelemente" A5, 1981, pp. 39/44 and 44/69, respectively); and (3) the correlation of rock formation with geodynamic or plate-tectonic position (see pp. 154/60). In all cases, only more recent, comprehensive papers (some containing extensive references) will be used.

For an overview of the geochemical variations of RE and/or Y in the geospheres refer to the papers given on pp. 138/41.

9.2.1.3.1   Use of Rare Earth Element Data for Deciphering of Crystalline Rock Formation

For the definitions of characteristic values of Nd isotope composition, see "Seltenerdelemente" A5, 1981, pp. 170/2. Generalized diagrams with discussion of the relation between $\varepsilon_{Nd}-\varepsilon_{Sr}$ or $\Delta Nd-\Delta Sr$ are given in "Seltenerdelemente" A5, 1981, pp. 381/6. Using the trace element concentrations (RE, Th, and Ba) measured in a series of cogenetic lavas, the method of inversion of trace element data for batch melting models allows one to find the degree of melting and the mineralogical composition for each lava, which, in turn, gives the chemical composition of the source (for the details, see original paper). There is no indication that the present theory could not be used for major elements as well [68].

Trace elements are generally more difficult to handle than isotopic ratios because their concentrations are modified by magmatic processes (partial melting + fractional crystallization + other processes such as seawater interaction). Some elements are strongly enriched in the liquid during magmatic processes (see bulk mantle/basaltic distribution coefficients $D \leq 0.01$, e.g., for La [1]) and are unmodified by interaction with seawater. Therefore, their ratios can be considered to be representative of their mantle source (see also [2], [3, p. 127]). Such elements, called H (hydromagmatophile) elements by [4], are Hf, Ta, Th, La, Zr, Nb [5]; see also hygromagmatophile or incompatible [6] and hygromagmaphile or incompatible elements [7]. Although the fractionation processes associated with basalt generation may have contributed to the range of hydromagmatophile abundances, they clearly have not significantly modified the ratios of the more hydromagmatophile elements, which must therefore be characteristic of the mantle source [8, p. 189]. If incompatible element ratios reflect these ratios in the mantle source, it is not simply a mixing of a uniformly depleted and a uniformly enriched source which is controlling the chemistry of intermediate basalt members. Rather, each segment of mantle seems to have its own characteristic ratios. Thus, regional heterogeneity in the mantle source of North Atlantic basalts is confirmed (see also p. 164). The reasons for the varying incompatible element ratios are only specula-

tive: (1) At greater depths, mineral phases such as garnet, or other high-pressure mantle phases, can fractionate these elements more effectively; and (2) processes of crustal extraction, operating since the early Archean, can lead to significant removal of selected trace elements from the mantle, and ratios such as Ce/Zr, Ce/Y, Ce/Ti, Ce/P, etc. are much higher in the continental crust than in oceanic basalts [9].

As shown previously (see [10, 11]), the RE along with Ti and P are partitioned in favor of the basic liquid in experimental immiscible systems (a trend opposite to that observed in crystal-liquid fractionation) and, thus, these elements can be used to test immiscibility as a possible origin of coexisting acidic and basic melts [12].

Regardless of the actual mechanism of crust-magma interaction, radiogenic Sr, Nd, and Pb isotopes act as tracers for this process. The mechanism probably involves mixing of mantle-derived magmas with a fluid phase containing incompatible elements derived from hydrous minerals of the country rock in close proximity to magma chambers and conduits, and (providing sufficient heat is available) can lead to a partial melting of the country rock. Thus, the geochemistry of the radiogenic isotopes (e.g., ^{143}Nd) is diagnostic and gives important constraints for deciding whether a given igneous rock suite or ortho-gneiss complex has been produced by melting of upper mantle material and/or basic lithosphere, or by melting of an older continental crust [13, pp. 491, 494/5]. The available Nd and Sr isotopic results on recent oceanic and continental volcanics may be conveniently considered on a graph of ^{143}Nd/^{144}Nd vs. ^{87}Sr/^{86}Sr in two groups: Group 1 includes most of the oceanic data and forms a steep, negative correlation; most of the isotopic compositions indicate derivation from source regions which have been depleted in LILE relative to bulk earth for a considerable time. Recent LILE enrichments are recognized in both oceanic and continental areas, and the elements have migrated from source regions which also have Nd or Sr isotopes on the trend of group-1 samples. Group 2, volumetrically clearly much less significant, has shallower slopes and plots to the right of the main correlation; the isotope data point to a significant influence of a different component to those in group 1. This component, most unlikely to be introduced by contamination during magma extraction, must be present in the upper mantle, and might reflect subducted crustal material which has retained its identity, or might result from mantle metasomatism [14]. Correlations between Pb-Sr-Nd isotopic data indicate that, on a worldwide scale, there are two reservoirs (which had been connected at some time in the past) for basalts: the MORB reservoir in the upper mantle and the OIB reservoir in the lower mantle. The OIB reservoir is probably partly contaminated by the MORB reservoir during ascent [5]; see also [67].

Since mantle and crust evolve with relatively high and low Sm/Nd ratios, respectively, it follows that initial ^{143}Nd/^{144}Nd ratios can provide useful criteria of characterization for the source region of any given igneous rock (see also examples on pp. 182/8). The rate of growth for the initial Nd ratio in sialic crust is retarded relative to the mantle. Further, Nd is enriched relative to Sm during magmatic processes leading to production of sialic crust from the upper mantle [13, p. 512]. The variations in initial ^{143}Nd/^{144}Nd compositions indicate, e.g., that long-lived (≥ 0.5 Gyr) light RE-depleted mantle reservoirs existed at least as early as 4 Gyr ago [15]. Large variations in Sm/Nd ratio have not survived from the earth's early history, compatible with the failure of differentiation products to survive at the surface until ~3.8 Gyr ago [16]. There are global and regional trends in isotope ratios which reflect the secular addition of radiogenic isotopes, such as of Nd from the decay of ^{147}Sm [17].

The perfectly flat (for middle to heavy RE) chondrite-normalized RE distribution patterns observed in Archean peridotitic komatiites, high-Mg basalts, and many MORBs suggest that mantle processes (such as magma generation and migration of metasomatic fluids)

do not significantly modify the relative RE abundances (this also applies to Y). Consequently, the mantle sources of the above rock types do not have Ce, Eu, or Yb anomalies ($\leq$2%) while such anomalies occur in some chondrites. Available data (see, e.g., [18, 19]) also suggest that chondritic ratios also exist among other refractory lithophile elements (such as Y and RE) in the earth's primitive mantle. Literature data for RE in the least-depleted mantle nodules and Alpine-type peridotites suggest that primitive mantle abundances are within the range of 2.0 to 2.5 times the ordinary chondrites (Archean peridotitic komatiite data give ~2.0 times ordinary chondritic abundances for RE [18]) [20].

Since chondrite-normalized RE distribution patterns are widely used in genetic discussions, the correspondence for Nd between isotopic growth and pattern should be noted. Qualitatively, two models can be considered, closed system and two-stage evolution. For the former, in a rock with a pattern depleted in light RE, the $^{143}Nd/^{146}Nd$ ratio grows faster, because of the higher Sm/Nd ratio than in a rock enriched in light RE; the isotopic growth in a system with flat patterns (chondritic Sm/Nd ratio) is in between these two cases. For the two-stage evolution it is supposed that: (1) the earth 4.55 b.yrs. ago had an initial $^{143}Nd/^{146}Nd$ ratio of 0.69973 (like that of eucrite Juvinas); and (2) the mantle had a chondritic Sm/Nd ratio (note that this assumption concerns only the ratio, not the absolute abundances) and had been closed with respect to these elements to time t, when chemical differentiation occurred resulting in various parts of the mantle with different Sm/Nd ratios (i.e., different RE patterns); and (3) basaltic magmas are formed today by partial melting of these different parts of the mantle, which differentiated t years ago. Therefore, a magma derived from an area with higher Sm/Nd ratio (the area is depleted in light relative to heavy RE) has a higher $^{143}Nd/^{146}Nd$ ratio than a magma derived from a part of the mantle with lower Sm/Nd ratio; and a magma derived from a part with chondritic Sm/Nd ratio has an intermediate $^{143}Nd/^{146}Nd$ ratio. A present $^{143}Nd/^{146}Nd$ ratio of 0.7080 is calculated for a system which has been closed for 4.55 b.yrs. and has chondritic Sm/Nd [21, pp. 269/70, 277]. For a compilatory diagram of $^{143}Nd/^{144}Nd$ variation in continental volcanic rocks believed to be of mantle origin, see [22]. Calculations for equilibrium melting of a modal mantle mineralogy which underwent no change in Sm/Nd until a present-day melting event show that δ_{Nd} for the residual mantle is constrained to be within the $+\delta_{Nd}$ and $-\delta_{Sr}$ quadrant. Natural samples which plot in this quadrant thus are most simply explained by a depletion event (which placed their residual source region in the $+\delta_{Nd}$ and $-\delta_{Sr}$ quadrant) and a subsequent melting event (which displaced the generated liquids into the $-\delta_{Nd}$ and $-\delta_{Sr}$ quadrant). The δ values can of course be further modified by a subsequent crystallization differentiation [23]. This simple model is essentially that proposed by [24]. Besides the $^{143}Nd/^{144}Nd$ ratio, $^{143}Nd/^{146}Nd$ is also used to clarify the genesis of oceanic basalts. In a closed system, the growth of this ratio can be written as $(^{143}Nd/^{146}Nd)_p = (^{143}Nd/^{146}Nd)_i + (^{147}Sm/^{146}Sm)_p \cdot (e^{\lambda t} - 1)$, where p denotes present, i the initial (i.e., t years ago) and λ the decay constant of ^{147}Sm ($= 0.6539 \times 10^{-11} yr.^{-1}$) [21, p. 269]. Isotopic evidence (from Sr, Pb, Nd) indicates that there are at least (due to density) two source regions of basaltic magma in the mantle which have remained separate for the order of 1 to 2 Gyr. Compared to the deeper source region for MORB, the subcontinental and hot-spot source region is enriched in incompatible elements. Eclogite and garnet peridotite xenoliths in kimberlites seem to have the appropriate characteristics to provide MORB and continental basalts, respectively. Melting in both layers may result from the thermal insulation provided by the thick continental lithosphere [25].

Due to ε_{Nd} values, the LILE-depleted source of MORB is likely to have formed as a residue after previous partial melting events in the mantle that formed part of, or all of the continental crust. Modelling of Sm-Nd fractionation patterns in the source of MORB strongly suggests that the data array cannot be explained by a single differentiation event to form the depleted mantle but instead most likely requires mixing of depleted and undep-

leted mantle sources [26, pp. 7439, 7443]. Comparing initial ε_{Nd} values for Paleozoic ophiolites and young oceanic and continental basalts, it is obvious that the Paleozoic rocks (from the Bay of Islands complex, Newfoundland) have slightly lower ε_{Nd} (+6.5 to +8.1) than present-day normal MORB (+8 to +12) and are clearly distinct from CFB (selected samples with ε_{Nd} near zero and negative values resulting from crustal contamination). The Paleozoic ε_{Nd} values are shifted down along the correlation line by ~2 to 3 ε-units from typical present-day MORB. This implies a relatively rapid mixing in the source of MORB for at least the last 1×10^9 yrs. [26, pp. 7437/8, 7443]. See also, a consistent isotopic contrast between MORB and CFB (the latter clustering near $\varepsilon_{Nd} = 0$) [27]. Young volcanics with low $^{143}Nd/^{144}Nd$ ratios, being interpreted in terms of enriched-mantle source, may possibly be explained also by processes involving the contamination of mantle-derived melts by crustal components [33]. As follows from Pb, Nd, and Sr isotope data for MORB glasses, either the process of basalt magma generation and evolution of mid-ocean ridges can affect the fractionation of Sm/Nd much more than is often appreciated, or some mantle process affects large, but transient fractionation before the melting event [34].

An initially homogeneous mantle which suffered an incipient equilibrium melting event(s) at an early stage of the earth's history is consistent with the constant La/Ta, but variable Th/La ratios in the mantle. This incipient melting may have involved migration of an alkali and hygromagmatophile element-rich liquid, leaving residual secondary sources still fertile enough to produce significant volumes of basalt. The steeper oceanic geotherm in the Precambrian might have induced such an incipient melting event on a global scale. The residues of this early solid-liquid process would have the same La/Ta, slightly different Th/La, and widely different Ce/Yb ratios. Over a period of ~2000 m.yrs., these residual sources would develop significantly different isotopic ratios and would then act as secondary sources from which the basalts erupted at the mid-ocean ridge of the northern Atlantic Ocean could be derived by subsequent partial melting events [28].

Incompatible elements can be used to determine relative degrees of partial melting (e.g., RE in basanitoids and alkali olivine basalts [29]), or to derive crystal fractionation constraints (e.g., the Ba/Ce ratio will not be altered, even by large amounts of crystallization of minerals such as plagioclase, clinopyroxene, or olivine). The concentration levels will of course be affected, with concentrations in the melt phase increasing as crystallization of these minerals proceeds (90% crystallization will increase melt concentrations of incompatible elements by ~10 times, and so on). The presence of garnet in a melting residue will tend to buffer the concentration of heavy RE (compatible elements with crystal/melt partition coefficients >1) in the melt, somewhat indepently of the degree of melting. Thus, due to garnet as a residual phase in the source region, alkali basalts tend to have RE patterns showing a wide variation of light RE abundances but are relatively constant for heavy RE (or they converge toward the heavy RE end). Conversely, due to missing garnet, MORB shows RE patterns which are parallel to each other, but show variable total RE abundances [3, pp. 129, 131]. Contents and compositions of RE in volcanic rocks have been widely used to evaluate such processes as partial melting and crystal fractionation, and to infer compositional features of mantle source regions (refer to, e.g., [24, 30, 31]). Where it can be demonstrated that crystallization has not been extensive, or else the bulk cumulate phases do not significantly fractionate the RE, relative abundances of RE in basaltic lavas may be considered representative of those in the parental magmas. To a first approximation, the values of mineral/liquid distribution coefficients (D) govern the trace element distribution in a magma. In the case of partial melting, calculated RE contents of liquids are somewhat model-dependent, and the resulting partial melts show increasingly different RE patterns with increasing degree of melting. The following main classes of partial melting models can be discerned: (1) batch equilibrium melting (liquid remains in equilibrium with bulk

residual solid until its extraction); (2) fractional equilibrium melting (liquid is separated continuously from residual liquid with or without collection of liquid in a common magma chamber); and (3) zone melting (liquid reacts continuously with wall rocks during its ascent). Crystal fractionation affects the element contents in magma during a pre-eruptive process. Its effectiveness in modifying trace element contents in a residual liquid depends upon the nature and amounts of precipitating phases, the relevant D coefficients, and the type of equilibrium (or lack thereof) maintained between crystals and liquids. Equilibrium may be of bulk or Nernst type (liquid remains in equilibrium with bulk cumulate crystals, which are homogeneous) and surface or Rayleigh type (liquid remains in equilibrium only with surfaces of cumulate crystals, which display compositional zoning) (refer for that also to [24]). Under conditions of moderate-to low-pressure crystallization, the RE are not significantly incorporated into near-liquidus phases that typically precipitate from basaltic magmas. A notable exception is Eu which may be concentrated into plagioclase relative to basaltic liquid [32]. Note also the data for partition coefficients of RE and/or Y between mineral and melt, and the discussion of the physico-chemical factors affecting this distribution given in "Seltenerdelemente" A5, 1981, pp. 33/44.

For an introduction to, or for discussion of models and/or RE data-based constraints of melt formation processes in the lithosphere refer to the following papers; only their main topics are briefly mentioned here (for details, see the original papers):

Closed-system [8] and open-system fractional crystallization models [8, 35, 36].

Zonal and fractional melting models [37, 38]; partial melting models for alkali-rich basalt [39] and granite [40].

Batch partial melting models for volcanic suites [41] and (containing data for N- and E-type MORB) [42].

Model for single-stage melting of lherzolitic upper mantle material [43].

Continuous convecting-magmatic fractionation model operating for a large part of the mantle [44].

Dynamic melting model involving continuous and simultaneous melting processes in an upwelling upper mantle [45].

Calculations for the equilibrium melting of a modal mantle mineralogy which underwent no change in Sm/Nd ratio until a present-day melting event [23].

Models for the evolution of the source of MORB (derived from ε_{Nd} and ε_{Sr} data) by a discrete differentiation event and modeling of fractionation patterns in the MORB source and the timing of fractionation events [26, pp. 7438/42]. Evolution of ε_{Nd} during mixing of mantle and crustal components [46, 47].

Models involving recycling of oceanic crust [48]. Model of multi-stage mantle melting with polybaric fractional crystallization [49].

Formation of the major magma types by mixture, or by hybridism of depleted and enriched magma [50].

Mixing model of a mantle component and recycled crust [51].

Dynamic binary mixing asthenosphere-plume or blob model for basalt genesis [52].

Model of concurrent assimilation and fractional crystallization (AFC model) [53].

Melting-mixing model for element recycling in the crust-upper mantle system [54].

Models derived from Nd and Sr isotope abundances for formation of tholeiitic flood basalts and MORB and continental basalts [55].

Partitioning of RE between minerals and coexisting melts during partial melting of a garnet lherzolite [56].

Influence of accessory minerals (particularly amphibole, phlogopite, and apatite) on distribution and composition of RE during melt formation [57].

Influence of apatite stability on the behavior of P and RE during crust-derived felsic magma production and evolution [58], see also [59 to 61]; and influence of fractionation of small portions of apatite on the La/Sm ratio of the residual liquid [62].

Influence of mesostasis and abundance of clinopyroxene and plagioclase on RE distribution for layered gabbro cumulates (especially of the Samail ophiolite, Ibra, Oman) [63].

Trace element fractionation (e.g., of La and Yb) during the origin of tholeiitic and alkaline magma types [24] (see also [21]).

Abundance patterns of RE as a function of the degree of melting of some hypothetical mantle assemblages [64].

Experimental determination of RE fractionation patterns in partial melts from peridotite in the upper mantle [65].

Type of RE distribution patterns for Tahitian rocks depending on pressure in the mantle source region [66].

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9.2.1.3.2 Relationship Between Geodynamic Position and Type of Magmatism

For the relationships between geodynamic or plate-tectonic position and the type of magmatic rocks (recent and old) refer also to [1], and for a thorough, general compilation of convection systems, thermal boundary zones, and magma production in the present earth, and for an idealized sketch of the plate-tectonic relations in the upper part (down to 600 km) of the earth, see [41]. Refer also to the data for characterization and discrimination of magma and rock types by their chondrite-normalized RE distribution patterns given in "Seltenerdelemente" A 5, 1981, pp. 313/63. Additionally, in more recent papers, the following statements are given.

Based on Nd isotopic and Sm-Nd geochemical data, it seems reasonable that upper-mantle depletion and creation of (enriched) continental, sialic crust are complementary processes. One very effective process of crust formation is correlated with plate tectonic processes in island-arc and continental margin environments. The initial radiogenic isotope ratios of a mantle-derived, crustally uncontaminated magmatic rock suite then will represent locally homogenized, regionally variable mixtures of isotopes derived from subducted oceanic lithosphere and from the overlying upper-mantle wedge. This is adequate to account for small initial ratio variations between different regions. Larger variations can be superimposed by crustal contamination processes of a different kind [2].

Subduction of material into the lower mantle (across the 650 km discontinuity) is prevented by physio-chemical constraints [3]. The distinctive isotopic signature (e.g., Sm/Nd and $^{143}Nd/^{144}Nd$ ratios) is preserved through the Phanerozoic, and melts derived from subducted oceanic crust must reflect these characteristics, which are very different from the isotopic signature of subducted sediments or old continental crust. Island-arc magmas appear to be dominated by melting of upper oceanic crust (see also p. 157). Magmas derived by melting of subducted oceanic plates (~upper mantle + crust) and forming magmatic arcs along continental margins are emplaced through older continental crust and subducted sediments. Thus, it is to be expected that these magmas would be blends of the different source materials [4]. Largely unaffected by the subduction process may be the Nd isotopic composition of destructive margin magmatic rocks and its relationship to their Sm/Nd ratios. In this case they will reflect the pre-subduction evolution of the overriding lithosphere. But in most of the cases, the combined Nd and Sr isotopic data provide strong evidence that magmas of destructive plate margins contain a contribution from the subducted ocean crust mixed with material from the overriding lithosphere. This contribution may be released during dehydration rather than melting of the downgoing slab [5], and aqueous fluids formed

during dehydration will mobilize the RE less efficiently than Sr [6]. High field strength elements (HFS; including Y and heavy RE) remain within the subducting oceanic crust (now occurring as eclogite) as it sinks into the lower asthenosphere. The LIL elements (including light RE) will be transported from the slab by hydrous fluids (of the dehydration process) and re-equilibrate with, and thus introduce LIL elements into the overlying mantle wedge [7, pp. 354/5].

The occurrence of veined mantle (due to metasomatic processes) beneath the Antarctic Peninsula (and other continental margin areas) has important implications for calc-alkaline magma genesis. Appropriate minerals capable of retaining HFS elements are present in the subcontinental mantle (e.g., ilmenite, rutile, zircon, titanite, apatite). The presence of enriched mantle component removes the problem of accounting for the high LIL element abundances in calc-alkaline magmas by fusion of depleted basalt in the subducted slab, or of depleted lherzolitic mantle above the slab. At low P_{H_2O}, such as during formation of intracontinental alkalic magmas, the vein component makes a significant contribution towards magma production which has both high LIL and HFS element levels. In the mantle wedge above the subduction zone, however, partial melting occurs under higher P_{H_2O} with production of high LIL/HFS ratios in the melt [7, p. 357]. Directly or indirectly related to dehydration and/or partial melting of subducted oceanic crust beneath a magmatic arc is the change in the condition of magma production, superimposed with a change in the composition of mantle magma sources (as is the case, e.g., for Quarternary tholeiitic, calc-alkaline, and high-K calc-alkaline basalt lavas from Java and Bali). If the lithosphere beneath an island arc previously lost a small basaltic melt fraction during a MORB or OIB magma generation event, it will be depleted in incompatible elements (such as light RE) with respect to the primitive mantle. And if this mantle later gains only water from dehydration of underlying oceanic crust, it (and its partial melts) will retain the "depleted" incompatible element signature. But, if the hydrous fluids derived from the subducted crust selectively transport incompatible elements, a selective re-enrichment of the sub-arc lithosphere may occur. Small amounts of acid-intermediate liquids rich in light RE relative to the lherzolitic mantle (and released into the overlying mantle wedge during melting of subducted oceanic crust in depths >100 to 150 km) react with the mantle, strongly influencing its geochemistry. Subsequent melting of this modified mantle produces the calc-alkaline and high-K calc-alkaline basaltic magmas [8]. Note also that partial melting of subducted oceanic crust is a probable mechanism to give rise to the distribution of several minor and trace elements (especially RE, Na, P, Ti, Zr, Hf, etc.) in the Namosi andesite formation of Viti Levu, Fiji Islands. The best fit would give a three-stage model involving reaction of slab-derived acidic magma with overlying peridotite to give wet garnet pyroxenite which subsequently can yield calc-alkaline magmas upon diapiric uprise and partial fusion [9]. For a re-evaluation of the hypothesis of deriving orogenic andesites as partial melts of subducted basaltic eclogite by use of RE fractionation calculations, see [10].

It appears that oceanic lithosphere globally is underlaid by an upper mantle zone uniformly depleted in light RE. Except for areas characterized by mantle plumes piercing the asthenosphere from below as well as perhaps the upper mantle beneath continental areas, it also appears that the source of the low-velocity layer has remained depleted for at least some 70 to 100 m.yrs., since no secular variations are apparent over this time span. This fact, despite the fact that a large quantity of magmatic material has been drawn out at mid-ocean ridges to produce new lithosphere by spreading, has at least some important implications: Only mantle material as a whole has been drawn out of the asthenosphere during spreading and not simply the low-melting basaltic fraction. But mass continuity requires that new material must enter the asthenosphere at some locations, such as regions below or near the trenches. Since the material replenishing the asthenosphere is likely

to have different RE distribution patterns, it requires that the thickness of the asthenosphere reservoir feeding mid-ocean ridges be large in comparison with that of the lithosphere being generated by sea-floor spreading. In variance with the foregoing, it can be assumed that the material replenishing the asthenosphere is of the same RE composition as the asthenosphere itself. Another distinct possibility is to hypothesize a steady state for the recycling, whereby only the low-melting basaltic fraction is removed at the ridge axis and similar material replenishes the asthenosphere from either below or near the trenches [11, pp. 1471/2].

There is much evidence that source materials of oceanic basalts derived from progressively deeper levels in the mantle approach bulk earth (or undepleted chondritic) elemental and associated isotopic ratios (as, e.g., $^{143}Nd/^{144}Nd$) [2]. Some relationship seems to occur between the geodynamic position of a basaltic rock and its ε_{Nd} values, as MORB significantly shows positive values, whereas OIB and continental basalts have less positive ε_{Nd} [12]. Note too that basalts (or andesites) of a given tectonic setting have a characteristic value of ε_{Nd} with a finite variability of about ± 2 to 3 units. Almost all oceanic basalts have ε_{Nd} between $+4$ and $+12$; continental flood basalts cluster at $\varepsilon_{Nd} \sim 0$. The tight clustering of ε_{Nd} for each group (representing worldwide sampling) indicates that the mantle reservoir from which MORB stems is relatively well mixed on a global scale and on a time scale which is short compared to the age of the crust. This apparently holds true also for island-arc and intraplate oceanic island basalts [13]. The Nd isotopic systematics in granitoids younger than ~ 350 Myr, and representing various geodynamic environments (island arcs, continental subduction zones, complex subduction areas, and continental collision zones), show that these granitoids contain some crustal recycled component (remelted old continental crust); mantle-type material is subordinate. Subduction-type orogeny involves more mantle material than collision-type orogeny, but with mass ratios of 0.5 to 2 for crust and mantle material. In contrast to Sr and Pb indicating selective contamination, for Nd a volume-to-volume mixture has to be considered [14]. The enrichment of La in active margin basalts of the Pacific Ocean (from drill cores obtained along a transect from the West Philippine Basin to the Marianas Trench) is consistent with a petrogenetic model involving metasomatism of the mantle wedge above a subducted zone (with hydrous fluids derived from the subducted crust) prior to, or at the time of partial melting in the mantle wedge [15].

As is partly derived from RE data, mid-ocean ridges should be subdivided into segments of three different genetic kinds, e.g., normal ridge segments, plume ridge segments, and transitional ridge segments. Along normal segments, diapirs made of crystal mush rise passively from the asthenosphere ($\sim$ depleted low-velocity layer) in response to spreading, and so does the tholeiitic melt produced by further partial melting and segregation during the rise and decompression of the diapirs. The tholeiitic sea-floor basalts (MORB) derived from such segments are relatively depleted in LIL elements and are low in radiogenic isotopes (with $[La/Sm]_N < 1$) [11, pp. 1459/60]. Thus, the spatial and temporal variations of RE abundance observed in basalts across three normal segments (Reykjanes Ridge, mid-Atlantic Ridge, and East Pacific Rise) are within the permissible range theoretically expected and caused by variation in the degree of partial melting (mostly between 10 and 30%), by some extent of fractional crystallization (up to 50% removal of plagioclase and olivine for the rare ferrolava occurrences), or, quantitatively not easily controllable, by posteruptional weathering or mild hydrothermal leaching effects [11, p. 1471]. Note also, trace element correlations (including RE) for MgO-rich basalts of the mid-Atlantic Ridge may reflect the combined effects of source heterogeneity and fractional crystallization, and probably also variations in the extent of partial melting. And as a general effect, may indicate rift-melting environment, but more lengthy transport and/or storage (hence fractionation) histories for enriched magmas from fracture zone melting, prior to hybridization [16]. Plume ridge seg-

ments lie directly over large plateaus which are assumed to be underlain by rising plumes or blobs (for definition, see [17]). Tholeiitic basalts from such areas are richer in LIL elements and in radiogenic Sr and Pb than the basalts derived from normal ridge segments, and have light RE-fractionated distribution patterns ($[La/Sm]_N > 1$) [11, p. 1459]. Related to the presence of a major upwelling blob of lower mantle material beneath several parts of the oceanic mantle is the mixing of material from two mantle sources distinct in LIL elements (namely, primordial hot mantle and the low-velocity layer) which leads to formation of tholeiitic basalts with a $[La/Sm]_N$ ratio of ~1 in the Afar region, northeastern Africa [18]; or to formation of basalts with progressively changing RE distribution patterns (from slightly light RE-enriched near Iceland to strongly depleted ones southward along the Reykjanes Ridge), although heavy RE remain constant. The mixing mechanism for the two melt components is believed to be a horizontal propagation over long distances (>100 km) and parallel to the Reykjanes Ridge Crest volcanic edifice [19]. Whereas the blob model explains only the secular variations, a composite dynamic model (involving rift propagation and its related thermal processes) may explain the spatial variations of the Iceland hot spot [20]. A progressive secular decline in light RE-enrichment from the Tertiary to present for Icelandic basalts suggests a pulsating mantle-plume activity with time beneath this region [43]. In an analogous way as for Afar and Iceland, the progressive change from light RE-enriched to light RE-depleted patterns is explained for recently erupted basalts along the mid-ocean ridge across the Azores platform [21]; note also that group-II volcanics (according to their Nd-Sr isotopic properties) of Sao Miguel island, Azores, is indicative for a two-component source (one of which may be subducted crustal material or metasomatized mantle) [22]. Trace elements and radiogenic isotope data (including RE) indicate that mantle sources of basalt which erupted at oceanic hot spots have had a complex, multi-stage evolution from the primordial mantle, and consist of more than one component. A mixing process involving the veining of parts of the mantle on a cm-scale by an undersaturated mafic magma (partial melts removed from the Archean mantle) is preferred against a simple mantle-plume mixing. Quantitative mixing models show that the trace-element chemistry of hot-spot mantle sources can be generated by introducing ~5% of an undersaturated mafic magma into a mantle source for normal-type MORB [23]. For a model relating hot-spot volcanism (mantle plumes) with subducted ancient crust, see [24, pp. 424/5].

Referring to concentrations of incompatible elements (such as light RE, U, Th, K, Rb), the source of OIB (i.e., plume material) is geochemically "enriched" to MORB which is more "depleted", but is neither primitive nor merely less depleted mantle peridotite. The evidence for a non-primitive source of OIB is twofold: Its observed incompatible element enrichments (for both alkali basalt and tholeiite) are so high that conventional melting models, based on primitive sources, indicate extraordinarily small degrees of melting which conflict with most of today's conventional petrological views. And Nd isotopic composition usually indicates lower-than-primitive Nd/Sm ratios. Therefore, one explanation for the "enriched" composition of OIB sources is that some metasomatic enrichment prior to the eruption of OIB has occurred, but subducted oceanic crust (garnet- and clinopyroxene-containing material with a typical MORB-type RE distribution pattern) suffering ~30% melting will fit better the requirements [24, pp. 421/2, 429]. OIBs and those island-arc basalts without an obvious crustal contamination are very similar in their Sr-Nd relationships, and therefore it is proposed that both come from the same source as can be explained by a plum-pudding model where OIB and MORB sources are intermixed on a relatively small scale (<10^2 km^2) with the OIB source embedded in a depleted MORB matrix (or vice versa). Metasomatically veined mantle models would be included here. The type of magma produced is a function of the degree of melting; lower degrees will favor melting of the less refractory OIB source. The Nd evidence for at least two different kinds of OIB suggests two different

sources: (1) plums and plumes from the lower mantle; and (2) nuggets of recycled previously subducted oceanic lithosphere [25]. Note also, the geochemical properties (e.g., the RE composition) of MORB, alkali basalts, and nephelinites suggest that the mantle sources for MORB have undergone more extensive melting than for the other two rock types. Also differing are the source locations, which must have a geometry that isolates them, for alkali basalt (the center of a mantle convection cell) and for MORB (the low-velocity zone above upriding parts of neighboring convection cells) [40]. As Nd–Sr isotope data suggest, island-arc lavas (in general showing higher values for Sr/Nd ratio than other basalt types) are derived from a mixture of suboceanic mantle and hydrothermally altered oceanic crust (MORB). However, these data for New Britain rocks deviate only slightly from the ε_{Nd}–ε_{Sr} mantle array, and the involvement of oceanic crust in magma generation must have been relatively less affected by element exchange with seawater than would appear to be the case for some other island arcs (e.g., the Marianas and Scotia Sea). There is no isotopic evidence for an involvement of ocean-floor sediments in the formation of island-arc magmas [26]. Note also, isotopic and trace element data (for recent lavas in the northern Marianas) imply a mantle source for island-arc basalts with negligible input from the crustal portions of a subducted slab. Depletion in RE (and other elements) and more chondritic values for incompatible element ratios (as, e.g., K/La) most likely indicate real differences between the mantle sources for island-arc basalt and ocean-ridge tholeiite [27]. The differences in ε_{Nd} between oceanic island-arc rocks and MORB ($^{143}Nd/^{144}Nd$ ratio is lower by about 1 to 2 ε-units than for typical MORB) are significant, and a plausible explanation is that the island-arc volcanics result from a melting of subducted slabs of oceanic crust and sediments with the proportions of the contributions being somewhat variable (by a factor of 2 to 3) in different stages of melting [28, pp. 273/4]. Island-arc lavas may result from melting in the subducted crustal slab at depths of 100 to 150 km as results from anomalous isotopic composition ($^{143}Nd/^{144}Nd$ ratios down to 0.5124) of recent lavas from the Banda volcanic arc, eastern Indonesia [29]; or the relatively low $^{143}Nd/^{144}Nd$ ratios (0.5124 to 0.5128) for calc-alkaline lavas (basalt to dacite, with predominating basaltic andesite) from the Banda arc and the Sunda arc, Java, suggest that at least some of the lavas reflect mixing of mantle-derived and sialic components. The most likely source of sialic material is terrigenous material subducted beneath the arc, but sialic contamination in an initial clastic wedge cannot be ruled out [30]. The amount of sedimentary rock which can be included in the source of island-arc magmas is reasonably constrained by the Eu anomaly that such mixing would impart on the source compositions (for a calculation of the maximum amounts of sediments that can be added without producing a signature of Eu depletion, see original paper) [31]. A common "arc-type" magma source is shown by the Nd isotopic data for an andesite sample from the Hakone volcano and samples from the Izu arc, Japan [28, pp. 269, 273]. For magmas of the Aleutian arc, an admixture of partially altered oceanic crust with up to ~8% entrapped sediments is derived from the combined Nd, Sr, and Pb isotopic systematics and the trace element ratios [32].

Single-stage melting (anatexis) of an upper mantle source already enriched in LIL elements and located above a descending oceanic crust slab is a suitable mechanism forming the Mesozoic to Recent volcanic rocks from a transect of the Central Andes between latitudes 26° and 28° south in northern Chile and Argentina. The spatial chemical variations across the volcanic belt (e.g., for the RE distribution pattern) probably reflect primary systematic changes in the composition of the magmas due to decreasing degree of partial melting with increasing depth, and possibly also due to the heterogeneity of the source materials. During ascent, magmas were affected by varying degrees of fractional crystallization and, possibly, by limited crustal contamination [33]. Also, the RE may not be mobilized significantly during the dehydration of subducted lithosphere giving rise to calc-alkaline andesites

and plateau lavas of northern Chile and Ecuador. The $^{143}Nd/^{144}Nd$ ratios of these destructive-margin volcanites are believed to reflect long-established heterogeneities in the lithosphere beneath the Andean chain [34]. A multi-stage model for andesites of the North Chilean Andes involves subducted oceanic crust which undergoes subsolidus transformation followed by partial melting and reaction with overlying mantle during diapiric uprise of melt [35].

In the Nd–Sr isotopic diagram, silica-undersaturated volcanic rocks from continental rift systems (as, e.g., Rio Grande Rift, Mexico; Oslo Rift, Norway; Ataq diatreme, south Yemen; Leucite Hills, Wyoming) plot in a diagram $^{143}Nd/^{144}Nd$ vs. $^{87}Sr/^{86}Sr$ to the left of the diagonal mantle array defining a near-vertical sector (which is comparable to that observed for apatite-rich pyroxenites of the Southern Highland Province, New South Wales, Australia) and perhaps signifies that several rift volcanic suites represent melts extracted from mantle locally modified (metasomatized) due to influx of large volumes of CO_2 exhalations (fluids) from the mantle released during uplift and rifting [37].

Probably formed above a subduction zone, for the Oman ophiolite complex two types of source variation must be considered: one existing prior to subduction (which can be ascribed to a pre–Cretaceous history of mantle enrichment and depletion events), and one directly caused by subduction (which can be ascribed to transfer of material from subducted oceanic crust into the overlying mantle wedge). Pre-subduction processes are only likely to affect elements that can be transmitted in CO_2-rich fluids or interstitial melts causing mantle heterogeneities in subduction-unrelated settings, i.e., those elements incompatible with garnet lherzolite. Thus, the most incompatible elements (as La) show the greatest variations, moderately incompatible elements (as Sm) show moderate variations, and compatible elements (as Y, Yb) show little or no variations. Although Tb is not significantly affected by processes causing mantle heterogeneity, it behaves as an incompatible element during partial melting and fractional crystallization. On the contrary, subduction-related processes mainly affect elements that are transmitted in aqueous fluids, e.g., light RE can be enriched especially in the source region for calc-alkali basaltic rocks, and are possibly derived from subducted sediments [37]. Only partly related to late Cenozoic subduction processes is the delayed partial melting of the source region for a few individual rocks of three volcanic provinces in Papua-New Guinea. The reason may be a modification of mantle lithosphere in the early Cenozoic or late Mesozoic by slab-derived fluids (rich in water and LIL elements), together with changes in the direction of subduction movement during the geological history [38].

Sufficient data are not yet available (1977) to show conclusively that differences between oceanic and continental tholeiites are generally inherent to the respective source regions, and other processes, such as crustal contamination, may account in part for some of the observed differences [42, p. 149]. For a thorough discussion on systematic differences in RE abundance patterns and Nd isotopic ratios between the above tholeiite types, see [42, pp. 159/61].

For indications, partly based on RE data, of different plate-tectonic processes operating in the Precambrian earth (1.2 to 2.6 Gyr ago), see [39]; and for hints of Precambrian granitoids derived partly from the mantle by complex magmatic fractionation processes (calc-alkaline differentiation), see [15].

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9.2.1.4 Geochemical Variations for Yttrium and/or Rare Earth Elements in Special Geospheres

9.2.1.4.1 Mantle

The upper and lower mantle are complementary products of early terrestrial differentiation. The lower mantle is the crystalline residue left after melt extraction (rather than primitive, undifferentiated material as is assumed in some recent models). The upper mantle is divided into a shallow LILE- and olivine-rich peridotite layer and an eclogite transition region (which is the depleted reservoir for MORB). The lower mantle differs by its major element chemistry and intrinsic density, and is isolated from the upper mantle [1, p. 49]. For an overview, based on Sr-Nd isotope geochemistry, describing box models for different structural units of the earth's mantle and crust, see [2, pp. 114/7]. The present asthenosphere is to be considered as a residual rock that has been maximally depleted in Rb and incompatible lithophile elements (including RE) during the continuous vertical filtration and elimination of the melted part, which at each stage was enriched in Rb and other incompatible lithophile elements [3, p. 106]. If the depleted mantle is represented by mean MORB or by extreme MORB values, the depleted upper mantle reservoir varies from 50 to 70% or from 35 to 60%, respectively, of the total mantle mass; the latter figure is more in accord with previous results (see, e.g., [2, 4 to 6]) [7, pp. 198/9].

Based on Nd isotope data, the lower mantle is undifferentiated with respect to Sm and Nd, and thus has retained its $\varepsilon_{Nd} = 0$ for the entire history of the earth. The upper mantle continuously cycles through the processes of ocean-floor formation at mid-ocean ridges and subduction. Associated with the subducting zones, new continental crust is continually made in magmatic arcs by extraction of chemically fractionated materials from the mantle. The upper mantle today, therefore, has a positive ε_{Nd} value ($+12$) which is counterbalanced by the negative value for continental crust (-15 as an estimated average) [8]. Correlations between Pb-Sr-Nd isotopic data indicate that the upper mantle is isotopically extremely coherent, but not homogeneous, and variations may occur on a regional scale. The variations are created by the geodynamical system linked with the sea-floor spreading which implies chemical fractionation. Imperfect homogenization results from convection. In contrast, the lower mantle may be more uniform for Nd and hygromagmatophile elements (e.g., La) than the upper mantle [19]. A critical evaluation of Nd and Sr isotope data for the representative mean values of the mantle states the following: Ratios like Sm/Nd measured on basalts are certainly fractionated relative to their source. The upper depleted mantle may be represented by a $^{147}Sm/^{144}Nd$ ratio ≈ 0.258, the lower mantle by ≈ 0.19 (more reasonable than the a priori value of 0.172 used in the DEL model; refer to p. 162). Therefore, the upper mantle should be represented by $\varepsilon_{Nd} + 13$ or $+15$, and not by the average MORB values of $+9$ or $+10$; the lower mantle may have an ε_{Nd} value closer to the bulk earth ($+3$) and not the average observed for OIB from lower reservoirs [7, p. 193]. The isotopic composition of Nd in oceanic basalts (MORB comprises nearly 80% of the earth's volcanic products) reflects the fractionation history of Sm and Nd in the mantle source regions, and therefore may throw light on several important problems of the earth's history (such as differentiation of mantle material to produce continental crust, or recycling of continental material, or degree of convective mixing in the mantle) [9]. As follows from Nd isotopic data, especially for rocks older than $\sim 2 \times 10^9$ yrs., they started with a uniform composition (± 2 to 3% that of average chondritic material), probably because of the mixing effect by rapid convection when the earth was hotter. Younger rocks show increasing scatter (on plots of $^{143}Nd/^{144}Nd$ ratio vs. time), indicating a gradual evolution of chemically different domains in the mantle [8]. It is assumed that the subcontinental upper mantle is overall at least as depleted as suboceanic upper mantle, yet contains a comparable degree of heterogeneity, as follows

from the range of observed ΔNd values $=[(^{147}Sm/^{144}Nd)_{t.i.} - (^{147}Sm/^{144}Nd)_{b.E.}/(^{147}Sm/^{144}Nd)_{b.E.}]$, with b.E. $=$ bulk earth and t.i. $=$ time-integrated value calculated from measured $^{143}Nd/^{144}Nd$ ratio. However, whereas for the bulk of suboceanic upper mantle ΔNd values in the range for MORB are assumed, it is far less clear what the bulk of subcontinental upper mantle is [10, pp. 481, 483].

Within the mantle, RE could occur to considerable depths with clinopyroxene, garnet, and perhaps perovskite structures. They are assumed to be distributed uniformly throughout the entire mantle [11]. Only garnet and clinopyroxene have large enough mineral/melt distribution coefficients to exert a pronounced effect on the RE distribution [12]; or garnet is the main factor controlling partition of trace elements (including heavy RE) between coexisting minerals in the upper mantle [13]. During partial melting of the mantle, in the crystalline residuum of later stages heavy RE may be retained by garnet, light RE by spinel, and Eu by Ca-rich pyroxene [14]; or the amount of Ce is inversely proportional to the degrees of partial melting. Y apparently is retained by clinopyroxene $\pm$ garnet, though the partition coefficients can be shown to have been <1 for both phases [15]. The concentrations of incompatible elements (including the RE) would be largely independent (for partial melting in excess of $\sim$5%) of the relative portions of olivine, orthopyroxene, and clinopyroxene in the residual phases [16, p. 714]. Possibly, at greater mantle depth, carriers of RE may be phosphides due to their high melting point and denser structure than for the corresponding oxides [17]. Apart from grain surface contaminations, fluid inclusions (containing a liquid and a vapor phase and, possibly, silicate glass) are demonstrated to be very important loci of light RE in upper-mantle minerals from anhydrous spinel–peridotite xenoliths of the Dreiser Weiher, Federal Republic of Germany. Olivine, poor in fluid inclusions, contains only negligible amounts of light RE against olivine rich in such inclusions [18].

The isotopic data for Nd, Sr, and Pb in the mantle indicate that, while a number of isotopically distinct materials may exist, they may all be described as linear combinations of (at least) three components (for any subdivision of the mantle into 2, 3, or n components is necessarily a simplification). Processes which involve the mobilization of silicate liquids, or silica-rich fluids within the mantle, are thought to fractionate parents from daughters in each of the isotope systems. In a gross sense, Nd isotope variations may be explained by two mantle components, but are better described by mixing between three chemically independent mantle components, which formed through differentiation from a well-mixed mantle subsequent to core formation. Two of the mantle components are undifferentiated or slightly enriched material and MORB-type or depleted mantle material. Possibly, subducted oceanic crust is the third component (but an accurate assessment of its suitability for the third component must await further work) [20]. Refer to recycled continental material as an important component of the upper mantle [21]. Using mass balance equations and the definition of the mean age of a reservoir, from Rb/Sr and Sm/Nd isotopic systematics several three-box models are derived for the evolution and chemical structure of the mantle, assuming it to be composed of two layers and the continental crust to be extracted out of the mantle (see also pp. 142/5). Depending on the assumed chemical nature of the lower mantle, two classes of models (each with two subclasses) are considered: (1) The lower mantle is virgin (with planetary or bulk-earth composition) and the upper mantle is depleted (VIL model); and (2) the whole mantle is depleted, but the lower part less than the upper part (DEL model) [22]. Using the results of a "total inversion" approach (for details, see original paper) to VIL and DEL models, the gross structure of the mantle can be described by a two-layer model (with the most depleted upper mantle being between 1200 and 1700 km, or between 750 and 1500 km thick using, respectively, mean or extreme MORB composition) or by a domain inclusion-type model (a set of domains statistically embedded in the normal mantle, and created by subducted plate material) [7, pp. 200/1]. From the Sm–Nd systematics

for a variety of mantle-derived rock samples, a static (non-convective) model is constructed for the upper 200 km of both the oceanic and continental mantle; below 200 km, the mantle has a most primitive, chondrite-like composition for both areas. The most important feature of this model is an increasing fertility with depth of the mantle. Below the continents, the most primitive zone (and source region of kimberlites) is overlaid by a zone of sheared xenoliths (with Sm/Nd ratios >chondrite), followed at ~150 km by a zone of granular xeno- liths and at 100 km by eclogites (both with Sm/Nd ratios≳chondrite) and uppermost by granulites (with Sm/Nd ratios <chondrite). Below the oceans, the most primitive zone is overlaid at ~150 km under ocean islands by a less primitive mantle, the "fertile zone" (with Sm/Nd ratios≳chondrite, and the source region of alkali basalts), and at 50 to some km under mid-ocean ridges by a "depleted zone" (with Sm/Nd ratios >chondrite, and the source region of MORB). The different trace element ratios result by the extraction of variable amounts of melt in the past (see p. 146) from an initially uniform mantle reservoir. The process of melt extraction and melting associated with diapirism within the mantle (see p. 156) causes the mantle to become heterogeneous, both vertically and laterally, with time (see pp. 164/7) [23]. For a mantle model composed of tholeiite-, harzburgite- and lherzolite layers formed by differently intense partial melting of pyrolite, see [24].

To achieve a chondritic mantle composition, models describing its chemical composition must use a priori assignments of mixing ratios for either the cosmic source material, or for the petrological components involved (e.g., basalt, peridotite, or ultramafic nodules). No a priori assignments are necessary to model a mantle in a four-component system crust, peridotite, LIL-depleted basalt (MORB), and LIL-enriched component. According to this, the contents of Y and of some RE in the primitive mantle (=total mantle +crust) and in the upper and lower mantle parts are as follows [25]:

element or ratio	content in ppm			
	chondrite C1	primitive	upper	lower mantle
Y	2.1	3.26	9.28	0.70
La	0.367	0.57	1.63	0.12
Ce	0.957	1.40	3.90	0.34
Nd	0.711	1.02	2.88	0.23
Sm	0.231	0.32	0.92	0.07
Eu	0.087	0.13	0.362	0.03
Tb	0.058	0.09	0.241	0.02
Yb	0.248	0.32	0.880	0.09
Lu	0.038	0.06	0.144	0.02
Sm/Nd	0.3249	0.319	0.319	0.318
La/Yb	1.48	1.77	1.85	1.43
Ce/Nd	1.35	1.37	1.35	1.49
Eu/Nd	0.12	0.13	0.13	0.13
Yb/Lu	6.53	5.80	6.10	4.77
U/La	0.038	0.034	0.035	0.032

There appears to be no primordial material in the mantle that serves as a source for present day magmas [26]. Mass balance calculations for Nd show that the fraction of mantle which has remained undepleted is subject to large uncertainties. Thus, the identification of the undepleted mantle with the lower mantle is speculative, and most (well over half) of the mantle may possibly have been depleted in LIL elements [27, pp. 209/11]. Up to 1983, there are no volcanic rocks analyzed which met the requirements for a single-stage (virgin, or bulk-earth) source evolution with respect to Nd isotope data. This does not mean virgin mantle does not exist, only that there is yet no evidence for it (and thus no compelling

evidence to favor the VIL models, see p. 162) [7, p. 200]. Most trace elements (e.g., RE) are incompatible with the mantle mineralogy; they are lithophile and concentrate in the first liquid formed during partial melting processes (see p. 168) [28].

Present upper-mantle sources from which a wide variety of mid-ocean ridge basalts (of the northern Atlantic Ocean) originates are heterogeneous and must therefore have suffered previous fractionation events if they have been derived from a homogeneous primordial mantle [29]. As evidenced by deep-sea drilling samples, mid-ocean ridge basalts of the northern Atlantic Ocean show a rather restricted range in concentration of less-hydromagmatophile elements (e.g., Y and heavy RE), which suggests that the different mantle sources are relatively homogeneous in these elements, but are markedly heterogeneous in respect to the more hydromagmatophile elements. This observation, together with nearly chondritic values of ratios between hydromagmatophile elements of similar ionic character (e.g., Y/Tb) indicate that the heterogeneous mantle sources have ultimately been derived from a homogeneous chondritic precursor mantle [30]. The constant and equal to chondritic ratios for Y/Tb (9 and 18) and other hydromagmatophile elements in numerous basalt samples from the Atlantic and Pacific oceans favor an initial chondritic composition of the "primordial" mantle for these elements [31]. A primary chondrite-type composition of the earth's mantle is supported by the RE distribution in ultramafic rocks as, e.g., picrites of Kamchatka or meymechites and picrite porphyry of the Meymecha-Kotui region, both Eastern Siberia [32].

Chemical heterogeneity in the mantle is readily identified from variations in the ^{143}Nd/^{144}Nd ratio, and both suboceanic and subcontinental mantles show comparable degrees of heterogeneity [10, p. 490], as do ε_{Nd} values which are positive and negative for xenoliths from kimberlites, whereas values around +8 are typical for MORB (see [53]) or around +4 and values ranging down to zero occur in alkali basalts of ocean islands [23]. Comparing RE characteristics and radiogenic isotope ratios for Pb and Sr in ocean-floor and continental tholeiitic flood basalts, the depletion in light RE for suboceanic mantle has persisted for times on the order of 10^9 yrs., implying that large volumes of subcontinental upper mantle material apparently have failed to mix by convective or other means with the more voluminous suboceanic mantle [91]. The Nd and Sr isotopic data clearly demand a mantle in which heterogeneities have existed for thousands of millions of years. The topology and distribution of the heterogeneities can be described by a layered-mantle model (see, e.g., [33]) with only vertical heterogeneities displacing sharp boundaries, or by a model which shows little or no mean vertical variation and the heterogeneities are isolated and have a range of chemical differences and show a large range of sites. The principal differences between these models lie in (1) the fraction of mantle which has been strongly LIL-depleted; (2) the topology of the heterogeneities; and (3) the existence of a reservoir of isotopically primitive material. No part of the spectrum of models discussed can confidently be excluded at present [27, p. 212]. From correlations between chemical elements, isotopic ratios, and, in particular, the "mantle" isochrons and Nd–Sr correlations, it follows that the chemical mantle heterogeneity cannot be created by mixing with continental crust material since this is the chemical complement of the mantle relative to the planetary values (refer to pp. 142/7). The chemical fractionation effects in the mantle lead to a mean variation and to a domain variation. Mean variation is created by continuous extraction processes which mainly involve solid-liquid partitioning and result in an evolution which differs from the planetary evolution. Local heterogeneities can be explained by mixing of different mantle domains which have different extraction parameters. Subducted sediments may participate in this domain heterogeneity, but it seems to be a minor phenomenon. The fractionation and mixing parameters have varied with time, but a time constant for this variation (essentially that for mantle convection) of ~2 Gyr appears reasonable. However, many features

are correctly explained by a steady-state model as a consequence of increased efficiency of both the balance between mixing and fractionation due to convection. Particularly the evolution of trace element concentrations is better explained if the oceanic crust material becomes isolated from the mantle [34]. Since at least the beginning of continental growth 3.8 Gyr ago, the Sm-Nd isotopic system has been fractionated in the mantle, compatible with continuous or multi-stage fractionation models. The present Sm/Nd ratio heterogeneities are mainly the result of more recent fractionations which occurred on a time scale closer to 10^8 than 10^9 yrs. If such fractionations of RE commonly occur in the upper mantle, then the isotope systematics of Recent basalts (e.g., from the northern Atlantic Ocean) require that they are short-lived heterogeneities [35]. The widespread depleted mantle of today seems perhaps to have existed 0.7 Gyr ago. At 1.8 Gyr ago, it was present as a major source of new continental material, but was not by any means universal. At 2.8 Gyr ago, combined Nd and Hf isotopic data suggest that the majority of mantle sources was not old depleted ones, but essentially undifferentiated in Sm/Nd and Lu/Hf. In pre-3.0 Gyr time, almost all Nd and Hf initials came from chemically unevolved mantles (except the Eastern Indian 3.8 Gyr crust-mantle differentiation of [36]). It is therefore generalized that from 3.8 Gyr to the present, long-lived depleted mantle regions have become increasingly ubiquitous [37, p. 87]. Mantle heterogeneity (e.g., different degree of light-RE depletion) may result from the higher heat productivity during the Archean, since violent mixing of depleted residual mantle with undepleted mantle could produce heterogeneity of the incompatible elements. Alternatively, migration of partial melts from previously undepleted parts of the mantle can produce enriched zones. Reprocessing of this heterogeneous material would keep elemental ratios fairly constant but would result in significant variation in abundances (perhaps up to a factor of 2) [38]. Mantle heterogeneity may result from the selective mobility of elements during migration within the upper mantle (low-velocity zone or below) of a melt, or fluid (possibly a H_2O-CO_2-enriched supercritical one) with RE concentrations similar to olivine melilitite, kimberlite, or carbonatite, thereby depleting some mantle regions and enriching others [39]. Note also that the upper part of the low-velocity zone is enriched in incompatible elements (including RE) relative to deeper levels [16, pp. 714, 716, 720]; and observed inhomogeneities (of Ce/Yb and Ta/Tb ratios in North Atlantic basalts) are probably generated by migration within the mantle of small amounts of an interstitial fluid (probably rich in H_2O and CO_2) most likely in the asthenosphere [40]; or metasomatism of the subcontinental mantle would progressively add light RE and is a viable mechanism to account for mantle heterogeneity (and the chemistry of continental tholeiites from the Ferrar Group, Antarctica) [41, pp. 99/101]. Relative increase of some mantle segments in Nd/Sm and decrease in other ratios are compatible with the removal or addition of these trace elements in silicate liquid phases [42]. If the incompatible elements (as, e.g., La, Ce, Nd, Sm) are selectively enriched in the source medium for ocean island alkali basalts and nephelinites, the enrichment must involve processes such as diffusion, or pneumatolytic liquids being able to discriminate effectively among the incompatible elements [43, p. 246]. For a discussion of the evolution of isotopic inhomogeneity in the upper mantle, based on initial $^{143}Nd/^{144}Nd$ ratios and $^{147}Sm-^{143}Nd$ systems, see [3, p. 99].

The present existence of mantle heterogeneity is universally accepted. The mantle varies from apparently unfractionated to quite LILE-depleted, though enriched mantle may occur occasionally. Mantle depletion is understood to be a significant change in key element ratios as Sm/Nd, Rb/Sr, Lu/Hf, etc. which will generate isotopic variation with time. This depletion normally involves partial melt extraction (refer to p. 168). During any mantle differentiation event, silicate liquid will acquire much of the available Hf and thus have a lower Lu/Hf ratio than the starting mantle, whereas the solid residue will retain Lu in preference and hence acquire a raised Lu/Hf ratio. The degree of mantle heterogeneity is comparable for all the crust generation events (see also pp. 174/8), and a little less than that of the

present oceanic mantle [44, pp. 279, 281, 293/4]. Mantle heterogeneity of incompatible trace element abundances (e.g., RE) may be reflected on an absolute basis by uniformly characteristic differences in content for high La–TiO$_2$ and low La–TiO$_2$ group basalts of the Suiko Seamount (DSDP–Site 433 C), Pacific Ocean [45]. A very large–scale heterogeneity in the mantle related to latitude is indicated by the values of 9 and 18 for La/Ta ratios which are closely related to the topography of the mid–ocean ridge, Atlantic Ocean, and remain constant along a specific "flow line" of the oceanic lithosphere [31]. Note also that fine–scale isotopic heterogeneity (on a scale of tens of km) in the sub–Atlantic mantle along a N–S axis is derived from a Sr–Nd correlation diagram [46]. Heterogeneous with respect to the relative RE concentrations and the ^{143}Nd/^{144}Nd ratios is the mantle beneath Reykjanes Peninsula, Iceland [47]. Upper mantle sources of basalts (as, e.g., from the Walvis Ridge, southeastern Atlantic Ocean) may have become heterogeneous on a small scale due to the introduction of small–volume melts and metasomatic fluids [48].

Heterogeneity in the Paleocene upper mantle beneath Skye and Hull, Scottish Hebrides, Great Britain, occurs on two scales, as (1) local variability on the scale of mantle volumes involved in the production of individual magma batches; and as (2) lateral heterogeneity on a larger scale between the igneous complexes [49]. A large–scale horizontal mantle heterogeneity is present beneath southern Africa as follows from a large disparity in RE data, together with K and incompatible elements, between the northern and southern Lebombo basalts. This is shown particularly by the Jurassic Karroo volcanics since their overall compositional variation appears to be best explained in this way rather than by variable partial melting, fractional crystallization, and crustal contamination. Indications of vertical heterogeneity are present for the central Karroo area, but its scale cannot yet be defined [50]. Regional mantle inhomogeneity is indicated by significantly different [Ce/Yb]$_N$ ratios for early Cretaceous ophiolite of the Sarmiento and Tortuga complexes, southern Chile. However, the differences may be interpreted as a secular change resulting from different degrees of evolution of a similar mantle source region (refer to "Rare Earth Elements" A6a, 1988, Paragraph 6.5.2.1) [51]. An extreme heterogeneity in the subcontinental mantle seems to be reflected by the considerable range in Sr and Nd isotope data of Cenozoic volcanic rocks from three (petrographical) provinces in the western United States [52].

In terms of RE composition, the Archean mantle was rather heterogeneous. The widespread occurrence of light RE–depleted peridotitic komatiites could suggest that the Archean mantle was not sufficiently homogenized by the presumably more rigorous convective motion. Though heterogeneity is convincingly shown by variable La/Sm ratios, it becomes less pronounced in terms of Sm/Nd ratios and even less so with respect to the Nd isotopic composition [54, p. 360]. See also evidence for long–lived heterogeneities in the Archean mantle derived from Sm–Nd data for greenstones of the Yilgarn Block, western Australia [55]; also, the Archean upper mantle (beneath Australia and South Africa) is heterogeneous with no apparent simple relation between major and incompatible element abundances (particularly light RE) [56]. Isotopic data for Sm and Nd of granitic and tonalitic gneisses, Singhbhum–Orissa iron ore province, eastern India, give direct evidence that parts of the earth's mantle were already differentiated from chondritic values before 3.8×10^6 yrs. ago [36]. Regions with both time–integrated light RE enrichment and depletion (Sm/Nd ratio $\gtrless$ bulk earth value, respectively), and supposed mantle heterogeneity, may be delineated by diopsides from South African lherzolite nodules in kimberlite [57]. The variations of ε_{Nd} among Archean rocks could be indicative of a long–scale chemical heterogeneity in the Archean mantle (2.7×10^9 yrs. ago), or of contamination effects by pre–existing continental crust with low Sm/Nd ratio [58]. The positive initial ε_{Nd} for rocks (3420 to 345 Myr old) of the Ancient Gneiss Complex, Swaziland, implies that their mantle source materials had been relatively

depleted in light RE by a much older episode of melt removal. Either a chondritic model for the Nd isotopic evolution of the earth's mantle is inappropriate, or the mantle was chemically heterogeneous for a considerable time prior to the formation of the oldest crustal section [59]. Whereas a probable mantle heterogeneity at 2.8 Gyr exists for Lu, it is not apparent for Nd and may partly reflect the $\varepsilon_{Hf} = 2\varepsilon_{Nd}$ relationship (derived, as a result of chondritic growth, from isotopic variations from 4.55 Gyr ago to present), or it may be that the appropriate samples have not yet been analyzed for Nd. The degree of ε_{Hf} and ε_{Nd} variation present in the mantle depends in a conceptual sense upon the local ratio between the frequency and history of geochemical differentiation events and the speed of convection [44, pp. 292/4]. A heterogeneous, or even stratified mantle could ensue from garnet crystallization and settling, due to its greater density than other phases, as follows from RE geochemistry and Sm-Nd age for early Archean komatiites of the Onverwacht Group, Republic of South Africa. From the different chemistry of some late Archean komatiites of Finland, Canada, Rhodesia, and Australia it appears that the upper mantle chemistry has evolved through Archean times. The characteristic Gd/Yb ratios in the Onverwacht Group rocks can also be explained as a result of local short-term mantle heterogeneity [60]. In contrast to the foregoing, most data for initial $^{143}Nd/^{144}Nd$ ratios of Precambrian rocks suggest that they have been derived from a rather uniform reservoir with chondritic Sm/Nd ratio. This implies that the Archean mantle was indeed quite homogeneous in terms of Sm/Nd ratio and the RE abundance pattern in general. Or, more likely, the compositional heterogeneity is not yet revealed by the limited data, or the true heterogeneity in RE characteristics (as observed in many komatiitic series) is only a short-term phenomenon [54, pp. 357/8]. Enrichment of light RE and Rb in the Antarctic mantle during, or prior to the Jurassic may have occurred (1) by addition of continental material from a Paleozoic/Mesozoic subduction zone (via a fluid rich in these elements resulting from dehydration of the downgoing slab); or (2) by metasomatism of volatile elements from the lower mantle; or (3) by a distinct mantle differentiation event (at ~2.0 to 1.6 b.yrs.), perhaps as a result of extensive partial mantle melting, rather than involving continuous changes in geochemical parameters [41, pp. 89, 98/101].

In studies of early mantle geochemistry, four types of problems arise and constitute a formidable barrier in the discussion of mantle evolution (and of locations for melt formation). Firstly, the extent of secondary open-system chemical redistributions associated with lava-seawater interaction, diagenesis, and burial and/or thermal metamorphism must all be taken into account. Secondly, because only primary magmas unaffected by crystal fractionation can be used to infer mantle composition, the role of crystal fractionation and the nature of the residual mineral must be evaluated. Thirdly, the nature of the partial melting process is unknown; the simplest assumption is that of an equilibrium batch melting which allows calculations based on Henry's law (see, e.g., [61 to 63]). However, more complex mechanisms are possible, including different types of melting (fractional, or continuous, or dynamic), mixing of liquids extracted from heterogeneous mantle sources and addition of LIL-enriched melt, or wall-rock reactions associated with selected introduction of incompatible elements into the magma. Fourthly, the incomplete knowledge of distribution coefficients between mineral and melt for trace elements in residual mantle phases (at different pressure, temperature, volatile content, and melt composition) makes estimates of primary abundances uncertain [64, pp. 253/4]. It need not, and probably does not mean that all the chemical units (e.g., of the bimodal suite in the Ancient Gneiss Complex, Swaziland) used to construct the Sm-Nd isochron were derived from exactly the same source during a single igneous event. Rather, the Sm-Nd data allow for a variety of mechanisms, from direct partial melting of the mantle to anatectic melting of slightly older crustal materials, as long as these events occurred within a time interval short enough so that significant Nd isotopic heterogeneity was not generated in the varied source materials [59].

If the earth originally had a chondritic RE abundance and later differentiated to form the core and the early (primitive) mantle, the latter would have retained the RE because they are lithophilic elements. This would result in a mantle with a greater RE abundance and a parallel RE distribution pattern relative to chondrites. Melting of the mantle to form basalts leads to a relative depletion in light against intermediate and heavy RE; thus, the evolving mantle should become relatively depleted in light RE, as is generally substantiated by Nd isotopic studies [65]. Deeper zones of the mantle should contain greater quantities of cerian RE than the upper mantle. But it is difficult to decide whether there is one separate deep-lying zone or various isolated chambers [66]. A secular depletion of mantle source regions is reflected by a progressive depletion of several Archean volcanic sequences in siderophile, lithophile (as, e.g., Y), and chalcophile elements with higher stratigraphic level as is reported for komatiite-tholeiite assemblages of South Africa (Barberton Mountain Land), Australia (Pilbara and Yilgarn blocks), and Canada (Superior Province). This may be caused by a depletion of mantle peridotite in components enriched in extracted mafic melts, but possible also because the Archean upper mantle was vertically zoned in incompatible elements, and magma extraction progressed with time from LIL-enriched high levels to LIL-depleted deeper levels [64, pp. 272/5]. If the light-RE depletion in Archean komatiites is found to be very widespread, the causal effect and the complementary part might be related (1) to the production of some contemporaneous light RE-enriched tholeiitic magmas; (2) to enrichment of light RE and other incompatible elements by adding some undersaturated melt to higher-level mantle source regions which later produced light RE-enriched rocks; or (3) to contemporaneous or previous continental crust-forming events [54, p. 363].

An early terrestrial development of Nd in an environment with approximately chondritic Sm/Nd ratio is corroborated by Archean igneous and meta-igneous rocks whose data points in a diagram of initial $^{143}Nd/^{144}Nd$ ratio vs. time lie close to the growth line, representing the evolution of a reservoir which had 4550 Myr ago ratios of $^{143}Nd/^{144}Nd = 0.50682$ and of Sm/Nd $= 0.308$ (the average chondrite value) [67]. There is a consensus from isotopic studies (e.g., $^{143}Nd/^{144}Nd$ ratio) that a significant fraction of parent/daughter element ratios has occurred in the oceanic upper mantle quite early in history. Relatively large volumes of mantle have fairly constant ratios, particularly of the more hygromagmatophile elements (such as La). The partial melting processes associated with basalt generation do not significantly change these ratios unless the degrees of partial melting are very small. Only very small and variable degrees of partial melting of an initially homogeneous source could produce residues with the observed ratios and abundances of the more hygromagmatophile elements found in ocean-ridge basalts of the northern Atlantic Ocean. Such melting could have occurred in a zone analogous to the present-day asthenosphere [68]. Because both Nd and Hf are very resistant to secondary alteration, the Hf-Nd isotope correlation yields substantial "hard" information about the mantle. Thus, it follows from a double plot of $^{176}Hf/^{177}Hf$ vs. $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ for oceanic basalts that the fractionations of the Rb/Sr, Sm/Nd, and Lu/Hf ratios in the suboceanic mantle have been essentially coherent through time. The latter two ratios were raised when the first was reduced. The point $\varepsilon_{Hf} = \varepsilon_{Nd} = 0$, corresponding to a theoretical present-day undifferentiated reservoir, lies within the array of observed isotopic compositions. This is evidence supportive of the assumption that present-day mantle sources evolved from a primitive mantle which was chondritic for Sm/Nd and Lu/Hf. On both diagrams, MORB defines a field corresponding to sources (the depleted mantle) with highest Lu/Hf and Sm/Nd, and lowest Rb/Sr integrated over time. In contrast, OIB, which represents a very small portion of mantle sources, is very variable and is responsible for defining mantle arrays; the correlation between $^{176}Hf/^{177}Hf$ and $^{143}Nd/^{144}Nd$ in OIB is very close [37, pp. 84/6].

Ascribed to fractionation in the mantle, the ratios of large-ionic, highly-charged elements to smaller, less highly-charged elements are low in ocean-ridge basalts compared to the solar or chondritic ratios. The combined time constraints of Sr, Pb, and Nd isotopes show that the fractionation had to occur long before upwelling of the mantle under the present ridge axis. Time on the order of billions of years is necessary to produce the observed isotope inhomogeneities [26]. Note also, the mantle source of mid-ocean ridge basalts samples long-lived heterogeneities that predate or coincide with the opening of the Atlantic Ocean. These domains (to be distinguished on the Sr-Nd correlation diagram) may be segmented by major transform faults [46]. The heterogeneity with respect to $^{143}Nd/^{144}Nd$ (or Sm/Nd) ratios in the immediate upper mantle source regions of oceanic basalt has developed over a period of time much greater than the development of present-day ocean basins [92]. A strict upper limit to the time of last chemical differentiation of magma sources from the chondritic uniform reservoir (CHUR, see "Seltenerdelemente" A5, 1981, pp. 170/1) is given by the Sm-Nd model ages $T_m(Nd)$ [69]; note also that the Sm-Nd data represents the time when the rocks of the bimodal suite, Ancient Gneiss Complex, Swaziland, solidified from partial melts derived from the mantle and/or slightly older basaltic material in the crust [59]. Thus, for Cretaceous MORB of the southern end of the Bermuda Rise, Atlantic Ocean, the time of mantle differentiation is on average $\leq 2.06 \times 10^9$ yrs., assuming a two-stage evolution model. However, in view of geological evolution and geodynamic consequences, a model of continuous fractionation-crystallization with later mixing of heterogeneous sources seems most reasonable [69]. Estimates of how long a rock and its source region have had a different Sm/Nd, and hence $^{143}Nd/^{144}Nd$ ratio, can be made by T_{CHUR}^{Nd} ages, which are model ages because a simple two-stage history is assumed (primitive chondritic mantle and present rock). If such a model is inapplicable, as, e.g., when light RE-enriched crustal rocks are derived from depleted mantle ($^{143}Nd/^{144}Nd > CHUR$), the time of separation from the mantle may be older than that implied by their T_{CHUR}^{Nd} age. Nevertheless, for mantle-derived volcanic rocks, such model ages reflect how long chemical variations have persisted in that part of the upper mantle; and for crustal-derived rocks they provide an estimate of the age of their source region [70]. If positive ε_{Nd}^T values are a general characteristic of Archean meta-igneous rocks (e.g., for metasediments and metavolcanics from West Greenland), then either the CHUR parameters are inappropriate for the bulk earth, or fractionation of Sm-Nd occurred in the source of these Archean crustal component prior to their generation. Possibly, Sm/Nd had increased in the mantle prior to 3.8 Gyr ago by formation of continental crust [71]. Because there is no significant temporal and spatial variation in $[La/Sm]_N$ depletion since the Jurassic, an implication is that "similar" (in grand scale) source materials (light RE-depleted) have existed at least since 150 Myr ago in the mantle. It further indicates that the depletion was a very large-scale phenomenon and may suggest an effective mixing with the asthenosphere in order to produce magmas of rather uniform chemistry over a time span of >150 Myr. However, small-scale heterogeneity in the mantle source(s) for basalts cannot be discounted, as may be inferred from the variable $\varepsilon_{(T)}^{Nd}$ values [69].

Colinearity in a diagram ε_{Nd} vs. time for very old (2790 to 4550 Myr) mafic-ultramafic rock sequences from Australia, South Africa, and Greenland suggests the possible existence of an ancient (>4000 Myr) ultramafic mantle source with an $^{147}Sm/^{144}Nd$ enrichment factor relative to CHUR of ~0.08. This reservoir would today have an ε_{Nd} of about +9 and could thus be the source of oceanic basalts with positive ε_{Nd}. This is contrary to previous suggestions (see [72, 73]) of a younger (1800 to 2000 Myr) source for recent oceanic basalts. To distinguish between both models, additional high-precision initial $^{143}Nd/^{144}Nd$ data are required from Precambrian oceanic basalts of different ages [55].

For the discussions of mantle evolution and magma generation, an important development in recent years has been the recognition of an LIL-enriched "metasomatic" component

in the mantle, or of a recently metasomatized reservoir [1, pp. 42/3]. Partial melting cannot explain all features of trace element distribution in the mantle; therefore metasomatism through the action of a vapor fluid phase may play an important role, and may be important in controlling element composition (including RE) in the upper mantle [74]. It is suggested that LIL elements were removed from the MORB reservoir in the mantle not only by extraction of the continental crust, but also by removal of a fluid or vapor phase which has enriched the continental lithosphere (see also p. 176) and the upper mantle peridotite [75]; and the Jurassic Antarctic mantle may have been contaminated by a fluid in light RE which resulted from dehydration of the downgoing slab (refer also to pp. 158/9) [41, p. 99].

Local metasomatic effects in the upper mantle, related to emplacement of partial melts (represented by dikes of pyroxenite, hydrous minerals, and gabbro that occur in mantle peridotites) are expressed by refractory rocks with light RE/heavy RE ratios greater than for chondrites. Those refractory rocks are xenoliths of various composition occurring in alkali basalt and kimberlites, or some oceanic peridotite massifs [76]. Also, mantle metasomatism with introduction of light-RE enrichment is viewed as an essential precursor to continental alkaline volcanism [77 to 79]. In the geochemical evolution of suboceanic mantle, metasomatic processes (leading to small, closely spaced veins in the mantle) may be able to discriminate more effectively between the incompatible elements (e.g., La) than do processes involving silicate melts (as partial melting, zone refining, fractional crystallization, or dynamic melting) [43, pp. 250/1]. Relative to estimates of primitive mantle composition, the source(s) of Honolulu volcanics was enriched in elements in the sequence $Ta \sim Nb > La > Ce \sim Sr > Nd > P > Hf \sim Zr \sim Sm \sim Ti \sim Y \sim heavy$ RE. This composition resembles that postulated for mantle compositions created by metasomatism [80]. Modification by metasomatic enrichment events is necessary for the (at least) two different mantle sources for the Early Proterozoic Scouri dike suite, northwest Scotland, Great Britain [81].

Influx of CO_2-rich metasomatic fluids into the mantle transforms the peridotite both petrographically and chemically producing a light RE-enriched pyroxenite (as, e.g., in the Southern Highland Province, New South Wales, Australia). A near vertical vector on the plot $^{143}Nd/^{144}Nd$ vs. $^{87}Sr/^{86}Sr$ results from the isotopes responding to the light-RE enrichment in a relatively short period of time (100 m.yrs.). This unique isotopic signature contrasts markedly with the diagonal mantle array in this plot and represents a response to a low Sm/Nd ratio [82]. In accordance with experimental results, at upper mantle pressures, the light RE are strongly fractionated into a CO_2-rich vapor phase relative to silicate melts, carbonate melts, and garnet lherzolite minerals. Thus, mantle metasomatism by a CO_2-bearing fluid phase, occurring as a precursor to magma genesis, may explain the high total RE contents and light RE enrichment of carbonatites, basic alkalic silicate magmas, and kimberlites [83]. Refer also to formation of an alkaline earth-rich, but alkali-poor liquid probably due to CO_2 emanation from inner zones of the mantle as a first stage in generating carbonatite-alkalic rock sequences [84]. Addition in various portions of a CO_2 fluid enriched in incompatible elements (and possibly containing some H_2O, Cl, and F) to segments of the mantle below northern Kenya could give rise to the observed correlation between silica undersaturation and incompatible element abundance ratios for basic lavas from the rift between lakes Barringo and Turkana [85]. Mantle metasomatism at shallow depths (>70 km) in a diapir by an RE-enriched vapor phase (H_2O, CO_2) is reflected by the common light RE enrichment and variable Zr/Y ratios in Archean metavolcanics from Karnataka state, Southern India [86]. Small amounts of partial melting in mantle pockets enriched in incompatible elements as a result of metasomatic processes would explain the content and composition of RE observed in Indian lamprophyres [87].

If mantle metasomatism has occurred, then one might expect to find a correlation between light RE and Sr isotope ratios in mantle-derived tholeiites. Although the data points for

only few examples are scattered in a plot $[La/Sm]_N$ vs. initial Sr isotope ratio $(^{87}Sr/^{86}Sr)_0$, there appears to be a general trend of increasing $[La/Sm]_N$ with increasing $(^{87}Sr/^{86}Sr)_0$. This would not be surprising, as a clear covariance of $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios occurs in recent volcanics (see [42]) [41, pp. 100/1]. The Nd and Sr isotope geochemistry of lherzolite and amphibole–megacryst inclusions of alkali basalt from Alaska requires a recent ($\ll$200 m.yrs.) metasomatic event in the source region. This event is believed to be represented by pargasite, mica, and kaersutite in the nodules [88]. Note also that the relative enrichment of light RE in tholeiitic basalt, Suiko Seamount, Pacific Ocean, resulted from a recent (relative to the half–life of ^{147}Sm) metasomatic event [45]; or there is clear evidence of a recent or subrecent metasomatic enrichment of light RE and LIL elements in the mantle source regions of oceanic and continental basalts. Effects of ancient enrichment events in the subcontinental mantle become visible by the Nd isotope data for diopside megacrysts of lherzolite nodules from kimberlites, South Africa. These metasomatic events are believed to be genetically related to the upwelling of mantle plumes or blobs [57]. Mantle metasomatism is confirmed by RE and other incompatible elements in various types of peridotite nodules from South African kimberlite [89]. Data for Sm/Nd and $^{143}Nd/^{144}Nd$ ratios of volcanic rocks from Roccamonfina, Campanian region, Italy, may be most simply interpreted in terms of a recent mixing event within this portion of the upper mantle between a LILE–enriched fluid (characterized by a low $^{143}Nd/^{144}Nd$ ratio of 0.5121 and Eu^{2+} depletion relative to the light RE) and the mantle through which this fluid migrates; in doing this, the fluid metasomatizes the mantle [90]. If not caused by fractionation during melting, the position of MORB points on the Sm/Nd isochron plot may be due to the operation of a recent Nd–Sm enrichment event in the mantle source region for MORB, such as metasomatism [7, p. 203]. Some part of the mantle sources for komatiites of the Onverwacht Group, South Africa, may have been metasomatized to various extent by invading of light RE–enriched fluids or magmatic liquids (shortly before a partial melting event) as is suggested by the nonuniform distribution of light RE in the predominant group II–rocks (with $[Gd/Yb]_N = 1.41 \pm 0.13$) and the highly enriched light RE in the subordinate group III–rocks (with $[Gd/Yb]_N < 1.0$) [60]. Furthermore, besides heterogeneity in the mantle, some lavas of the central Karroo province, South Africa, are apparently derived (together with earlier lavas in the southern African volcanic record) from enriched mantle sources caused by earlier and non–Karroo–related mantle metasomatic processes [50].

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9.2.1.4.2 Crust

Crust Formation

The RE, which are enriched in the crustal rocks, are generally enriched most strongly for the large-size (La) end of the element series. Since the RE elements have a very smoothly decreasing ionic radius with increasing atomic number (refer to "Seltenerdelemente" A4, 1979, pp. 1/2), their relative abundances are sensitive to the details of the processes leading to their enrichment in the crust [1]. Constraints on overall crustal composition are limited, but an index is provided by the RE distribution in sedimentary rocks. In these, the RE patterns are sufficiently uniform to suggest that they represent an effective sampling of the upper crust (refer also to pp. 179/80) which is exposed to weathering processes. If the total crust has the composition of island-arc volcanic rocks, such a RE pattern could be produced via intracrustal melting from an island arc-type RE pattern. The presence of residual plagioclase in the lower crust can produce the Eu depletion (of the upper crust, see p. 179) while a light-RE enrichment is consistent with equilibration with clinopyroxene [2]. To explain the lanthanide abundances for the average crust in relation to the formation of the mantle, successive solidification with arithmetically progressional partition coefficients for lanthanides is the sole tenable interpretation, and neither zone nor partial melting can account for this problem [3]. The major fractionation of the RE is assumed to occur during the derivation of crustal rocks from a mantle reservoir (associated with formation of the protoliths) rather than with subsequent metamorphic events [4]. No fractionation of Sm and Nd during internal differentiation of the continental crust is indicated by statistically identical Sm/Nd ratios for granulite-facies rocks (32 samples with ages from 2900 to 200 Myr) and granitoids from the upper crust, whereas the Rb/Sr ratios are highly variable [5].

An important mechanism in the formation of oceanic crust may be two-stage (or more complex multi-stage) melting of upper mantle source rocks (pyrolite) which itself are residual diapirs from which picritic liquids have earlier been extracted [6]. The oceanic crust shows a range in $f^{Sm/Nd}$ from ~0 to +0.6, so variations in $^{143}Nd/^{144}Nd$ of about 3 ε-units may develop due to decay during plate motion over 200 m.yrs. But ε_{Nd} is not changed by alteration. This distinctive isotopic signature of oceanic crust (and mantle) is preserved through the Phanerozoic [7].

An absence of layered intrusions prior to 2.80 b.yrs. ago suggests that the crust was not rigid and/or thick enough to support large magma chambers, which seem to be essential for plagioclase fractionation and crustal melting processes which produce Eu anomalies in igneous rocks. Significantly, magma older than 2.8 b.yrs. rarely show Eu anomalies whereas they are common in younger igneous rocks [8].

Initial ε_{Nd} values for crustal rocks of different ages give constraints on crustal growth from the mantle through time, which may proceed according to three models: continuous linear growth, episodic growth, or rapid early linear growth followed by a slower growth (for the details, see original paper). No significant positive deviation from $\varepsilon_{Nd} = 0$ is found in rocks older than 2.5×10^9 yrs, but marked deviations occur in younger rocks. These data appear to fit reasonably with the first two models. But interpretation of initial ε_{Nd} is complicated by possible effects of crustal recycling and by the mantle heterogeneity. The general effect of recycling on the ε_{Nd} curves will be to make them more parallel to the $\varepsilon_{Nd} = 0$ line. For sufficiently fast recycling in comparison to crustal growth, the system will approach a steady state. Based on theoretical calculations, a steady-state model of crustal history is inconsistent with the existing data set, while small recycling rates (see below) accompanying gradual crustal growth are consistent with the ε_{Nd} data. It appears that with time, an early cycling-dominated mantle-crust regime gives way to a regime dominated by crustal growth with subordinate cycling [9]. According to two models for mantle evolution of ε_{Nd} (constant or increasing with time), the calculated values of the relative crustal recycling rate through time for a constant-mass crust are relatively modest at present (<0.3 crustal masses per 10^9 yrs., or ~ 1.6 km^3/yr.; refer also to p. 178). The results for both models do not differ drastically over the past 2 to 3×10^9 yrs., and give plausible crustal age distributions and a mean age in the 1.5 to 2.0×10^9 yrs. range [10]. Thus, the apparent single-stage growth of initial Nd isotope ratios in ancient rocks is simply a consequence of rapid recycling of continental crust on a near-steady-state no-continental growth earth. It does not require, or imply chemical homogeneity [11, pp. 458, 462, 466]. Note also that Nd and Sr isotopic data do not rule out recycling as the major process in crustal evolution [12]. If the crust is not formed with $\varepsilon_{Nd} = 0$ but from depleted mantle with $\varepsilon_{Nd} > 0$ (as, e.g., for North America), the T_{CHUR} age does not give a reliable crust formation age; it underestimates the true crustal age. Instead, it should be calculated relative to a mantle evolution curve $\varepsilon_{Nd}(T) = 0.25T^2 - 3T + 8.5$ (with $T = $ age). As a mantle having this ε_{Nd} evolution can be assumed to be depleted in incompatible elements, this revised model age is donated T_{DM} (depleted mantle) [13]. Mean ages $\bar{T}$ of the crust derived from VIL and DEL growth models (see p. 162) strongly support the concept of continuous or episodic growth of continents [14].

The earth's crust, in spite of prolonged and complex history with repeated reworking by sedimentary processes, metamorphism, and granitization, has inherited the features found in the products of tholeiitic magmatism, i.e., of the most common type of mantle magmas, in accordance with current petrological concepts [15]. Considering both that the dominant rocks in Archean greenstone terrains appear to be tholeiitic basalts and felsic volcanics and intrusive rocks, and that contemporaneous sediments are effective overall-samplers of exposed rock types (refer also to pp. 186/8), a popular **model for growth of** new continental **crust** assumes the addition of material derived from island-arc volcanism, ultimately derived via multi-stage melting processes from the upper mantle [2]. Note also that the RE distribution patterns of Archean sediments most closely resemble those of present-day island-arc volcanics [16, p. 538]. On the basis of RE evidence, the island-arc model can be inferred to act uniformly back to the base of the Proterozoic. This uniformitarian approach does not appear to hold for the Archean. At the Archean-Proterozoic boundary a significant change in RE distribution patterns occurs (less light-RE enrichment, $[La/Yb]_N = 4.8$, and no significant Eu anomaly; refer also to pp. 179/80) [16, pp. 536/7]. The RE data for post-Archean sediments strongly support a two-stage model for growth and evolution of the continental crust (as proposed by [17 to 19]), which extended back to at least the middle Proterozoic [20, p. 1550]. Continental crust, or only parts of it, formed by one (or by a number of) partial melting process of the mantle (leaving the MORB reservoir as a residuum, see also p. 161) [21]. For growth of Precambrian continental crust by predomi-

nantly differentiation from the upper mantle, refer also to pp. 145/6. For a recycling model of crustal evolution, the sedimentary RE data would call for a particularly vigorous period of crustal consumption and regeneration during the late Archean. Thus, geochemical model-ling of RE in sedimentary rocks in conjunction with isotopic data suggest a major period of growth of the continental crust during the late Archean. Model-dependent, 65 to 75% of this crust is formed between ~3.2 and 2.5 Gyr, or as much as 70 to 85% of the crust has formed by ~2.5 Gyr. Such a model is able to predict relatively constant "freeboard" (for definition, see [22]) during the past 2500 m.yrs., thus compromising the idea of constant freeboard as evidence of large-scale recycling of continental material through the mantle (see [11, p. 466]) [23, p. 358]. Simple igneous fractionation of tonalitic additions to the crust could produce a gross crustal layering with an upper component derived from the hydrous, residual melt with negative Eu anomalies. This model does not imply a mantle sink for Eu (see [24, p. 155]) nor an unseen, major anorthositic component in the lower crust (see [25]). A more complex model, involving the production of similar layering through a lengthy metamorphic differentiation by evolving vapor phases originating in the mantle (see [26]), is equally adequate. However, its requirement for addition of Eu to the lower crust from the mantle is not borne out by modern views on Sr and Nd isotope systems in some granulite-facies terrains [27]. Refer also to a model involving the role of fluids in the formation and subsequent development of early Archean sialic crust [28]. Models involving half the mantle in generating the crust yield $^{143}Nd/^{144}Nd$ ratio of the residual mantle which does not deviate significantly from the bulk earth until the Proterozoic (<2.5 Gyr). This coincides with the observation that initial $^{143}Nd/^{144}Nd$ ratios of Archean volcanics and orthogneisses are consistent with a source region which evolved with a chondritic Sm/Nd ratio [29]. Note also, that, from Nd mass balance calculations, it follows that well over half of the mantle may be LILE-depleted [30]. The vast volume of granitic rocks intruded into the upper crust represents a new crustal addition of material from the mantle and does not represent recycled ancient crust. Thus, a preferred model for crust formation involves two stages where material is added to the crust and subsequently remelted (within 100 to 200 m.yrs.) and intruded into the upper crust. The events related to the Archean-Proterozoic boundary are clearly not synchronous world-wide (depending on location, rang-ing from ~3.2 to 2.5 Gyr) [23, p. 351]. Note also that the strong upper crustal Eu anomaly is compelling evidence of the importance of intracrustal melting to the formation of the upper crust [20, pp. 1547/8].

There are two main ways that **matter** may be **transferred from the mantle to** continental **crust**: as silicate melts, or as fluids. (For the detailed discussion, see original paper) [31]. Water liberated during dehydration under granulite-facies metamorphism probably acts as a solvent and transport medium for soluble complexes of LIL elements (e.g., as carbonate complexes of heavy RE) and transports them to higher crustal levels as a result of diffusion, or by incorporation in partial melts. Since diffusion would not result in large-scale mass transfer, it is most likely that large-scale migration in the crust occurs via melts, which emanate from, or pass through (see also pp. 169/70), lower crustal regions. Moreover, this water would influence the kinetics of melting processes in the lower crust [28]. The observed upward concentration of incompatible elements in the continental crust, and the relative depletion of Eu in the upper continental crust since the Archean, may be explained by a mechanism leaving granulite-facies rocks as a residuum after generation and removal of granitic melts [32]. Metasomatic zones rich in K within strongly retrogressed granulites (with heavy RE-depleted distribution patterns) are explained by loss of a (fluid?) phase enriched in heavy RE complexes [28]; note also heavy RE-depleted RE patterns of Archean granulites, pp. 188/9. A two-way transport of incompatible elements between the two reser-voirs, mantle and a 50 km thick outer layer of the earth (including the continents), is proposed

with time-dependent flux rates, each with different time constants. Acceptable models are those in which: (1) only 50% (by mass) of the mantle contributed to crustal formation (i.e., the gradual accumulation of K and the other lithophile elements in the outer layer), and (2) the return flux transport coefficient is initially much greater than that for the outward flux. But to provide for the segregation of the bulk of the continental crust between 3.5 and 3.0 Gyr, the two transport coefficients (for return and outward flux) become equal about 3.0 Gyr ago. The residence (process) time thereafter becomes long in both reservoirs, and today is very much longer in the outer crustal layer [33]. For additional data on transport models for continental crust formation, see also p. 144.

The RE data and isotopic evidence suggest **episodic rather than uniform growth** rates for the addition of new continental material, as is shown by changes with time for total RE content, for Eu/Eu* ratio, and for the slope of the RE distribution pattern (La/Yb and light RE/heavy RE ratios). A rather sudden change from a "tonalitic" to a "granodioritic" upper crust occurs $\sim 2.5 \times 10^9$ yrs. ago [34, pp. 370/1]. Note further, a LILE-enriched upper crust and a depleted lower crust, with Eu retained in the lower crust, is formed within a short time interval (~ 0.2 Gyr) between derivation of material from the mantle and final differentiation to produce an evolved continental crust [35, p. 394]; and a substantial portion of the continental crust evolved rapidly during the late Archean in connection with major crustal thickening processes which culminated in the formation of deep-seated granulites [24, p. 169]. Periods of continental growth are sharply episodic, and the period 2.5 to 2.7×10^9 yrs. ago was a major epoch of formation of new continental crust [36]. The production of continental crust in the Front Range, Colorado, was probably not a continuous process, but a fairly sharply defined event at 1800 ± 10 Myr ago as follows from Nd isotope data [12]. Subcontinental lithosphere (e.g., beneath Antarctica) may have been enriched in light RE by a distinct differentiation event, perhaps as a result of extensive partial melting of the mantle about 2.0 to 1.6 b.yrs. ago [37].

The constant and uniform nature of the upper crustal RE distribution pattern over the past 1500 m.yrs. (for Australia) does not favor models of slow crustal evolution. It seems to be more likely that new crustal material rapidly evolves to a stratified and stable form. In contrast, the increase of ΣRE content in younger rocks would indicate a slow evolutionary process, which would need to increase ΣRE in the upper crust without changing the relative RE distribution [20, pp. 1544, 1546, 1549]. Note too that an interpretation involving a rapidly evolving upper continental crust seems to be consistent with the RE data for Huronian (late Proterozoic) sedimentary rocks of North America [38].

Data on radiogenic isotopes (Nd, Sr, Pb) indicate a prolonged and directional process of crust formation due to the inflow of new batches of material from the upper mantle during discrete tectonic-magmatic cycles. Starting 2.5 b.yrs. ago, a considerable part was played by reworking (recycling) of the existing crust [39].

Both the portions of Sm and Nd released from the mantle to the continental crust, and the **effect of recycling** on the (crustal) $^{143}Nd/^{144}Nd$ ratio are small [40, pp. 480/1]. But Sm-Nd data for Proterozoic and Phanerozoic granitic rocks show clear evidence for the recycling of pre-existing continental crust into younger granites (of the Caledonian, Great Britain) both by basement recycling and sediment incorporation (see, e.g., [41 to 44]) [45]; note also that recycling of continental crustal materials (that have had a prior crustal residence time ≥ 500 Myr) is suggested for many of the Caledonian granites from Scotland and northern England [46]. Partly, recycled sediment may be a component responsible for the Nd isotope composition observed in various island-arc basalts [41]. A complex present-day crustal recycling process (with calculated rates from 45 to 90%) is indicated by the large range

in model ages for modern sediments (900 to 1800 m.yrs. for pelagic sediments, see [47, 48]) [49].

Divergences for initial Nd and Hf isotopic compositions of modern and ancient mantle-derived rocks are most likely explained by a semi-continuous recycling of continental material back into the mantle over the past 2 b.yrs. The required rate of return of continents to the mantle, calculated from a simple transport model, is about 0.35 ± 0.15 of the continental mass per billion years (or ~ 2.5 km³/yr.). This result indicates that the mass of the continents has been approximately constant since the late Archean [50].

The initial ε_{Nd} value (according to T_{DM} ages, see p. 175) for a 1800 Myr old crust (of Colorado) could be accomodated for by a model of a growing continental crust without recycling, or of a constant-mass crust with decreasing crustal recycling rates towards the present. In either case, the amount of mantle which interacts with the crust must be limited to a small fraction ($\leqq 0.3$) of the total mantle. This supports a two-layered mantle model and suggests that it applies over most of the earth's history [12].

Recycling of older, consolidated continental crust on a large scale in Finland is clearly ruled out by the high initial $^{176}Hf/^{177}Hf$ ratios of the Precambrian samples studied. These high ratios result from a period of evolution with high Lu/Hf, such as is only attained in mantle residual from previous partial melting events. The Hf (and Nd, Sr) isotopic data are only capable of detecting recycling of crust which predates the sampled event by >150 Myr or so [51].

Spatial and Temporal Variations in Crust Composition

The RE distributions in the upper mantle are characterized by a significant Eu anomaly and hence a compensating positive Eu anomaly might be located in the lower crust. This positive Eu anomaly might be large, even if the lower crust is considered to comprise two-thirds of the total crust volume [24, p. 155]. When continental crust is formed, it generally is fractionated relative to the mantle with an Sm/Nd ratio about 40% lower on average. A simple model for crust and mantle Nd isotopic evolutions suggests that the crust is enriched in Sm and Nd, relative to the mantle, by factors of ~ 25 for Nd and ~ 16 for Sm [52]. Against chondrites, light RE are enriched in both the lower and upper crust. The enrichment is relatively higher in the upper crust relative to the lower crust, which is depleted in light RE while enriched in heavy RE [53]. The continental crust is a light RE-enriched reservoir compared to the upper mantle [54]. The characteristics of the present-day crust were established about 2.5 Gyr ago, caused by a two-stage process (model) comprising addition to the crust of igneous rocks derived from the mantle and subsequent intracrustal melting leading to the granodioritic upper crust [35, p. 393].

Taking the Baldwin volcanogenic graywacke, Australia, as representative of new sialic contributions to the crust, it can be used as a model composition for the whole continental crust. Comparing the RE distribution patterns for such a model composition and those of the observed upper crustal sedimentary rocks, the following becomes evident for the upper crust: It is enriched in light RE and depleted in Eu; it is nearly unfractionated with respect to heavy RE; and it is enriched in total RE by a factor of ~ 3. There is also good qualitative agreement between the predicted RE pattern of partial melts of a crust of island-arc basalt composition and the observed upper crustal RE distribution [20, pp. 1547/9].

The origin of upper crustal composition demands at least two stages of chemical fractionation from the mantle to provide the observed upper crustal material of granodioritic composition: addition of material from the mantle during island arc-type volcanic processes followed by intracrustal melting and invading of the upper crust. It is assumed that the crust

has grown with time (in contrast to recycling). Based on this model, the production of upper crustal Eu depletion is an intracrustal process and requires the presence of a stable Eu-bearing phase in the lower crust. Since the production of the Eu depletion requires liquid-crystal equilibria, partial melting rather than metamorphism appears to be the dominant process [34, pp. 359/62]. If partial melting of lower crustal materials (of island-arc composition) produces the rhyolitic magmas and the series of great batholiths ranging from tonalite to granite which characterize the crust, then the lower crust must be depleted in elements enriched in such rocks (including RE). In the lower crust, where partial melting takes place under wet conditions, plagioclase will preferentially retain Eu, and thus deplete it in the upper crust. Sediments derived from weathering of upper crustal material will inherit this Eu depletion [18]. The Eu depletion in upper crustal rocks must be intracrustal in origin and is most likely produced by partial melting where feldspar is a residual phase. Since plagioclase is unstable below ∼40 km (or >10 kbar), Eu anomalies due to this cause are thus produced by shallow intracrustal processes involving crystal-liquid equilibria rather than aqueous transfer [16, pp. 535/6]. Although plagioclase is indicated as a major component of the lower crust, most anorthosites do not show the predicted RE distribution (overall Eu enrichment, depletion in light RE and ΣRE relative to the whole crust), except positive Eu anomalies, thus indicating that the lower crust is more enriched in pyroxene and/or amphibole than anorthosites (sensu stricto). Garnet is relatively unimportant as a residual phase in most crustal melting episodes [20, pp. 1547/9]. Some real heterogeneities in age and/or initial Nd isotope ratios of the lower crust are reflected by two of seven xenoliths (with a pronounced light-RE depletion) from the Calcutteroo kimberlite pipes, South Australia. At least for the samples studied (garnet clinopyroxenite, garnet granulite, and felsic garnetiferous gneisses), retention of plagioclase in the lower crust has not been the major factor controlling RE abundances. Variations in abundance of RE-enriched accessory phases (as, e.g., allanite, zircon, apatite) could substantially influence the RE contents in the lower crust, and perhaps compensate the positive Eu anomaly produced by plagioclase. It is suggested that more basic rock types, as granulites of intermediate, basic, and ultramafic composition (with lower absolute contents of light RE, occasionally even light RE-depleted), may be an important constituent of the lower mantle [55].

Considering that a possible lower/upper crust interface may occur in the pre-2.6 Gyr Lewisian complex at Barra, Outer Hebrides, Great Britain, the tonalitic pyroxene gneisses (characterized by enriched light RE, depleted heavy RE, and positive Eu anomalies) may contain the excess crustal Eu needed to complement the Eu deficiency in post-Archean sediments and the upper crust. These features are compatible with two models for lower crustal evolution: (1) the purging of hydrous tonalitic precursors in the lower crust of H_2O and K, Rb, and Th by mantle-derived, CO_2-rich fluids carrying Sr and Eu during granulite-facies metamorphism; or (2) the primary igneous crystallization under high P_{CO_2} of new tonalitic additions to the crust from which the hydrous residual melt fraction was expelled upwards [27].

Assuming a deep-crust composition as for granulite-facies rocks of the Scourian complex, northwestern Scotland, the continental crust may be stratified with respect to RE [32].

Secular trends in chemical and isotopic composition (including RE) of sediments support a major mafic-to-felsic development in the continental crust (or its precursor) during the late Archean-early Proterozoic period [56]. And, as emerges from Sm-Nd systematics, there is a quasi-continuous development of Archean continental crust (formed between 3.77 and 2.45 Gyr ago) from a reservoir sufficiently large to maintain bulk-earth characteristics. From similar studies of Phanerozoic crust material, a more complex crustal evolution becomes visible [40, p. 475]. In contrast to Archean upper crust (showing less fractionated RE distribu-

tion patterns without an Eu anomaly, see [35, pp. 387/9]), the younger upper crust of the past billion years shows a constancy in RE composition [49], which is inferred to be a consequence of massive intracrustal partial melting which forms magmas primarily of grano-dioritic composition. During this melting process, the melt becomes increasingly enriched in light RE and depleted in Eu (due to different crystal-liquid partition behavior). This major crustal evolution event, reflected by the change from Archean to post-Archean RE distribution patterns, is not isochronous (see also p. 176) [35, pp. 390/2]. Large volumes of K-rich granitic rocks intruded into most shield areas of the earth were suggested to be responsible for the change of RE distribution patterns at the Archean-Proterozoic boundary. About one-third of K-rich granitic rock must be added to the upper-Archean crust to produce typical post-Archean sedimentary RE patterns. The contribution from K-rich granites and granodio-rites appearing sporadically throughout the Archean must have been below 10% [16, pp. 538/41]. Note also that changes in the RE pattern at the Archean-Proterozoic boundary can be related to the gradual unroofing of K-rich granitic batholiths (with negative Eu anomalies) that intruded into the crust at the end of the Archean. Thus, the generation of negative Eu anomalies in the upper crust is a consequence of intracrustal melting where feldspar (mainly Ca-rich plagioclase) containing abundant Eu is retained in the residue [23, p. 351]. There is no evidence for a general Eu excess relative to chondrites in Archean crust exposed to weathering, or for an early anorthositic crust. Most of the Archean sedimentary rocks from Kalgoorlie, Australia, have RE distribution patterns indistinguishable from those of recent island-arc calc-alkaline rocks, and so could constitute evidence that the Archean crust was principally formed by processes analogous to present-day island arc-type volca-nism. However, similar patterns may be produced by an appropriate mixture of the common bimodal tholeiitic-felsic igneous rock suite commonly observed in Archean terrains. The RE data presented here do not distinguish between these two models [57]. As follows from Nd-Sr isotope correlation for specific Precambrian crustal materials (of the Archean Lew-isian complex, northwestern Scotland), Archean crust may, to a first approximation, comple-ment the lithophile element depletion observed in modern MORB mantle sources. The Pre-cambrian crust, and particularly its lower part, must have significantly higher Sm/Nd (and hence higher $[Ce/Yb]_N$) ratios than is suggested by the andesite model for crustal growth (refer to p. 145) [58].

A general uniformity of RE distribution patterns (characterized by an overall enrichment of RE, a relative enrichment of light RE, and a relative depletion in Eu) for post-Archean sediments is not dependent on lithology and is not restricted to one continent, and may be indicative of the average RE pattern of the upper crust [34, pp. 355/6]. Note also that very uniform RE distribution patterns develop during the formation of post-Archean sedimen-tary rocks of Australia from extremely diverse igneous rock patterns. There is little change in either the absolute abundances or the relative patterns during diagenesis and metamor-phism [20, p. 1543]. The use of "average Archean sedimentary rock" (AAS) for reconstruct-ing the composition of Archean continental crust is rejected as unrepresentative, as it in-cludes a strong volcanic component and is heavily weighted in favor of fine-grained material [59], see also [35, pp. 382/3].

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9.2.1.4.3 Lithosphere, Hydrosphere, and Atmosphere

Lithosphere

In the lithosphere, the ideal geochemical cycle begins with the initial crystallization of a magma, proceeds through the alteration and weathering of the igneous rocks and subsequent transportation (partly via the hydrosphere and/or atmosphere) and deposition of the material thus produced with sediments, and continues through diagenesis and lithification to metamorphism of successively higher grade. Eventually, by anatexis (palingenesis, granitization in part) new magma is generated (regenerated). This ideal geochemical cycle may not be completely realized in practice; at some stage it may be indefinitely halted or short-circuited, or its direction reversed [1]. Refer also to a general overview, with a rough draft of the processes involved, for the geochemical cycle given in [2].

Although data for Y and RE elements (especially its chondrite-normalized distribution patterns and characteristic ratios) are widely used for genetical discussions (e.g., of igneous and sedimentary rocks, of individual geospheres, of melting or crystallization processes, etc.), the complete geochemical cycle for Y and/or the RE elements has not been outlined hitherto (1983) in the literature. Therefore, in the following sections and paragraphs only hints are given concerning fragments (mostly already described in this handbook) that can lead to a first approximation of the geochemical cycle. Additionally, some more recent, mainly post-1980 references will be given. The vast number of papers using RE data for a discussion of geological or geotectonic problems (in connection with, or without igneous rock or sediment formation) will be left out of consideration.

The distribution and behavior of Y and/or RE in the **magmatic cycle** are influenced mainly by its crystal-chemical behavior (refer to "Seltenerdelemente" A4, 1979, pp. 1/4 and 87/96) during the melt-forming processes and solidification. As is described in "Seltenerdelemente" A5, 1981, there is an influence (due to several factors, see pp. 32/44) of the crystallization of rock-forming (see pp. 44/69) and accessory minerals (see pp. 69/85) on the distribution of Y and/or RE during solidification of magmas. A relationship occurs between content or composition of $RE \pm Y$ and petrological factors (expressed by characteristic petrological indexes), or the alkalinity of a magma; refer to "Seltenerdelemente" A5, 1981, pp. 188/92

and 192/5, respectively. For distribution and behavior of Y and/or RE during the formation of aplites and pegmatites, or in the pneumatolytic–hydrothermal phase, refer to "Seltenerd-elemente" A5, 1981, pp. 387/415 and 416/48, respectively.

The petrogenetic significance of trace element constraints (including RE data and Nd isotopics) on magma genesis, especially of basalts and granites, is reviewed in [3]. For a classification and discrimination of magma types and magmatic rock groups by means of parameters regarding Y and RE (e.g., ratios between individual elements, or between groups of RE elements, and isotope ratios for Sm and Nd) in relation to the geodynamic (plate–tectonic) position, refer to "Seltenerdelemente" A5, 1981, pp. 237/313. Since mantle and continental crust evolve with relatively high and low Sm/Nd ratios, respectively, it follows that initial $^{143}Nd/^{144}Nd$ ratios can provide a useful criterion for characterization of the source region of any given igneous rock suite or orthogneiss complex; i.e., these ratios give impor-tant constraints if a rock has formed by melting of upper mantle material and/or basic lithosphere, or by melting of older continental crust. The rate of growth of $(^{143}Nd/^{144}Nd)_i$ in sialic crust is retarded relative to the mantle [4]. Melts derived from subducted oceanic crust must reflect its Sr–Nd isotopic characteristics, which are very different from the isotopic signature of subducted sediments or old continental crust. Thus, island arc magmas appear to be dominated by melting of upper oceanic crust. Magmas derived by melting of subducted oceanic plates along continental–margin magmatic arcs are emplaced through older conti-nental crust and subducted sediments and would display a blend of these different source materials, in general agreement with the large range in ε_{Nd} and ε_{Sr} for this type of magma [5]. Nd and Sr isotope data indicate that some magmas in continental regions may be derived from old reservoirs with low Sm/Nd ratio, or are heavily contaminated with old continental crust material [6].

As is widely accepted, magma generation for special types of igneous rocks is connected with the cycles of plate–tectonic processes. For a corresponding characterization and dis-crimination of igneous rock or magma types by chondrite–normalized RE distribution pat-terns, and by diagrams using the contents of Y, or of trace elements other than the RE, or of the main and minor rock-forming elements, refer to "Seltenerdelemente" A5, 1981, pp. 313/63 and 363/75, respectively. Starting with MORB, the following more general state-ments can be derived from RE data for a relationship between igneous rock type and plate–tectonic processes (refer also to pp. 154/60):

Correlations of RE content and light RE/heavy RE ratio with P_2O_5 contents in a wide range of mafic magmas (refer also to "Seltenerdelemente" A5, 1981, p. 229) suggest that apatite may be a minor but important mantle phase controlling the release of RE (fluoropatite is stable in the mantle down to 200 km or more). Thus, MORBs are readily generated from an apatite–bearing (0.5%) plagioclase– or spinel–lherzolite source (with 3 times chondritic RE concentrations and a chondritic light RE/heavy RE ratio) by relatively small degrees of melting (~5%) when apatite is a residual phase. Magmas enriched in P_2O_5 and light RE (e.g., basanites and potassic nephelinites) cannot be derived from either of the above sources, nor from an undepleted garnet lherzolite with similar RE contents. Such magmas appear to represent progressively smaller degrees of partial melting from progressively refractory sources (smaller amounts of apatite, clinopyroxene, garnet) as their P_2O_5 and light RE contents increase. These refractory sources have light RE/heavy RE ratios>chon-drite and represent residues of a material which has lost a light RE–depleted MORB fraction [7]. In contrast, when garnet is given the key role, light RE-rich basic magmas are viewed as products of low-degree melting with large amounts of residual clinopyroxene and garnet relative to light RE-poor melts produced by higher degrees of melting with less residual clinopyroxene + garnet [8]. But the role of garnet in fractionating RE might be better thought

as the result of heavy RE depletion due to its retention in garnet, with the light RE largely being contributed by other phases. Thus, in the case of apatite–bearing sources, light–RE enrichment results from a proportionally larger contribution to the melt from apatite as is reflected in high P_2O_5 content [9].

The source of OIB is geochemically "enriched" relative to MORB which is more "depleted", but it is neither primitive nor merely depleted mantle peridotite. The evidence for a non–primitive source of OIB is twofold: (1) The observed enrichments of incompatible elements (such as light RE, U, Th, K, Rb) in OIB (both alkali basalts and tholeiites) are to high that conventional melting models using primitive sources indicate extraordinarily small degrees of melting which are in conflict with most of today's conventional petrological thinking; and (2) Nd isotopic composition usually indicates lower–than–primitive Nd/Sm ratios. One explanation for the paradox that OIB sources are enriched in magmaphile elements but also relatively depleted in Nd (with respect to Sm) is that OIB may have undergone metasomatic trace element enrichment prior to eruption (but mantle xenoliths giving evidence for mantle metasomatism (refer to pp. 169/71), are normally not related to the source of basalt). The other, preferred explanation assumes subducted oceanic crust to be the source material for OIB (for the detailed discussion, see original paper) [10].

Island–arc lavas appear to be derived from a reservoir depleted in light RE and with a high Sm/Nd ratio. Consideration of both Nd and Sr isotope data suggests seawater involvement in generation of some island–arc lavas and thus indicates that they are derived from altered subducted oceanic crusts. Others may be derived from mantle reservoirs with affinities to the source of OIB [6]. For the percentage of elements (La, Nd, Yb, Ba, Rb, K, Sr) derived from different sources (as recycled from continents, oceanic crust, or undepleted and depleted mantle) in a multi–source model for generation of high–Al basalt, shoshonite, and island–arc tholeiite, refer to [11]. A multistage melting model may relate both tholeiites and komatiites to a common source, perhaps in a rising mantle diapir. Tholeiites would be the first–formed liquids extracted, whereas komatiites are produced by further melting of the residual mantle [12].

The analysis of RE distributions shows that the formation conditions for the calc–alkali rocks are similar in different regions with heterogeneous types of crust, which involves extensive granitization and palingenesis (refer also to p. 189) and which corresponds to the geodynamic settings of active margins and intra–continental activation regions. Thus, the origin of plutonic calc–alkali rocks (granodiorite to granite) from Mongolia is determined by a relatively complete melting of variously granitized substrates differing in basicity (up to basites). The resulting rocks have RE distributions of the types I and IIa (for the patterns, see original paper) with relatively high Eu contents. These magmas may then evolve in accordance with the basic models for crystallization differentiation (trends a and b) with fractionation of the accessory and rock–forming minerals, with the effect from accessory minerals predominating (trend a). The second trend has a joint fractionation of the rock–forming and accessory minerals, with fractionation of salic minerals predominating over the femic ones, leading to RE distributions of the types IIb and III (which show a definite relationship between the slope of the distribution pattern and the depth of the Eu minimum, or degree of negative Eu anomaly) [13]. The possible minerals involved as residual phases during partial melting or differentiation to form granitic melts are the feldspars, quartz, amphiboles, clinopyroxene, hypersthene, olivine, the micas, cordierite, kyanite or sillimanite, scapolite, and accessory minerals (e.g., apatite, zircon, oxides, and sulfides). Eu is retained by the feldspars. Relative to the other RE, the heavy RE are retained somewhat by clinopyroxene but to a greater extent by hornblende, garnet, and zircon; the intermediate RE by clinopyroxene, hornblende, and apatite; and the light RE only by apatite. Different Eu anoma-

lies in the melt result from garnet, apatite, hornblende, clinopyroxene, and hypersthene (leading to a positive one) or from plagioclase or K-feldspar in the residue (leading to a negative one); equal portions of plagioclase and clinopyroxene or twice as much plagioclase as hornblende in the residue result in negligible Eu anomalies in the melt. It is not clear how important complexing of RE is in late-stage supercritical fluids (which may be responsible for the formation of aplites and pegmatites) affecting seriously the trace element composition of a granitic body. Although data are limited, it is suggested that complexing may not be important for the RE (refer also to "Seltenerdelemente" A5, 1981, pp. 389/90 and 420/4) [14]. For Nd isotopic characteristics of I- and S-type granites, originating by partial melting or fusion of either mantle-derived (igneous) or pelitic (sedimentary) material, respectively, see [15]. A thorough discussion, partly based on RE data, of magma genesis in relation to geodynamics in the coastal Cordillera, northern Chile, states the following: Connected with subduction and melting of oceanic crustal material, the genesis of magmas starts with production of primitive tholeiitic material at the continental margin or island arc (with low ΣRE contents and balanced La/Yb ratio) followed by formation of calc-alkaline and shoshonitic lavas (with higher ΣRE contents, higher La/Yb ratio, and more or less Eu depletion which successively is shifted into the continental region). Especially for the genesis of Mesozoic to modern andesites, the following theoretical steps are considered: anatexis of lower crust; amphibole-controlled fractionation of basaltic magmas or partial melting of amphibolite; garnet- and pyroxene-controlled fractionation of basaltic magmas or partial melting of amphibolite; garnet- and pyroxene-controlled fractionation of basaltic magmas or partial melting of quartz eclogite; or partial melting of garnet peridotite at high P_{H_2O} [16].

According to a model for Archean crust evolution (see [17]), partial melting in the mantle produces basalts, which are recycled back into the mantle and are transformed to eclogite. Partial melting at depths where garnet is stable produces tonalites and trondhjemites (but not K-rich granites) with steep RE distribution patterns [18]. Note also that partial melting of amphibolite or eclogite of basaltic or gabbroic composition at depths >30 km, leaving a residue consisting predominantly of garnet and clinopyroxene, is assumed for the origin of quartz dioritic rocks (of the northeastern Minnesota – northwestern Ontario region), whether plutonic tonalite, dacite porphyry, gneissic or plutonic trondhjemite, or trondhjemite dikes [19]; refer also to trondhjemite formation on p. 189. And increasingly smaller amounts of equilibrium melting of a continuously replenished eclogite or garnet amphibolite source may lead to tholeiites (by ~50% melting), andesites (by 30 to 20% melting), or rhyolites (by ~10% melting) in the Archean Bulawayan Group of the Midlands Greenstone Belt, Rhodesia [20].

As follows from initial Nd isotopic composition, continental flood basalts (from the Central Siberian Plateau and other major occurrences) appear to be the product of partial melting of mantle sources that consist of relatively primitive undifferentiated material and are clearly distinct from MORB [21].

The genetic relation between carbonatites and alkali-ultrabasic rocks (refer also to p. 170) is confirmed by their positions in a plot of ΣRE+Y content vs. La/Yb ratio (see [22]), all falling in the same range characterized by high values for both components of the plot and comparable with kimberlites and alkali basalts in rift zones (i.e., explicitly mantle rock bodies), or with ultrabasic xenoliths of mantle origin. All this indicates indirectly that there is a plutonic and obvious mantle source for the primary alkali magma, whose differentiation gives rise to an association of alkali-ultrabasic rocks and carbonatites [23].

For the behavior of Y and RE during (auto-)metasomatic alteration of the various magmatic rock types (acid to intermediate, basic to ultrabasic, alkali-rich, and carbonatitic),

or during metasomatic alteration of their country rocks, refer to "Seltenerdelemente" A5, 1981, pp. 448/67 and 467/73, respectively.

Due to its significance in discussion of the earth's crust evolution (refer to pp. 174/82), there are a number of investigations concerned with Y and/or RE in the **sedimentary cycle**. For an overview on trends or regularities in RE distribution in the sedimentary shell, see [24, 25], and for a summary of RE elements in the sedimentary cycle (especially marine sediments), see [26, pp. 292/9]. Refer also to the following topics described in "Rare Earth Elements" A6a, 1988; note that the page numbers given in parentheses for the present paragraph relate only to the above volume of the handbook: Behavior and distribution of Y and RE during weathering of rocks (general, see pp. 9/13) under marine conditions (leading especially to palagonitization of the basaltic glass component, see pp. 13/7) or under terrestrial conditions (of igneous rocks, see pp. 18/25, and sedimentary rocks, see pp. 25/8. Formation of laterite/bauxite over basic and ultrabasic rocks, see pp. 28/30, and formation of bauxite over carbonatic rocks, see pp. 30/4). Behavior of Y and RE during migration and precipitation in weathering and oxidation zones (mostly influenced by the prevailing physico-chemical conditions, e.g., pH, Eh, complex formation, see pp. 37/42). Influences of climate, geological facies (pelagic to continental), and geotectonic position on distribution and composition of Y and/or RE during sedimentation (see pp. 46/61). Distribution of Y and/or RE in relation to physical and/or spatial factors in clastic (see pp. 77/87) and in chemogenic and/or biogenic sediments (as, especially, phosphorites and metalliferous sedimentary depositions, see pp. 87/100), and within special sedimentation basins and/or stratigraphic series (see pp. 100/16). Mobilization, migration, and precipitation during diagenesis (see pp. 126/8), especially the rearrangement in newly-formed concretions (both marine and non-marine ferromanganese nodules and phosphorites) and other diagenetic products (see pp. 128/58).

The observation that RE distribution patterns in crustal sedimentary rocks are essentially uniform, coupled with the fact that these elements are not significantly affected by weathering, diagenesis, and most forms of metamorphism, leads to the assumption that erosion and sedimentation carry out a wide-scale averaging of upper exposed crust for the RE [27]. And elements which are transferred more directly into detrital sediments preserve a record of the source rock composition. The RE appear to be transferred almost quantitatively into clastic sediments, and thus the average RE distribution in sedimentary rocks reflects their distribution in the exposed continental crust of the source region [28]. Very uniform RE distribution patterns develop during the formation of sedimentary rocks from extremely diverse igneous rock patterns. There is little change in either the absolute abundances, or the relative patterns during diagenesis and metamorphism [29]. With the possible exception of total RE content in some units, the RE distribution in Lower Proterozoic (Huronian) sedimentary rocks is not severely affected by secondary processes, so these samples should reflect a fairly effective sampling of the contemporaneous exposed upper crust for a large region north of Lake Huron, Canada [30]. The similar chondrite-normalized RE distribution patterns (characterized by lower overall abundance of RE, less enrichment of light RE, and without Eu depletion) for several Archean sedimentary rocks from various locations, and spanning a time interval >1000 m.yrs., indicate that sedimentary processes were carrying out an effective sampling of the Archean crust, and thus provides evidence for its composition which is andesitic or tonalitic and which is similar to that proposed for the present-day whole crust. RE evidence of an early anorthositic crust is lacking (refer also to p. 176) [31]. But note that the common (above) assumption that RE proportions are not influenced by weathering should perhaps be re-examined [32, 33].

The Sm-Nd isotopic system is substantially not disturbed during sedimentation or diagenesis [34], or minimal fractionation of Sm/Nd accompanies the generation of clastic sedimenta-

ry rocks from their precursors [35]. Regardless of whether most, or only some of the sediments were generated during the early terrestrial history, they would inherit Sm–Nd systematics from their igneous precursors. In a closed (cannibalistic) sedimentary recycling these ancient systematics will be perpetuated (and consequently Sm–Nd ages of all second-stage sediments should exceed their stratigraphic ages) [36].

Except for Eu (see also below), the relative RE abundances at the earth's surface appear to have remained constant over the past 3 b.yrs. The average relative abundance of Eu in older sediments is significantly greater (at least 1.3 to 1.5 times) than in younger sediments. It is supposed that Eu was relatively more abundant at the earth's surface during early Precambrian times than it now is, perhaps in an amount equal to its relative chondritic abundance [37]. Typical RE distribution patterns of Archean sedimentary rocks differ from those of the post-Archean (refer also to "Rare Earth Elements" A 6a, 1988, pp. 116/26). The former have somewhat more variable patterns and have lower La/Yb ratios (average $[La/Yb]_N = 4.6$), no detectable Eu anomaly (Eu/Eu* ratio ~ 1), and lower total RE contents (ΣRE 70 ppm) [18, p. 387]. The latter show distinctly different patterns (similar to granodioritic rocks) with a nearly constant light RE/heavy RE ratio (9.7 ± 1.8) and a negative Eu anomaly of constant magnitude [38]. The change in composition of the post-Archean upper crust, as is documented by the RE patterns, is inferred to be a consequence of massive intracrustal partial melting which forms magmas primarily of granodioritic composition, and is not isochronous [18, p. 390]. The parallel RE patterns in sedimentary rocks since 2.5 Gyr indicate no fresh input from other than granodioritic material (of the upper crust) over this period of time. The slow increase in ΣRE content is best explained by recycling of sedimentary material in a rather stable cratonic environment (see [36]) [18, p. 393].

Sediments derived from weathering of upper-crustal material will inherit an Eu depletion, because in the upper crust, where partial melting takes place under wet conditions, plagioclase will preferentially retain Eu and thus generate a negative Eu anomaly in upper-crustal material [39]. For the Eu anomalies in Archean graywacke from Wyoming and from the Fig Tree Group, South Africa, an unequivocal reason can not be found. A significant correlation between excess Eu and Sr is not obvious in the graywackes studied: Either Eu^{2+} is not geochemically similar to Sr^{2+}; the genesis of the Eu anomaly involves a change to Eu^{3+} during weathering, erosion, deposition, or diagenesis; or the resulting Eu anomalies are produced by compensating enrichments in feldspar and depletions in the other RE concentrating minerals [40]. The Eu-enriched nature of Precambrian sediments, in general, may be partly explained by the Eu enrichment in seawater and subsequent precipitation and/or adsorption of seawater RE. It is not necessary to invoke a changing RE composition of the exposed upper crust to explain Eu behavior in chemical sediments. It does appear, however, that the Eu contents of clastic sediments may also be related to a changing bulk RE content of the upper crust. This change appears to be abrupt between the Archean and early Proterozoic. Some of the Eu depletion in early Proterozoic shales associated with bounded iron formations may be due to preferential leaching of Eu^{2+} as well as to an inherited source depletion [41].

To get an indication of the degree of sedimentary recycling during continental evolution, the difference $\Delta_{(Sm/Nd - str.age)}$ between Sm/Nd age and stratigraphic age can be used, which should increase towards the present with a 45° slope (the upper limit for a completely closed system). In order to generate smaller Δ, sediments formed from a young source have to be added. This can be achieved by a simple addition; by a partial loss of the original old sediments (e.g., metamorphism) and their replacement by freshly derived young sediments; or by a combination of the above. Sm–Nd data indicate that t_0 (=beginning of simulated growth and recycling) for the bulk of the continental sedimentary mass is

>3.0 Gyr (perhaps 3.5 to 4.0 Gyr). A single sedimentary turnover (cycle) is about 65% (and not more than 85%) for the closed system [36]. Model ages calculated from $^{147}Sm/^{143}Nd$ data for sediments may be expected to provide estimates of their average crustal residence time (τ_{CR} age). The appropriate model age should be an estimate of the time at which the sample possessed the same $^{143}Nd/^{144}Nd$ ratio as the mantle reservoir from which its parental crustal material was derived. Provided that the Sm/Nd ratio of the sediment is close to that of the parental crustal material, and the selected Sm-Nd parameters for the mantle are appropriate, the model age should be a good estimate of τ_{CR}]35].

During the different types of prograde (progressive) and retrograde normal transformation in the **metamorphic cycle**, the changes are only minor for both the absolute contents of RE±Y and the relative RE distributions with increasing degree of metamorphism (i.e., increasing pressure and/or temperature). In contrast, there are indications of increasing mobility of Y and RE with higher intensity of a metasomatic influence, in most cases related to, or in combination with, mechanical weakening of the rock (shearing, mylonitization); sometimes the metasomatism is connected with retrograde alteration of special rock types. For an overview on the behavior of Y and/or RE elements during the metamorphic cycle (especially their mobility and the influence of a fluid phase thereon), and during specific and metasomatic processes, refer to "Rare Earth Elements" A 6a, 1988, pp. 161/8 and 168/71, respectively.

The metasomatic (or, incorrectly, "metamorphic", better named metamorphogenic) solutions or fluids affecting transport and fractionation of RE±Y may originate from one or more sources as, e.g., (1) late- or post-magmatic fluids (effective in contact-metamorphic processes); (2) pore water (from sedimentary source rocks) and/or crystal water (released from decomposed minerals); (3) juvenile fluids/solutions from the depth (mantle) and/or crystal water (effective in the formation of meta-igneous and granitized rocks); or (4) fluids mobilized from a subducting mantle wedge (effective in the formation of ophiolites and eclogites). For additional details, refer to the relevant sections and paragraphs in "Rare Earth Elements" A 6a, 1988, "Metamorphic Cycle".

Migration of Y and RE, mobilized during the normal metamorphic processes, occurs mostly over a short distance mainly by redistribution from primary into secondary minerals. But transport over some distance occurs during very extensive penetration of rocks by metasomatic/metamorphic fluids (high fluid flux) due to complexing of Y and RE predominantly with the halogens and carbonate ions (somewhat influenced by p, T, and ligand concentration; refer also to "Seltenerdelemente" A5, 1981, pp. 420/8). Thus, at lower temperatures, different types of alkali metasomatism promote transport of light RE predominantly in solutions rich in Na and Cl (in the course of albitization or spilitization); heavy RE and Y are more effectively transported in solutions rich in K and F (in the course of biotitization, sericitization, or feldspathization). At both higher temperature and pressure, fluids with increasing amounts of CO_2 (derived from country rock or from the mantle), and due to stability of complexes, seem to be more effective in transporting heavy than light RE, especially during processes influencing acid granulite-facies rocks and charnockites. Only in cases of extreme development of water-dominated metasomatic processes (as, e.g., serpentinization, rodingitization, amphibolitization, epidotization, or chloritization), predominantly light RE are influenced.

Compared to average crustal data, the low absolute RE concentrations (≤100 ppm), the enrichment of light RE, and an Eu excess must be characteristic of "primary" anatectic melts. When fractional crystallization of granitoid melts is suppressed or lacking (e.g., at the stage of anatectic magma formation), the relative Eu content approaches that of the crust [42]. In palingenic melting of various rocks, the RE contents should be determined

by their contents in apatite subject to equilibrium melting and by the contents of K. Compositions of RE in the primary mantle magmas are richer in light RE (La, Ce, Nd) relative to primary crustal-sialic magmas (especially those produced from gneisses). Crustal magmas, on a first and fairly crude evaluation, should differ from mantle ones by lower light RE/heavy RE ratios [43]. The total RE content in magmas formed from sediments by anatexis is higher than in magmas formed in the mantle, because RE are enriched into the upper crust and its silica-rich differentiates [44].

According to a model for development of early continental crust, partial melting of mafic granulites leads to Archean tonalitic and trondhjemitic magmas which would be enriched in mantle and/or lower-crust volatiles (as CO_2, halogens, and SO_2) which are all capable of forming soluble complexes with certain incompatible elements. The most soluble complexes (of, e.g., heavy RE and Y) can migrate out of the system resulting in the heavy RE-depleted character of Archean tonalitic gneisses. The more potassic granitic rocks are regarded as derived mainly by volatile-induced melting of these tonalites. Melts thus derived are expected to show variable fractionation of heavy RE, depending on their content in the source region, the composition of the volatile phase and the extent to which it was entrapped in the crystallizing magma [45]. Note also that early Archean tonalites (impoverished in Y) of Karelia, European USSR, are mainly derived from melts of mantle and crustal material. Predominantly ultrametamorphism of tonalites and supracrustal rocks, with addition of mantle fluids, produced gneissic granites and migmatites during the late Archean [46]. Partial melting of an amphibolite at relatively shallow depths (<50 to 60 km), in which the residue is largely hornblende, is suggested as the source of two high-Al_2O_3 trondhjemites (with chondrite-normalized RE patterns enriched for light RE and flat, slightly depleted for heavy RE) from the basement near the Archean Favourable Lake volcanic complex, northwestern Ontario, Canada [47]. Probably formed by equilibrium melting of a low-K_2O tholeiite or an island-arc basalt during anatexis in an orogenic zone is the highly homogeneous, high-Al_2O_3 and low-K_2O trondhjemite at Follstad, Trondheim region, central Norwegian Caledonides, which has a highly fractionated chondrite-normalized RE pattern (heavy RE relatively depleted against light RE) [48]. The most satisfactory models for formation of trondhjemitic gneiss and tonalite plutons of the Archean migmatite complex near the Gwenoro Dam area, Zimbabwe-Rhodesia, are those involving partial melting of an amphibolite parent, ranging in composition from undepleted to variably depleted Archean tholeiite. The former can lead to tonalite plutons, the latter, mixed with undepleted tholeiite, gives trondhjemite gneiss. Distribution of RE (e.g., strong, 25 times chondritic light-RE enrichment and slightly negative Eu anomaly in tonalite plutons) do not allow garnet as a residual phase. Amphibolite inclusions in trondhjemite gneiss apparently have been produced by partial melting of ultramafic rocks in the mantle in which neither amphibole nor garnet remains in the residue (the observed light-RE depletion probably reflects a partially depleted source) [49]. Partial melting of eclogite or amphibolite (of subalkaline basaltic or gabbroic composition) at mantle depths, leaving a residue of clinopyroxene and garnet, generates igneous rocks of quartz-dioritic composition (with low total, and near-chondritic heavy RE contents). Thus, as follows from the low heavy RE content and application of a partial-melting model (see original paper), 20% partial melting of a quartz eclogite (with a composition similar to that of early Precambrian basalt), leaving a high portion of garnet in the residue, is suggested for two samples of Saganaga tonalite, Thunderbay district, western Ontario, Canada. Partial melting of eclogite could produce the observed low RE content as well as the positive Eu anomaly in a leucocratic trondhjemite dike if the parent eclogite had a RE distribution similar to early Precambrian basalt or gabbro. Possibly, partial melting of a gabbroic source with low RE content, leaving a residue primarily composed of clinopyroxene with only minor garnet, hornblende, or plagioclase, is the source of the trondhjemitic

Burntside gneiss, St. Louis county northeastern Minnesota, which also has a low total RE content but no strong depletion of light relative to heavy RE. The similarity in chondrite-normalized RE patterns for rocks of such diverse occurrence suggests that the patterns reflect a similar, primary origin of the magmas, and are not the result of later events (such as differentiation of a minor phase like zircon, apatite, or titanite; loss of a RE-enriched late-stage hydrothermal solution; or effects of metamorphism) [19]. Permissive of a large variety of generative mechanisms by partial melting of basic source rocks, with garnet in the residue at mantle depths (without assigning a precise geotectonic setting), are the high $[Ce/Yb]_N$ ratios for three Archean synkinematic plutons from near Yellowknife, Northwestern Territories, Canada. Both the western and southeastern granodiorites show similar chondrite-normalized RE patterns with an enrichment of light relative to heavy RE (average $[Ce/Yb]_N$ ratio of 22.0) and without significant Eu anomalies (average Eu/Eu^* ratio of 0.93) [50]. Note also that an origin by 5 to 15% partial melting of a basaltic source, leaving garnet and/or amphibole as residual phases, is supported by the similar RE contents for synkinematic granites from the Archean Yellowknife supergroup and associated dacitic volcanic rocks from the Banting Formation [51].

Because eclogites, or its mineral constituents (garnet and clinopyroxene, mainly omphacite), are viewed as an important source component for magmatic/metamorphic melts (e.g., refer to pp. 185, 189, and "Rare Earth Elements" A6a, 1988, Paragraph 6.5.2.2), or are involved in models describing mantle-crust evolutions (e.g., refer to pp. 161, 163), one should take notice of the two main types of eclogite with different RE characteristics: (1) almandine eclogite (or basaltic eclogite) of crustal origin (and associated with basalts and gabbro-diabase of continental or island-arc type) has high RE content up to 170 ppm ΣRE and Ce/Nd ratios between 0.8 and 1.2; and (2) pyrope eclogite (or kimberlitic eclogite) of mantle origin (and associated with plagioclase- or garnet peridotite and olivine gabbro) has low RE content between 10 and 30 ppm ΣRE and Ce/Nd ratios between 3.5 and 5 [52].

Hydrosphere

A thorough compilation for the migration of Y and RE elements in the marine environment shows the dominating influence of terrigenous matter in supplying the oceans with these elements. Also discussed is the theoretical basis for RE differentiation in oceanic waters during transportation (due to the presence of suspended, colloidal, or dissolved forms of RE), or during precipitation with sedimentary, chemogenic, or biogenic formations. For the details, see original paper [53], and refer to the relevant paragraphs in Chapter 7 (see pp. 1/89) describing the factors and/or processes governing the behavior of Y and/or RE elements during the geochemical cycle in the marine and non-marine environments.

As is suggested by the lateral and vertical RE distribution (refer also to pp. 34/9), seawater displays a typical, negative Ce anomaly (due to its redox behavior, see below) which is caused predominantly (or exclusively) by the formation of ferromanganese nodules (showing a complementary enrichment in Ce, refer to pp. 76/7) on the sea floor. Besides polymetallic Fe-Mn nodules, palagonitization of basaltic glass (selectively enriched in Ce (refer to "Rare Earth Elements" A 6a, 1988, pp. 13/7)) is another possible process which might explain the Ce depletion in seawater [54].

Dissolved Ce occurs mainly as Ce^{3+} under Eh-pH conditions appropriate for seawater-rock interactions, and the $Ce(OH)_2^{2+}$ species predominates only in oxidizing alkaline solutions. However, the effective Eh at the surface of Mn nodules is elevated 200 to 400 mV above that of seawater, and thus precipitation of Ce dioxide may take place according to $Ce(OH)_2^{2+} \rightleftharpoons 2H^+ + CeO_2$ [55]. The strong fractionation of Ce from the trivalent RE in seawater apparently is due to its oxidation to the highly insoluble tetravalent state and

precipitation as hydroxide [26, pp. 286, 291/2]; refer also to p. 32. The range of Eh values for the oxidation reaction $Ce^{3+} + 4OH^- \rightleftharpoons Ce(OH)_4 + e^-$ is between 0.15 and 0.27 V [56], and the solubility product of Ce^{4+} hydroxide is almost two orders of magnitude lower than that of the RE^{3+} hydroxides. The preferential separation of Ce as a solid phase by sorption on suspended matter is provided by the beginning of Ce^{4+} hydrolysis at a pH 3.8, which is much lower than that of seawater or of the precipitation of the other RE [57]. At pH 8, the above reaction has Eh 0.34 V, and since CeO_2 is more stable and might actually control the oxidation of Ce, the Eh value probably is lower than this value [58].

According to the value of normal redox potential in seawater, the oxidation of Ce does not take place if it occurs in ionic form, whereas elements such as Mn, occurring as slightly dissociated compounds (complexes), are more readily oxidized, and this mechanism may also be assumed for Pr with a normal redox potential higher than that for Ce. Supposedly, the oxidation of Ce (and Pr) takes place most readily at the contacts with colloidal particles (suspensions) of hydrated Mn dioxide and Fe hydroxide; diminished contents of the former elements in seawater become understandable [59]. An enrichment of Ce in manganese nodules caused by oxidation occurs in most marine environments, since the Eh in seawater and sediments mostly ranges from 0.25 to 0.45 V (clustering around 0.35 V). If Eh is lower, or within the lower range, Ce oxidation would not be sufficient and, consequently, manganese nodules would lack a Ce enrichment [60]. Note also that an addition of Ce directly from seawater into ferromanganese nodules and sediments (siliceous ooze, glacial silt, and ridge–flank clay) of the Pacific Ocean (mainly its northern equatorial part) is due to oxidation of Ce in seawater and subsequent uptake as Ce^{4+}. This is inferred from a significant correlation for contents of Co and Ce in the ferromanganese nodules, which suggests similar enrichment processes and is not observed for the trivalent RE [61]; and precipitation of Ce due to its oxidation and hydrolysis and the localization of ferromanganese nodules in the northwestern part of the Black Sea may explain the Ce minimum in the water of the Karkinit Gulf and its absence off Poti in the southeastern Black Sea [62]. Further, precipitation of Ce as $Ce(OH)_3$ on the surface of manganese nodules with subsequent spontaneous oxidation to the tetravalent state is suggested [63]. For additional data on RE incorporation (including Ce anomaly) in ferromanganese nodules by direct precipitation from seawater, refer to pp. 75/8.

Biological fractionation as a possible cause of the negative Ce anomaly in seawater is deduced from RE concentration factors CF (ratio between RE contents in g/g dry plankton (average) and g/g in seawater) in mixed phyto– and zooplankton samples (comprising living and dead particles) from surface seawater of both the coastal and open eastern Pacific Ocean (CF for Ce is 4.6 times greater than for La and Sm, and 5.7 times greater than for Eu), as well as from minimum residence times in the photic layer τ (ratio between content in g/cm^2 for the photic layer and assumed rate of annual uptake in g/cm^2 yr.; assuming that removal per year equals production, the average annual biological production of the Pacific Ocean is 7.5×10^3 g C/cm^2 yr.). Thus, elements with τ much lower than the age of Pacific seawater (1600 yrs.) are rapidly removed from the water column; and since a linear relationship occurs between log CF and τ, biological transport via phases with an approximate relative chemical scavenging ability as the above mixed plankton samples is suggested to be an important mechanism for cycling of elements with $CF \geq 10^2$. The concentration factors and minimum residence times in the photic layer for some RE in the Pacific plankton samples are as follows [64]:

	La	Ce	Sm	Eu
$CF \times 10^3$	760	3500	760	620
τ in 10^2 yrs.	0.0053	0.0011	0.0011	0.0064

For definition of various other residence times, and for statements from them on migration of RE in seawater, refer to pp. 65/7.

Both negative and positive Ce anomalies have been observed almost exclusively within the marine environment. Therefore, Ce fractionations are more likely to be the result of strictly marine cycling processes: All trivalent RE (including Ce^{3+}) are removed from seawater by adsorption, and an additional removal of dissolved Ce^{III} by oxidation to solid Ce^{IV} is suggested. Post-depositional reduction to Ce^{III} may occur in organic matter-rich inshore sediments, at which point Ce behaves again as the other, strictly trivalent RE. Nevertheless, a regenerative flux of all RE (including Ce^{3+}) from these sediments would still carry the memory of a positive Ce anomaly. Relatively slow oxidation rates, in analogy with Mn, would allow some diffusion of dissolved Ce^{III} across oxic surface sediment layers and subsequent lateral transport into the center of an ocean basin leads to the observed enrichments in the surface waters. Then marginal sediments would act as a source for both the positive Ce anomaly and Ce itself. In surface water transects one expects both these properties, like Mn, to decrease in an offshore direction (refer, e.g., to pp. 34/6) as a result of oxidative scavenging removal. According to an observed Ce depletion of deep waters (refer, e.g., to pp. 39/41), one would expect to find a positive Ce anomaly for the authigenic fraction of particles settling towards the sea floor, but this has yet to be verified [65]. Note further that, although a negative Ce anomaly is characteristic for the deep-ocean environment, in some cases also divergent anomalies occur during the beginning of submarine weathering and with the change of smectite composition. Whereas Fe-rich varieties formed early in palagonitized glass have a positive Ce anomaly, a negative one occurs in later-formed authigenic smectites from solutions in equilibrium with seawater. This makes it difficult to distinguish by the RE distribution alone between detrital and authigenic minerals without regard to its regional volcanic-sedimentary connection [66].

Atmosphere

Besides mainly terrigenous material from the continents (see pp. 93/101), there is an anthropogenic source (industrial emission, burning of fossil fuels) for RE elements in the atmosphere (see pp. 103/5); origin from marine sources is minor (see pp. 101/2). A probable mechanism of RE migration from the ocean into the atmosphere is shown to be evaporation of high-molecular organic compounds (which are concentrated in the surficial parts of the sea), for the distribution of RE in plankton differs only little from that in sea- and rainwater of the Atlantic, Pacific, and Indian oceans [67]. Experiments with radioactive tracers on physical evaporation of seawater confirm a loss of elements, especially RE, into the atmosphere [68].

In the atmosphere, RE elements are connected mainly with coarser aerosol particles (see pp. 105/12) and, aside from variable near-source contents, are distributed homogeneously throughout the atmosphere (see pp. 112/25), but there are temporal variations with the seasons and/or meteorological conditions (see pp. 125/31).

Removal of RE from the atmosphere occurs predominantly by wet deposition (rain or snow); dry fallout (governed by particle size, shape, and density) is negligible (see pp. 132/6).

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9.2.1.5 Mean Contents of Yttrium and/or Rare Earth Elements in Terrestrial Environments and Balance for Individual Geospheres

Mean contents in the earth crust (Clarke values) and average contents in the main igneous rock types (ultrabasic, basic, intermediate, and acid) of the lithosphere are given for Y and the individual RE in [1].

Additionally to the mean contents of Y and RE elements for total earth, mantle, and crust given in "Seltenerdelemente" A5, 1981, pp. 2/9, the following more recent data have been determined. Based on data for (meta-)sedimentary rocks, the abundances of these elements for the primitive earth mantle and different parts of the present and Archean crust [2, pp. 384/5] and for the post-Archean crust [3] are as follows (note partly differing values for individual RE given in [4]):

	primitive mantle	present crust total	upper[1]	lower	Archean upper crust[2]	post-Archean crust total	upper	lower
Y	2.9	22	22	22	15	22	27	20
La	0.50	19	30	14	12.6	19	38	9.5
Ce	1.30	38	64	25	26.8	38	80	17
Pr	0.19	4.3	7.1	2.9	3.1	4.3	8.9	2.0
Nd	0.967	16	26	11	13.0	16	32	8.0
Sm	0.314	3.7	4.5	3.3	2.78	3.7	5.6	2.8
Eu	0.12	1.1	0.88	1.2	0.90	1.1	1.1	1.1
Gd	0.42	3.6	3.8	3.5	2.85	3.6	4.7	3.1
Tb	0.079	0.64	0.64	0.64	0.48	0.64	0.77	0.58
Dy	0.52	3.7	3.5	3.8	2.93	3.7	4.4	3.4
Ho	0.12	0.82	0.80	0.83	0.63	0.82	1.0	0.73
Er	0.34	2.3	2.3	2.3	1.81	2.3	2.9	2.0
Tm	0.048	0.32	0.33	0.32	0.26	0.32	0.41	0.28
Yb	0.34	2.2	2.2	2.2	1.79	2.2	2.8	1.9
Lu	0.052	0.30	0.32	0.29	0.28	0.3	0.4	0.25

content in ppm for

[1] Note also that contents of individual RE in loess samples from various deposits of America, Europe, China, and New Zealand are indistinguishable from average upper-crustal contents [5]. — [2] An estimate for the most fractionated Archean exposed crust allowed by sedimentary data gives in ppm: La 25.0, Ce 51.6, Pr 5.50, Nd 21.3, Sm 3.72, Eu 1.13, Gd 3.24, Tb 0.55, Dy 3.24, Ho 0.69, Er 1.92, Tm 0.27, Tb 1.79, and Lu 0.27; the Eu/Eu* ratio is 1.0 [6, p. 349].

For contents of Y and RE elements in the upper and lower mantle, refer also to p. 163. Average continental crust calculated from three sections of the Canadian Shield (northern Quebec, Baffin Island, and southern Saskatchewan) contains in ppm: Y 20.7, La 32.3, Ce 65.6, Nd 25.9, Sm 4.51, Eu 0.937, Gd 2.79, Tb 0.481, Ho 0.623, Yb 1.47, and Lu 0.233 [7]. Average oceanic crust calculated from analyses of fresh ocean-ridge basalts (taken from the literature) contains in ppm: Y 40, La 3, Ce 10, Pr 1, Nd 10, Sm 3, Eu 0.7, Gd 4, Tb 0.7, Dy 4, Ho 1, Er 3, Tm 0.8, Yb 2, and Lu 0.5 [8].

For the mantle source of normal- and enriched-type MORB, the following contents and ratios for Y and some RE are calculated [9]:

	content in µg/g						ratios		
	Y	La	Ce	Nd	Sm	Tb	La/Th	La/Ta	Zr/Y
N-type	4.1	0.31	0.95	0.86	0.32	0.08	15	14	2.8
E-type	2.7	0.66	1.68	1.11	0.42	0.08	11	11	4.2

The calculated average Sm/Nd ratio is 0.30 for the lower crust, similar to chondrite values of 0.325, but much higher than 0.18 for the upper crust [2, p. 386].

Computer-derived element abundances of Y and RE (from numerous literature data up to 1963) are as follows for individual lithologic categories [10, pp. 285/6]:

	content in ppm					
	igneous rocks	shale	sandstone	carbonate rocks	oceanic clay	oceanic carbonate
Y	41.4	20.4	16.2	14.9	57.3	36.4
La	48.1	28.1	18.6	9.42	68.2	16.3
Ce	130	44.7	55.0	10.8	203	35.3
Pr	16.7	5.50	7.05	1.28	26.0	4.64
Nd	56.5	18.0	23.9	7.99	87.5	20.9
Sm	15.5	4.97	6.63	1.08	24.2	4.53
Eu	2.28	1.07	0.944	0.187	3.35	0.822
Gd	9.90	4.10	4.41	0.773	14.7	4.44
Tb	1.78	0.540	0.745	0.145	2.77	0.741
Dy	9.82	4.15	3.06	0.528	14.9	4.47
Ho	2.40	0.824	1.11	0.180	3.67	0.880
Er	3.62	1.75	0.884	0.449	5.43	1.75
Tm	0.938	0.286	0.303	0.0750	1.40	1.07
Yb	4.76	1.58	1.61	0.197	7.54	1.42
Lu	1.13	0.284	0.298	0.111	1.80	0.860

The computed abundances in relation to four domains of sedimentary rock deposition are as follows [10, pp. 286/7]:

	content in ppm			
	continental shield	mobile-belt shelf	hemipelagic region	pelagic region
Y	17.8	18.2	55.2	54.3
La	21.6	23.5	63.0	60.9
Ce	40.8	46.4	186	179
Pr	5.09	5.80	23.9	23.0
Nd	17.5	19.4	80.9	78.2
Sm	4.66	5.34	22.3	21.5
Eu	0.861	0.974	3.10	3.00
Gd	3.54	4.03	13.6	13.2
Tb	0.518	0.590	2.56	2.48
Dy	3.14	3.56	13.9	13.5
Ho	0.776	0.889	3.39	3.28
Er	1.24	1.36	5.07	4.92
Tm	0.248	0.279	1.37	1.36
Yb	1.32	1.52	6.93	6.68
Lu	0.252	0.277	1.71	1.67

The RE contents and Eu/Eu* ratios for average shale composites from post-Archean samples of North America (NASC) [11] and from the Paleozoic of Europe (ES) [12], and for post-Archean sediments (shale, siltstone, and subgraywacke) from five areas of Australia [13] are as follows:

	content in ppm				content in ppm		
	NASC	ES	Australia[*]		NASC	ES	Australia[*]
La	32	41.1	38	Dy	5.8	—	4.4
Ce	73	81.3	80	Ho	1.04	1.20	1.0
Pr	7.9	10.4	8.9	Er	3.4	3.55	2.9
Nd	33	40.1	32	Tm	0.50	0.56	0.50
Sm	5.7	7.3	5.6	Yb	3.1	3.29	2.8
Eu	1.24	1.52	1.1	Lu	0.48	0.58	0.50
Gd	5.2	6.03	4.2	Eu/Eu*	0.70	0.70	0.67 ± 0.05
Tb	0.85	1.05	0.77				

[*] Additionally 2.8 ppm Y; the values for Tm and Lu are only calculated.

New analyses of the (not strictly) North American shale composite document that significant portions of RE and other trace elements are contained in minor phases and that their uneven distribution in the NASC powder appears to have resulted in heterogeneity among analyzed aliquants. Consequently, caution should be exercised in the interpretation of RE distributions of sediment samples as they may be variable and biased relative to average RE distribution of the crustal rocks supplying detritus. These effects appear to be largely averaged out in sediment composites, with the result that their RE distributions are more likely to be representative of their provenances [55]. For the matrix of 15 tillite samples from three areas of the Gowganda Formation (Lower Proterozoic) north of Lake Huron, Canada, the mean contents of some RE are as follows and given in ppm: La 25, Ce 55, Nd 23, Sm 4.3, Eu 1.2, Gd 3.8, Dy 3.1, and Er 2.0; the weighted Eu/Eu* ratio is 0.89 ± 0.13. These values may be comparable to upper crustal abundances [14].

Calculating bulk earth ($\sim$ undifferentiated mantle) parameters assuming (1) that the earth has the same relative abundances as carbonaceous chondrites, or (2) that heat lost from earth equals heat generated, the respective contents of Sm and Nd are calculated to be 0.32 and 0.97 ppm for (1), and 0.74 and 2.2 ppm for (2); in both cases the Sm/Nd ratio is 0.32 [15]; refer also to [16, p. 6093] and the isotopic data given in "Seltenerdelemente" A5, 1981, p. 9. Using a self-consistent, near-steady state recycling earth model, the chemical characteristics of major domains are calculated as follows [17]:

	crust		mantle			bulk
	upper	lower	upper	lower	total	earth
Sm (ppm)	5	3	0.46 to 0.54	0.49 to 0.52	0.5	0.35
Nd (ppm)	25	12	1.4 to 1.6	1.46 to 1.55	1.5	1.08
$^{147}Sm/^{144}Nd$	0.12	0.15	—	—	0.20	0.917

But note in contrast that only a small portion of the earth's total Sm and Nd budget is found in the crust [59]. Average southern Australian lower crust, calculated by weighing xenoliths (garnet pyroxenite, garnet granulite, felsic garnetiferous gneiss) according to their relative abundance, has 3.2 ppm Sm, 11.8 ppm Nd, and ratios of 0.16 for $^{147}Sm/^{144}Nd$ and 0.51179 for $^{143}Nd/^{144}Nd$; $\varepsilon_{Nd}(0)$ is -1.0 [18]. The $^{147}Sm/^{144}Nd$ ratio of average Precambrian surface crust is $\sim$0.110 (see [19]), similar to that of average North American shale with $\sim$0.115. These upper crust values are essentially identical to crust values of 0.108 ± 0.01 derived from two models (VIL and DEL, see p. 162) [20, p. 194]. A present-day $^{143}Nd/^{144}Nd$ ratio of 0.5129 is calculated for the residual mantle after generation of crust <2.5 Gyr ago

[16, p. 6098], and the $^{143}Nd/^{144}Nd$ ratio of the mantle source (for MORB) is close to 0.5130; that of average continental material will be < 0.5120 [21].

If the mean age of the continental crust is as great as 2500 Myr and with estimates of enrichment factors f_{Nd} from −0.35 to −0.48 for it (see, e.g., [16, 22 to 24]), an ε_{Nd} of −0.30 for the continental mantle is quite plausible [25].

There are global and regional trends in isotopic ratios (which reflect the secular addition of radiogenic isotopes such as of Nd from the α-decay of ^{147}Sm) and are given in a scheme for the possible distribution of Nd isotope compositions (mean ε_{Nd} values) in mantle, crust, and various geotectonic positions [26]. Whereas the Sm–Nd isotopic system is not substantially disturbed during sedimentation or diagenesis (refer to pp. 186/7 and "Rare Earth Elements" A6a, 1988, "Sedimentary Cycle"), Nd is enriched relatively to Sm during magmatic processes leading to the production of sialic crust from the upper mantle [61].

Elements derived from upper continental crust may be transported back into the mantle by dissolution in seawater and reprecipitation in fresh oceanic crust by low-temperature alteration (refer also to "Rare Earth Elements" A6a, 1988, pp. 13/7) and hydrothermal interaction. To estimate the maximum possible concentration increase of the oceanic crust due to uptake of U, Th, Rb, Sr, and Nd dissolved in seawater, calculations have been performed considering the production rate of oceanic crust (~ 20 km^3/yr.) besides river influx (or pelagic precipitation) and the assumptions that this crust is the only sink for these elements and that steady state prevails. The results for Nd are: 0.2 to 1.4×10^{10} g/yr. pelagic precipitation and < 0.24 ppm net concentration increase of crust, or < 2% concentration increase of crust via fresh MORB [27]. Note also that ocean floor basalt is not an important sink, and that the oceans may be small ($\sim 4 \times 10^9$ kg) but well-mixed reservoirs for Nd [21].

An analysis of the initial Nd and Hf isotopic composition of modern and ancient mantle-derived rocks shows that the divergence of the mantle ratios for $^{143}Nd/^{144}Nd$ (and $^{176}Hf/^{177}Hf$) from the chondritic ratios over the past 2×10^9 yrs. has been much less than would be expected from data based on these ratios for the mantle source of MORB. The most likely explanation is that rock material from the continents has been recycled semi-continuously back into the mantle over this period of time (refer also to pp. 177/8). As is calculated from a simple transport model, the required rate of return of continents to the mantle is about 0.35 ± 0.15 of the continental mass per 10^9 yrs. (or ~ 2.5 km^3/yr.). This is consistent with the hypothesis of an approximately constant mass for the continents since the late Archean [28].

For a compilation of published data (up to 1971) on the levels of radioactivity (including isotopes of Y, Ce, and Eu) in seawater, sediment, and marine biota from fallout and waste-disposal operations, see [54].

A balance of Ce and Yb concentrations for the undifferentiated earth (= crust + mantle) and the differentiated parts is as follows [29]:

	ppm Ce	ppm Yb	Ce/Yb ratio
undifferentiated earth[1]	3.1	0.68	4.6
mantle equivalent concentration			
removed to crust[2]	0.39	0.018	21.7
residual mantle	2.7	0.66	4.1

[1] Values calculated using a mean heat flow of 1.95 μcal/cm^2 sec. — [2] Calculated from crustal abundances given in [31].

For basic principles of balance calculations for Nd and Sr budget in the crust–mantle system, considering the concepts of mean and modal ages, see [30].

The results of mass balance calculations for a post–Archean composition (D) assuming the simple equation $D = xA + (1 - x)B$ (where A = Archean composition, B = late Archean upper crustal addition composition, and x = mass fraction) are given in the following and compared with known post–Archean upper crust compositions (C) [6, pp. 349, 353/4]:

	A	B	C	D*)
Sm (ppm)	3.72	4.86	4.5 ±0.36	4.62 or 4.35
Eu (ppm)	1.10	0.93	0.88±0.07	0.97 or 1.01
Gd (ppm)	3.24	4.10	3.8 ±0.30	3.92 or 3.72
Eu/Eu* ratio	0.95	0.62	0.65±0.03	0.68 or 0.75
Th (ppm)	6.9	12.3	11.1 ±1.2	11.2 or 9.9

) First number is for the maximum value of x (0.21) to explain composition C (particularly the mean Eu/Eu ratio) within uncertainties; second number is for the respective value of x (0.44) to explain the Th abundances.

A computer–derived geochemical mass distribution and balance between primary igneous rocks, sediments, and seawater for Y and the RE in various geological domains (columns (1) through (7)) gives the following results, which show a material balance between the sum for columns (1) to (6) and column (7) [10, pp. 280/4, 287/8]:

	continental shield (1)	mobile-belt shelf (2)	hemi-pelagic region (3)	pelagic region (4)	connate water (5)	sea-water (6)	weathered igneous rocks (7)
Y	0.0455	0.140	0.411	0.248	4.40*	42.1*	0.844
La	0.0553	0.180	0.469	0.278	0.00425*	0.0407*	0.982
Ce	0.105	0.356	1.38	0.818	0.00188*	0.0180	2.66
Pr	0.0130	0.0445	0.178	0.105	0.000935*	0.00895*	0.341
Nd	0.0448	0.149	0.602	0.357	0.00336*	0.0321*	1.15
Sm	0.0119	0.0409	0.166	0.098	0.000638*	0.0061*	0.317
Eu	0.00221	0.00747	0.0231	0.0137	0.000166*	0.00159*	0.0464
Gd	0.00906	0.0309	0.102	0.0604	0.000893*	0.00854*	0.202
Tb	0.00133	0.00452	0.0191	0.0113	–	–	0.0363
Dy	0.00805	0.0273	0.104	0.0615	0.00106*	0.0102*	0.200
Ho	0.00199	0.00682	0.0253	0.0150	0.000322*	0.00309*	0.0491
Er	0.00319	0.0104	0.0377	0.0224	0.000893*	0.00854*	0.0738
Tm	0.000635	0.00214	0.0102	0.00619	0.000191*	0.00182*	0.0192
Yb	0.00339	0.0116	0.0516	0.0305	0.000765*	0.00742*	0.0972
Lu	0.000644	0.00212	0.0127	0.00762	0.000170*	0.00163*	0.0231

content in 10^{14} metric tons [1]

[1] Values marked with an asterisk are given in 10^8 metric tons!

For a first approximation one can assume that the total river loading of an element (including dissolved and particulate forms; see also below) is deposited in estuaries and continental shelves (in sediments with typical shale composition) and on the deep-sea

floor (with oceanic pelagic clay). Mass balance is calculated by

$$M_T \cdot C_p^i + F \cdot C_R^i = (M_T + F \cdot \Sigma \, C_R^i - M) \, C_{sh}^i - M \cdot C_{op}^i \tag{1}$$

where M_T is the total suspended particulate flux from rivers to the ocean $(18 \pm 3 \times 10^{15}$ g/yr.), M is the total sedimentation rate of pelagic clay $(1.1 \pm 0.4 \times 10^{15}$ g/yr., obtained from an average pelagic clay sedimentation rate of $0.3 \pm 0.1 \times 10^{-3}$ g/cm yr.), and F is the total river water flux $(33 \pm 3 \times 10^{18}$ g/yr.); C_p^i, C_R^i, C_{sh}^i, and C_{op}^i are the concentrations of element i in river–suspended particles, filtered river water, shale, and oceanic pelagic clays, respectively; $F \cdot \Sigma \, C_R^i$ $(\sim 0.9 \times 10^{15}$ g/yr.) is the summation of the dissolved river loadings (excluding Ca^{2+} and HCO_3^- which are deposited separately in the oceans as oceanic carbonates) and the recycled sea salt components (assuming Cl^- is recycled through the atmosphere). Dividing equation (1) by M_T, and substituting various coefficients with known values, one obtains

$$C_p^i + 1.8 \times 10^3 \, C_R^i = 0.99 \, C_{sh}^i + 0.66 \, C_{op}^i \tag{2}$$

where all C^i are in ppm [32, pp. 2076/8]. As a first approximation, the chemical composition of river–suspended matter is very close to that of surficial rocks (see table below). However, owing to the importance of chemical weathering and the resulting transport of dissolved material, the suspended matter is relatively enriched in elements such as the lanthanides. The use of an average earth rock composition may therefore significantly change mass-balance computations. The mean contents of Y and some RE in continental material (rocks and soils), rivers (diss. = dissolved and part. = particulate), and ocean water and deep-sea clays are as follows [33] (except for soils, refer also to [34]); approximate values are given in parentheses:

	contents in µg/g or µg/L *)					
	continental		rivers		ocean	
	rock	soil	diss.*)	part.	water *)	clay
Y	33	40	—	30	0.0013	32
La	41	40	0.05	45	0.003	45
Ce	86	50	0.08	95	0.001	100
Pr	9.6	—	0.007	(3)	0.0006	9
Nd	37	35	0.04	35	0.003	40
Sm	7.1	4.5	0.008	7	0.0005	7.0
Eu	1.2	1	0.001	1.5	0.0001	1.5
Gd	6.5	4	0.008	(5)	0.0007	7.8
Tb	1.05	0.7	0.001	1.0	0.0001	1.0
Ho	1.6	0.6	0.001	(1)	0.0002	1
Er	3.7	2	0.004	(3)	0.0008	2.7
Tm	0.5	0.6	0.001	(0.4)	0.0002	0.4
Lu	0.45	0.4	0.001	0.5	0.0002	0.5

Except for the migration diagram given in [35] depicting the change in RE composition during its way from continent to ocean, complete budgets for Y and/or RE that attempt to balance the fraction of elements entering the ocean as dissolved material with their accumulation in authigenic and biogenic sedimentary phases are missing, only parts of this cyclus have been mentioned or are investigated in detail, as can be seen from the following.

Relating only to the data for river input (as, e.g., derived for the Gironde River estuary), the balance is insufficient by a factor of 11 to 12 to account for the present rate of RE accumulation in authigenic and biogenic phases of pelagic sediments in the Pacific Ocean.

This discrepancy becomes even larger if one considers: (1) the rather high rates of accumulation of biogenic sediments in the hemipelagic environment; (2) the omission of several phases, particularly fish-bone apatites; (3) the neglect of possibly high accumulation rates of seawater-derived RE along the East Pacific Rise; and (4) the use of what is possibly a conservative estimate for the RE concentration in amorphous phases. Several explanations may account for this apparent imbalance: (1) either the Gironde input is low for the average of world rivers, or a fraction of the suspended load is present as a loosely absorbed phase which is released to solution on contact with seawater; (2) diagenesis of buried sediments maintains a relatively high concentration of authigenic phases in surface and near-surface sediments; and (3) marine volcanism may contribute significant RE to pelagic sediments, principally as volcanic material that is rather quickly altered to montmorillonite and phillipsite or precursors of these two minerals [36, pp. 301/2]. Regarding the Garonne and Dordogne river values for La (475×10^{-10} g/L) as an approximation to world river La concentration, and assuming that estuarine (Dordogne) removal is affecting roughly 50% of the supply (the world river discharge taken as 36.4×10^{15} L/yr. and the ocean area to be 3.6×10^{13} km^2), the river input would be 0.25×10^{-9} g/cm^2 yr. But the total output of 2.26×10^{-9} g/cm^2 yr. is higher by an order of magnitude (see table below). A small percentage of dissolution of suspended matter in the ocean would easily balance the input deficiency. It may also be suggested that a fraction of the particulate supply is incorporated in the various authigenic phases (as montmorillonite and phillipsite), and that volcanic influx could be an alternative explanation. The discrepancy in balance could also result from the representation of RE data of the Garonne and Dordogne rivers and the Gironde estuary, and the La concentration of 2000×10^{-10} g/L found in Swedish rivers and the Columbia River may be more realistic. On this basis, a smaller amount of estuarine removal of 25% is necessary, and the fluvial global input to the ocean would become 1.5×10^{-9} g/cm^2 yr. which is of the same order of magnitude as the oceanic output and thus eliminates the problem of RE imbalance. The quantitative data calculated for the individual phases involved for La output from the ocean are as follows [37]:

phase involved for La output	accumulation rate in 10^{-6} g/cm^2 yr.	content ppm La	La accumulation rate in 10^{-6} g/cm^2 yr.
CaCO$_3$	60	1	0.06
polymetallic nodules	0.2	250	0.05
fish bones	0.15	2000	0.30
montmorillonite	15	100	1.60
phillipsite	1.5	150	0.25
barite	1	—	—

Note also that, according to two models, the calculated accumulation rates (in 10^{10} g/yr.) for Y (6.4 or 3.1) and La (4.3 or 3.6) in the deep-sea area show a considerable discrepancy against dissolved input with rivers (Y 0.29 and La 0.82). Addition of continental detritus (with Y 1.55 and La 1.80×10^{10} g/yr.) does not equalize the balance [38]. The imbalances given above for the overall RE budget based on river input only may be equalized by a major atmospheric input and by deep sources (sediments). Equally, a benthic flux of the magnitude of the river flux would allow the long riverine residence times to be compatible with the short scavenging residence times (see pp. 191/2). The RE are rapidly cycled in the marine environment [39]. The balance of RE in the oceans (as given by [36, 37]) shows that the equilibrium between supply and extraction (by precipitation or fixation into sediments) is difficultly to maintain, in particular for Ce between ferromanganese nodules, phosphate debris, calcareous sediments, submarine alteration products of basalt (palagonitization), and seawater. For the quantitative data, see the original paper [40].

The ocean–rock system has run so close to a steady state that, for more than 60 elements, the rate of input to the ocean by river transport is almost exactly balanced by the rate of removal by sedimentation (see [56]). Using a simple chemical reactor model (igneous rocks + acid volatiles + water → seawater + sediment + atmosphere), a strong correlation is established between the mean oceanic residence time $\bar{t}_y$ and the ocean–rock partition coefficient $K_{y(sw)}$ of an element (for the data of log K_y for RE elements, see p. 22). This relationship can be used to rationalize the observed composition of seawater (and a similar correlation also exists for world average river water). For details, see the original paper [57]. The mean $\bar{t}_y$ calculated from river input of dissolved material for some RE elements is as follows and given as log $\bar{t}_y$ in yrs.: La 3.31, Ce 2.63, Eu 3.53, Gd 3.47, and Lu 3.83. The relative oceanic enrichment can be calculated from log $\bar{t}_y - 4.53$ [58]. For considerably lower minimum residence times of La, Ce, Sm, and Eu in the photic layer of the eastern Pacific Ocean, see p. 191.

The total quantities of La buried on the floor of the Pacific and Indian oceans are 21 and 11×10^3 t/yr., respectively, corresponding to a mean La content of 18.4 ppm for the Pacific and 18.5 ppm for the Indian ocean (which is very close to the mean content of 19 ppm La for sedimentary rocks of continents and subcontinents given in [41]). Calculations indicate that pelagic zones of both oceans receive only 6.4% and 2.9%, respectively, of all the La supplied by rivers. Most of the river–derived La is deposited at their mouths, in marginal seas, and near the coasts [42]. Based on data given in [43], the annual influx of Y and La by rivers into the Pacific, Indian, and Atlantic oceans is calculated for Y to be 0.2014, 0.2304, and 0.0899×10^6 t, and for La, 0.2807, 0.3225, and 0.1257×10^6 t, respectively. Without consideration of the shelf and the upper part of the continental slope, the annual accumulation of Y in sediments restricted to landward sites with depths of 1 to 3 km is 0.03144×10^6 t (or 15.60% of the river runoff) for the Pacific Ocean and 0.0120×10^6 t (or 5.21% of the river runoff) for the Indian Ocean [44]. For the sedimentation rates (in $\mu g/cm^2 \cdot 10^3$ yr.) of La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu in authigenic and biogenic phases of pelagic sediments of the Pacific Ocean, see [36, p. 300].

Abundance patterns of RE in seawater, and the calculated enrichment factors $f_{Sm/Nd}$ for ferromanganese modules (assuming that the North American shale composite represents an average continental source) indicate that the RE balance is controlled to some extent by precipitation into these nodules (see also pp. 76/7). Clearly, there must be other substantial sedimentary deposits or other sinks in the oceans which have f-values (and Ce abundances) which would balance the RE abundances by a steady-state model. Ocean floor basalts could be one possible sink [45]; though of minor importance (p. 198). Even though some 98% of the annual river flux of Nd is in particulate matter (refer also to p.11), the estimated mean concentrations of dissolve Nd in river water are over an order of magnitude higher than in the seawater. If these dissolved Nd concentrations in seawater are at a steady state, the excess Nd in river water must be sequestered by particulate material in the oceans and may constitute a portion of Nd in the hydrogenous RE component of pelagic clays (which thus became the largest repository of Nd in the oceans). Assuming steady state and a mean content of 37 ppm Nd (as for the North American shale composite), the mass balance of Nd in ocean basins is as follows (according to the constraints density of dry abyssal sediment = 0.7 g/cm^3; abyssal non-carbonate sedimentation rate = 10^{-4} g/cm^2 yr.; mean ocean depth = 3729 m; pelagic sediment ~90% carbonate; Mn accumulation rate in nodules = 10^{-6} g/cm^2 yr.; Nd content in river water = 3.79×10^{-7} g/L; and H_2O flux from rivers into oceans = 3.2×10^{16} L/yr.): 2.8×10^{-9} g/L as average Nd concentration in seawater (see [46]) is equivalently contained in a 0.4 mm-thick layer of pelagic sediment (averaged), or the mass of clay particulate containing an equivalent amount of Nd as 1 L seawater is ~7.5×10^{-5} g. The average amount of non-carbonate detrital particulate in seawater

is 5×10^{-5} g/L [47]. A source of dissolved Nd from bottom sediments may be necessary to bring the dissolved oceanic RE budget into balance. Whereas the dominantly continental nature of Nd in ocean water is well established, it is not yet possible to identify and assess the importance of processes active at the sediment–seawater interface that may affect the RE budget of the oceans [48]. Although there is a first direct evidence of RE–enriched hydrothermal solutions pouring into seawater from the east–Pacific Rise (at $30°$ N latitude), the budget of these elements in the ocean and the crust is not modified, because the hydrothermal RE component in seawater is orders of magnitude less than the continent-derived components [49]. Note also that mid–ocean ridges are not important sinks or sources for elements with a mass balance ratio $c_{out}/c_{in} > 0.7$ (as, e.g., the RE elements) [32, pp. 2077/8, 2082]. For the Nd budget in seawater refer also to pp. 46/7.

Assuming Nd in seawater is in soluble form with a $^{143}Nd/^{144}Nd$ ratio between 0.51245 and 0.51264, it is clear that the seawater budget is strongly skewed toward mantle-type Nd (introduced by submarine and subaerial volcanism and hydrothermal circulation at mid-ocean ridge crests) [20, p. 197].

An assessment of natural and anthropogenic sources of atmospheric emissions gives for Sm the following fluxes in 10^8 g/yr.: from continental dust 32; from volcanic dust 9; from industrial particulate emissions 7; and from fossil fuel 5. An estimate of trace metal fluxes to the atmosphere from burning of wood and forest fires gives for Sm 0.1×10^8 g/yr. Calculated from (total emissions/continental+volcanic fluxes) $\times 100$, the atmospheric inter-ference factor is 29%, indicating that anthropogenic sources are of small importance [50, pp. 512/5, 520]. Refer also to p. 104 for mobilization of RE into the atmosphere. For a discus-sion of the relationship between calculated interference factors and observed enrichment factors, and for a quantitative model representing the change with time of the mass of a given metal in atmospheric particulates, see [50, pp. 515/8]. The transport of Sm into the oceans occurs mainly by stream load $(890 \times 10^8$ g/yr.); atmospheric rainout is minor $(3 \times 10^8$ g/yr.) [50, p. 519]. Aerosol-rock enrichment factors $EF_{Fe}(x)$ (see p. 91) have been used to calculate the world emission from natural and anthropogenic sources [51]; and compared with the world emission (1967) from fossil fuels (coal and lignite) [52]; the values for some RE elements are as follows:

| | world $EF_{Fe}(x)$ | emission in 10^6 g/yr. | |
		natural and anthropogenic	fossil fuels[*)]
La	1.5	1060	1400
Ce	1.4	2050	1600
Sm	1	150	220
Eu	2.2	70	100
Tb	0.8	17	42
Dy	1.4	100	—
Ho	0.9	10	42
Yb	0.05	3.5	70

[*)] The emission from oil combustion is for La 0.8, Ce 2.0, and Er 0.2×10^6 g/yr.

For samples taken between February and April 1976 at middle-latitude and tropical regions of the southern parts of the Atlantic and Pacific oceans, the calculated mass flux of La into the atmosphere according to transfer in marine spray and terrigenous material is 1.2 and 6.0×10^4 t/yr., respectively. The content of La (range and mean) in fractionated

marine spray is 1.0 to 6.1, 2.9 mg/L [60]. Refer also to p. 101 for mass flux of La with terrigenous material entering the atmosphere.

Annual deposition of Σ light and Σ heavy RE by rain and dry deposition over the Atlantic, Indian, and world oceans, and total deposition of La, Ce, Sm, and Eu from the atmosphere over Great Britain, are given on pp. 134/5.

For a balance of RE distribution and composition in the mineral content of individual metasomatic rocks, see "Seltenerdelemente" A5, 1981, pp. 445/8.

For a schematic quantitative flux diagram (in units 10^4 gm/yr.) for solids in the earth's crust and upper mantle, see [53].

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Table of Conversion Factors

Table of Conversion Factors

Following the notation in Landolt-Börnstein [7], values which have been fixed by convention are indicated by a bold-face last digit. The conversion factor between calorie and Joule that is given here is based on the thermochemical calorie, cal_{thch}, and is defined as 4.1840 J/cal. However, for the conversion of the "Internationale Tafelkalorie", cal_{IT}, into Joule, the factor 4.1868 J/cal is to be used [1, p. 147]. For the conversion factor for the British thermal unit, the Steam Table Btu, Btu_{ST}, is used [1, p. 95].

Force	N	dyn	kp
1 N (Newton)	1	10^5	0.1019716
1 dyn	10^{-5}	1	1.019716×10^{-6}
1 kp	9.80665	9.80665×10^5	1

Pressure	Pa	bar	kp/m²	at	atm	Torr	lb/in²
1 Pa (Pascal) = 1 N/m²	1	10^{-5}	1.019716×10^{-1}	1.019716×10^{-5}	0.986923×10^{-5}	0.750062×10^{-2}	145.0378×10^{-6}
1 bar = 10^6 dyn/cm²	10^5	1	10.19716×10^3	1.019716	0.986923	750.062	14.50378
1 kp/m² = 1 mm H₂O	9.80665	0.980665×10^{-4}	1	10^{-4}	0.967841×10^{-4}	0.735559×10^{-1}	1.422335×10^{-3}
1 at = 1 kp/cm²	0.980665×10^5	0.980665	10^4	1	0.967841	735.559	14.22335
1 atm = 760 Torr	1.01325×10^5	1.01325	1.033227×10^4	1.033227	1	760	14.69595
1 Torr = 1 mm Hg	133.3224	1.333224×10^{-3}	13.59510	1.359510×10^{-3}	1.315789×10^{-3}	1	19.33678×10^{-3}
1 lb/in² = 1 psi	6.89476×10^3	68.9476×10^{-3}	703.069	70.3069×10^{-3}	68.0460×10^{-3}	51.7149	1

Work, Energy, Heat

Work, Energy, Heat	J	kWh	kcal	Btu	MeV
1 J (Joule) = 1 Ws = 1 Nm = 10^7 erg	1	2.778×10^{-7}	2.39006×10^{-4}	9.4781×10^{-4}	6.242×10^{12}
1 kWh	3.6×10^6	1	860.4	3412.14	2.247×10^{19}
1 kcal	4184.0	1.1622×10^{-3}	1	3.96566	2.6117×10^{16}
1 Btu (British thermal unit)	1055.06	2.93071×10^{-4}	0.25164	1	6.5858×10^{15}
1 MeV	1.602×10^{-13}	4.450×10^{-20}	3.8289×10^{-17}	1.51840×10^{-16}	1

1 eV $\cong$ 23.0578 kcal/mol = 96.473 kJ/mol

Power

Power	kW	PS	kp m/s	kcal/s
1 kW = 10^{10} erg/s	1	1.35962	101.972	0.239006
1 PS	0.73550	1	75	0.17579
1 kp m/s	9.80665×10^{-3}	0.01333	1	2.34384×10^{-3}
1 kcal/s	4.1840	5.6886	426.650	1

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Key to the Gmelin System
of Elements and Compounds

System Number	Symbol	Element
1		Noble Gases
2	H	Hydrogen
3	O	Oxygen
4	N	Nitrogen
5	F	Fluorine
6	**Cl**	**Chlorine**
7	Br	Bromine
8	I	Iodine
8a	At	Astatine
9	S	Sulfur
10	Se	Selenium
11	Te	Tellurium
12	Po	Polonium
13	B	Boron
14	C	Carbon
15	Si	Silicon
16	P	Phosphorus
17	As	Arsenic
18	Sb	Antimony
19	Bi	Bismuth
20	Li	Lithium
21	Na	Sodium
22	K	Potassium
23	NH_4	Ammonium
24	Rb	Rubidium
25	Cs	Caesium
25a	Fr	Francium
26	Be	Beryllium
27	Mg	Magnesium
28	Ca	Calcium
29	Sr	Strontium
30	Ba	Barium
31	Ra	Radium
32	**Zn**	**Zinc**
33	Cd	Cadmium
34	Hg	Mercury
35	Al	Aluminium
36	Ga	Gallium

System Number	Symbol	Element
37	In	Indium
38	Tl	Thallium
39	Sc, Y La—Lu	Rare Earth Elements
40	Ac	Actinium
41	Ti	Titanium
42	Zr	Zirconium
43	Hf	Hafnium
44	Th	Thorium
45	Ge	Germanium
46	Sn	Tin
47	Pb	Lead
48	V	Vanadium
49	Nb	Niobium
50	Ta	Tantalum
51	Pa	Protactinium
52	**Cr**	**Chromium**
53	Mo	Molybdenum
54	W	Tungsten
55	U	Uranium
56	Mn	Manganese
57	Ni	Nickel
58	Co	Cobalt
59	Fe	Iron
60	Cu	Copper
61	Ag	Silver
62	Au	Gold
63	Ru	Ruthenium
64	Rh	Rhodium
65	Pd	Palladium
66	Os	Osmium
67	Ir	Iridium
68	Pt	Platinum
69	Tc	Technetium[1]
70	Re	Rhenium
71	Np,Pu...	Transuranium Elements

HCl

$CrCl_2$

$ZnCrO_4$

$ZnCl_2$

Material presented under each Gmelin System Number includes all information concerning the element(s) listed for that number plus the compounds with elements of lower System Number.

For example, zinc (System Number 32) as well as all zinc compounds with elements numbered from 1 to 31 are classified under number 32.

[1] A Gmelin volume titled "Masurium" was published with this System Number in 1941.

A Periodic Table of the Elements with the Gmelin System Numbers is given on the Inside Front Cover