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Special Paper: Adakite-Like Rocks: Their Diverse Origins and Questionable Role in Metallogenesis

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Abstract

Based on a compilation of published sources, rocks referred to as adakites show the following geochemical and isotopic characteristics: SiO_2 ≥56 wt percent, Al_2O_3 ≥15 wt percent, MgO normally <3 wt percent, Mg number ≈0.5, Sr ≥400 ppm, Y ≤18 ppm, Yb ≤1.9 ppm, Ni ≥20 ppm, Cr ≥30 ppm, Sr/Y ≥20, La/Yb ≥20, and $^{87}Sr/^{86}Sr$ ≤0.7045. Rocks with such compositions have been interpreted to be the products of hybridization of felsic partial melts from subducting oceanic crust with the peridotitic mantle wedge during ascent and are not primary magmas. High Mg andesites have been interpreted to be related to adakites by partial melting of asthenospheric peridotite contaminated by slab melts. The case for these petrogenetic models for adakites and high Mg andesites is best made in the Archean, when higher mantle geotherms resulted in subducting slabs potentially reaching partial melting temperatures at shallow depths before dehydration rendered the slab infusible. In the Phanerozoic these conditions were likely only met under certain special tectonic conditions, such as subduction of young (≤25-m.y.-old) oceanic crust.

Key adakitic geochemical signatures, such as low Y and Yb concentrations and high Sr/Y and La/Yb ratios, can be generated in normal asthenosphere-derived tholeiitic to calc-alkaline arc magmas by common upper plate crustal interaction and crystal fractionation processes and do not require slab melting. An assessment of several arc volcanic suites from around the world shows that most adakite-like compositions are generated in this way and do not reflect source processes. Similarly, rare adakite-like intrusive rocks associated with some porphyry Cu deposits are the evolved products of extensive crustal-level processing of calc-alkaline basalt-andesite-dacite-rhyolite series magmas. If slab melts contribute to such magmas, their geochemical signatures would have been obliterated or rendered ambiguous by subsequent extensive open-system processes. In Archean terranes, where adakitic and high Al tonalite-trondhjemite-granodiorite (TTG) magma series rocks are more common, porphyry Cu deposits are rare and, where found, are associated with normal calc-alkaline suites rather than adakites. The two different magma series are compositionally distinct in terms of several major and trace element parameters.

Common upper plate magmatic processes such as melting-assimilation-storage-homogenization (MASH) and assimilation-fractional-crystallization (AFC) affecting normal arc magmas can be demonstrated to explain the distinctive compositions of most adakite-like arc rocks, including high Mg andesites and especially those rare examples associated with porphyry Cu deposits. In contrast, slab melting can in most cases neither be proved nor disproved and is therefore unsatisfactory as a unique factor in porphyry Cu genesis.

Introduction

MAGMAS produced by melting of subducted oceanic crust, commonly referred to as adakites, have recently been proposed by several authors to be an important source for metals in giant porphyry Cu deposits (e.g., Thiéblemont et al., 1997; Sajona and Maury, 1998; Oyarzun et al., 2001). In this paper we first explore the definition of, and various petrogenetic models for producing, adakitic magmas both in the Phanerozoic and Archean. We then examine several arc volcanic and intrusive suites from around the world that include adakite-like rock compositions and show that in many cases these compositions can be explained more simply by crustal-level fractionation and contamination processes affecting mantle wedge-derived magmas, than by slab melting. We similarly show that a number of global porphyry suites that include rocks with adakite-like compositions can also readily be explained by such processes. In the Archean, when adakitic magmatism was more widespread than in the Phanerozoic, we show that not only are porphyry Cu deposits rare (whereas they might be expected to be more abundant if

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adakitic magmas were key to their generation), but also that those which do occur are not specifically associated with adakite-like rocks.

We conclude from this assessment that, although slab melting may well occur under restricted circumstances in the Phanerozoic, the vast majority of arc rocks that have been termed adakitic are probably simply evolved magmas that have undergone crystal fractionation and crustal contamination processes. This also applies to adakite-like rocks associated with some porphyry Cu deposits, whose crustally evolved compositions are more likely to be key to their metal enrichments than a unique magma input from slab melting.

What are adakites?

The term "adakite" was first coined by Defant and Drummond (1990), following the work of Kay (1978), to describe an unusual type of magnesian andesite found near Adak Island in the Aleutians. As originally described by Kay (1978), these rocks were characterized by high La/Yb ratios (i.e., high ratios of light rare earth elements to heavy rare earth elements; LREE/HREE), high Sr concentrations (~1,800 ppm), and relatively high Mg number, Cr, and Ni concentrations compared with normal andesites, but nonradiogenic Pb and Sr isotope compositions. Kay (1978) suggested that these chemical characteristics were consistent with an origin as partial melts of subducted, garnetiferous (i.e., eclogitized) oceanic crust, which had then reacted and partially equilibrated with the peridotitic asthenospheric mantle wedge during ascent. The intermediate bulk compositions roughly matched those of experimental partial melts of hydrated basalt, as later confirmed by Rapp et al. (1991), Sen and Dunn (1994), and Rapp and Watson (1995); the HREE depletions (high La/Yb ratios) indicated residual garnet in the source (which preferentially partitions Y and HREE relative to LREE); the high Sr concentrations reflected absence of residual plagioclase in the source (replaced by garnet and jadeitic pyroxene at high pressure, which do not preferentially partition Sr); and the nonradiogenic Pb and Sr isotope compositions precluded continental crustal contamination effects. Only the high Mg number characteristics and high Cr and Ni contents did not simply fit a slab-melting model, necessitating the additional step of variable degrees of hybridization of primary dacitic slab melts with the overlying mantle wedge to form adakites. Rocks with these compositional characteristics from Baja California have also been termed bajaites by Saunders et al. (1987), who similarly proposed a slab-melting origin.

Kay (1978) noted that the magnesian andesites of Adak Island were geochemically unusual, and that this petrogenetic model could not be generally applied to island-arc magmatism. Instead, normal tholeiitic to calc alkaline arc magmas are thought to be derived from partial melting of hydrated peridotite in the asthenospheric mantle wedge above a dehydrating subducting slab (e.g., Ringwood, 1977; Gill, 1981; Plank and Langmuir, 1988; Hawkesworth et al., 1993; Pearce and Peate, 1995; Schmidt and Poli, 1998; Poli and Schmidt, 2002; Gaetani and Grove, 2003).

Defant and Drummond (1990, 1993) and Drummond and Defant (1990) later refined Kay's (1978) model and proposed geochemical ranges for adakitic magmas to distinguish them from normal island-arc basalt-andesite-dacite-rhyolite suites (Table 1). In particular, Defant and Drummond (1990, 1993) used a plot of Sr/Y versus Y to highlight the mutually exclusive roles of garnet fractionation in adakites (yielding high Sr/Y, low Y magmas) versus plagioclase fractionation in normal tholeiitic to calc-alkaline rocks (yielding low Sr/Y, normal to high Y magmas; Fig. 1a). Following Jahn et al. (1981) and Martin (1986), Drummond and Defant (1990) also used a plot of La/Yb versus Yb (Fig. 1b) to emphasize the strong HREE depletion relative to LREE in adakitic lavas compared to normal arc rocks. These two diagrams are now widely used as diagnostic criteria for the identification of adakites and, by extension, for an origin via slab melting. We argue below that these criteria are nonunique and are therefore not diagnostic of slab melting.

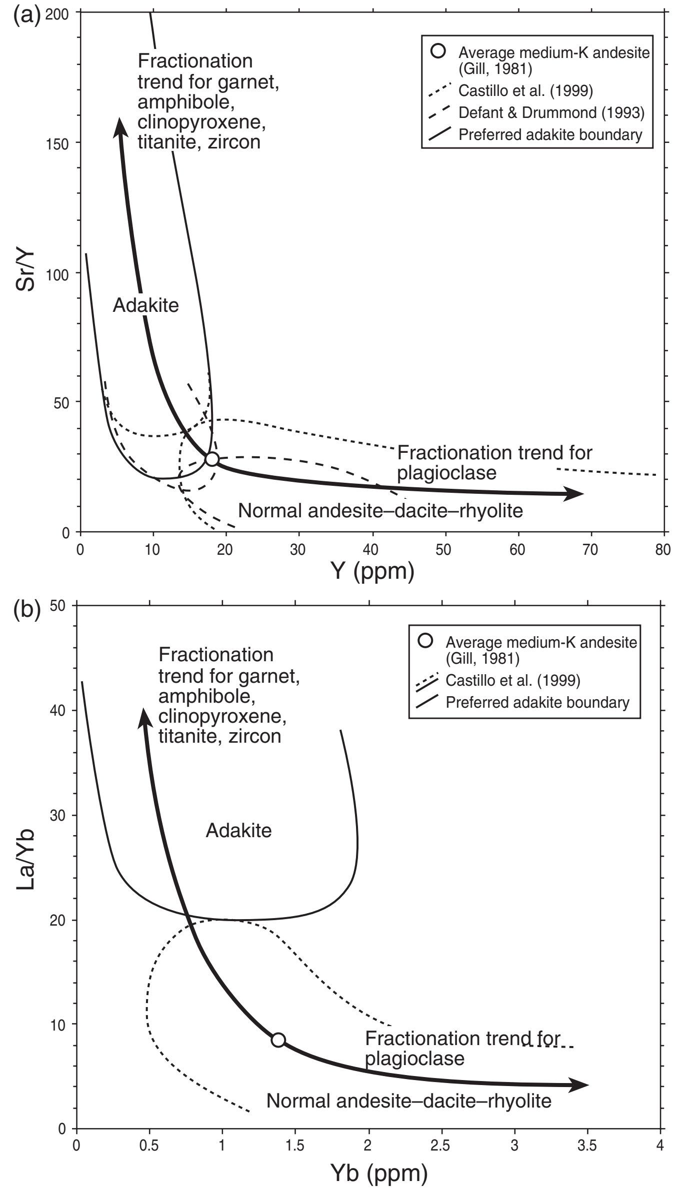

FIG. 1. Plots of (a) Sr/Y vs. Y (Defant and Drummond, 1993), and (b) La/Yb vs. Yb (Castillo et al., 1999), showing fields for adakite and island-arc andesite-dacite-rhyolite lavas. Typical differentiation paths resulting from fractionation of various minerals shown schematically (modified after Castillo et al., 1999).

TABLE 1. Temporal Evolution of the Definition of Adakites

Parameter	Defant and Drummond (1990)	Drummond and Defant (1990)	Defant and Drummond (1993)	Drummond et al. (1996)	Castillo et al. (1999)	Martin (1999)	Defant and Kepezhinskas (2001)	Martin et al. (2005)	Restrictive range	Permissive range	Range used in this paper
SiO_2	≥56 wt %					>56 wt %	>56 wt %	>56 wt %	>56 wt %	≥56 wt %	≥56 wt %
Al_2O_3	≥15 wt %		>15 wt % at 70% SiO_2	>15 wt % at 70% SiO_2			>15 wt %		>15 wt % at 70% SiO_2	≥15 wt %	≥15 wt %
MgO	Usually <3 wt %; rarely >6 wt %								<3 wt %	≤6 wt %, rarely higher	Normally <3 wt %
Mg no.[1]						~0.51		~0.51	~0.5		~0.5
Na_2O						3.5–7.5 wt %	>3.5 wt %	3.5–7.5 wt %	3.5–7.5 wt %	>3.5 wt %	≥3.5 wt %
K_2O				≤3 wt %					≤3 wt %		≤3 wt %
K_2O/Na_2O						~0.42		~0.42	~0.42		~0.42
Rb				<65 ppm					<65 ppm		≤65 ppm
Sr	≥400 ppm					300–2000 ppm	>400 ppm		>400 ppm	300–2000 ppm	≥400 ppm
Y	≤18 ppm		≤18 ppm		<15–18 ppm	≤18 ppm	≤18 ppm	≤18 ppm	<15–18 ppm	≤18 ppm	≤18 ppm
Yb	≤1.9 ppm		≤1.9 ppm		<1–1.5 ppm	≤1.8 ppm	≤1.9 ppm	≤1.8 ppm	<1–1.5 ppm	≤1.9 ppm	≤1.9 ppm
Ni						20–40 ppm		24 ppm	20–40 ppm		≥20 ppm
Cr						30–50 ppm		36 ppm	30–50 ppm		≥30 ppm
Sr/Y			≥20		>40		≥40		>40	≥20	≥20
La/Yb		≥~8			>20		≥20	≥~15	≥~8	≥20	≥20
$^{87}Sr/^{86}Sr$	<0.7040			<0.7045					<0.7040	<0.7045	≤0.7045
Age of subducted oceanic crust	≤25 m.y.			≤25 m.y.		≤20 m.y.			≤20 m.y.	≤25 m.y.	≤25 m.y.

[1] Mg no. = Mg/(Mg + Fe), where Mg and Fe are atomic proportions

Table 1 compares various chemical criteria used to define adakites by several authors since Defant and Drummond's initial paper in 1990 and shows that there has been some evolution and broadening of these ranges. This has led to confusion in the literature as to what exactly constitutes an adakite, especially in terms of the commonly used Sr/Y and La/Yb ratios, for which there is significant disagreement (e.g., ≥20 or ≥40 for Sr/Y; ≥~8 or ≥20 for La/Yb). For the purposes of comparison of data in this paper we have selected in the final column of Table 1 a set of criteria that errs toward the permissive end of the range for most parameters. However, it is clear that, like many other rock types, adakites encompass a range of magma compositions that broadly overlaps with other more common rock types. Thus, the usefulness of the term adakite, particularly when imbued with petrogenetic significance, is immediately called into question. Where possible in this paper, we therefore refer to rocks that fall within these compositional ranges as adakite-like.

Several other magmatic rock types of basalt-andesite-dacite-rhyolite composition share the high La/Yb, low Y, and elevated MgO, Cr, and Ni features of adakitic rocks, including high Mg andesites and Nb-enriched basalts found in several Cenozoic arcs in association with adakite-like rocks (e.g., Kepezhinskas et al., 1996; Sajona et al., 1996) and some Archean tonalites and trondhjemites. Rare flows and intrusions of adakitic composition, associated with high Mg andesites, Nb-enriched basalts, and normal tholeiitic to calc-alkaline arc basalts, have been described from Archean greenstone belts (Hollings and Kerrich, 2000; Polat and Kerrich, 2001; Cousens et al., 2002; Svetov et al., 2004). Late- to post-tectonic, batholithic, high Al tonalite intrusions are prevalent in Archean terranes (Drummond et al., 1996; Condie, 2005; Martin et al., 2005), and rare, post-tectonic intrusive bodies in Archean greenstone belts, variously termed sanukitoids or Mg diorites, show similar trace element compositions (Shirey and Hanson, 1986; Smithies and Champion, 2000).

Prior to the term adakite being coined, Na- and Al-rich magmatic rocks of Archean and younger age were described as belonging to the tonalite-trondhjemite-granodiorite (TTG) magma series, and intermediate compositions were known as low K dacites. Unlike the calc-alkaline basalt-andesite-dacite-rhyolite magma series, the TTG series does not include andesitic compositions (Barker, 1979; Gill and Stork, 1979). High Al tonalites and trondhjemites are compositionally similar to adakites in possessing high La and Sr but low Yb and Y concentrations (high La/Yb and Sr/Y ratios). However, high Al tonalites and trondhjemites, as well as adakites, are more sodic and less potassic than most calc-alkaline intermediate magmas and accordingly plot in separate fields or on different trends compared with calc-alkaline rocks on K-Na-Ca or normative Ab-An-Or ternary diagrams, or the Q' versus ANOR normative diagram (Q' = Q/(Q + Or + Ab + An), ANOR = An*100/(An + Or), where minerals are CIPW normative values; Barker and Arth, 1976; Barker, 1979; Streckeisen and Le Maitre, 1979; Martin, 1986; Drummond et al., 1996; Polat and Kerrich, 2001; Condie, 2005; Martin et al., 2005).

The first part of this paper therefore examines the geochemical uniqueness of adakites, addresses the association of adakites, high Mg andesites, and Nb-enriched basalts, and evaluates the suggested connection to slab melting (i.e., the relationship: slab melting + mantle hybridization = adakite). The greater abundance of adakitic rocks and compositionally similar rock types in the Archean is also discussed.

We then show (as has been demonstrated previously by numerous authors referenced below) how melting-assimilation-storage-homogenization (MASH; Hildreth and Moorbath, 1988) and/or assimilation-fractional crystallization (AFC; DePaolo, 1981) processes that control the crustal evolution of normal tholeiitic to calc-alkaline arc magmas can result in similarities to some of the geochemical characteristics of adakites, such as high Sr/Y and La/Yb ratios. Defant and Drummond (1990) and Drummond et al. (1996) originally studied adakitic rocks from intraoceanic arcs specifically to avoid these compositional complexities that arise from continental crustal interaction.

Adakite-like rocks in arc metallogeny

The term adakite was virtually unknown in the economic geology literature prior to the late 1990s. The first explicit suggestion that these rock types might be related to mineralization was made by Thiéblemont et al. (1997) based on studies of porphyry and epithermal ore deposits in the Philippines. Although Thiéblemont et al. (1997) referred only to basalt melting for the origin of these rocks, Sajona and Maury (1998) specifically called for melting of subducted young oceanic crust. Oyarzun et al. (2001) later suggested that adakites were uniquely responsible for the formation of giant porphyry deposits in northern Chile because of their inferred high sulfur and water contents and high oxidation states (argued to be derived directly from the subducting slab by partial melting; see also Mungall, 2002; Borisova et al., 2006). Since that time, claims of adakite occurrences have been made in an increasing number of porphyry districts around the world, including Ecuador, Mexico, Tibet, and southern and eastern China. Many of these claims are based on a fit to only some of the criteria listed in Table 1, most commonly high Sr/Y ratios; other parameters, such as broader magma associations, major element compositions, and other geochemical and isotopic indices, are either not assessed or are ignored.

Despite the recent interest in adakites, a relationship between porphyry deposits and magmas with fractionated REE patterns and low Y concentrations has been known for some time. Baldwin and Pearce (1982) and López (1982) independently noted that "productive intrusions" associated with porphyry deposits in northern Chile had large negative anomalies for Y, Mn, Th, and HREE relative to barren plutons, and suggested that these characteristics might be due to partial melting processes or fractional crystallization of hornblende, titanite, and/or garnet from hydrous magmas. Maksaev and Zentilli (1994), Cornejo et al. (1997), Ossandón and Zentilli (1997), Lang and Titley (1998), Kay et al. (1999), Kay and Mpodozis (2001), and Richards et al. (2001) similarly noted HREE depletions in porphyry-related intrusions from Arizona, northern Chile, and northern Argentina, and attributed these effects to amphibole and/or deep-crustal garnet fractionation. Thus, an alternative model for high Sr/Y, high La/Yb porphyry-related magmas based on common and expected magmatic processes (fractional crystallization of observed phenocryst phases coupled with deep crustal interaction) has existed for some time but was not considered by

Oyarzun et al. (2001; for a discussion of Oyarzun et al., 2001, see Rabbia et al., 2002, and Richards, 2002, and reply by Oyarzun et al., 2002).

The final part of this paper therefore examines the relationship between high Sr/Y and La/Yb magmas and porphyry deposits and critically evaluates the proposed sequence of slab melting plus mantle hybridization to produce adakites, which then produce giant porphyry deposits, for both the Phanerozoic and Archean geologic records.

Constraints on the Origin of Subduction Zone Magmas

Slab dehydration and partial melting in subduction zones

In the first decades of the plate tectonic revolution, it was widely assumed that arc magmatism was caused by melting of the hydrated subducting oceanic crust, and many first-year geology text books still depict this process in simplistic arc cross sections. However, even as early as 1962, Coats proposed that the slab does not melt but instead dehydrates, adding water and "hyperfusible materials" (Na, Si, Al) derived from underthrust basaltic volcanic and sedimentary rocks to the overlying peridotitic mantle, which subsequently melts (see also Perfit et al., 1980).

Nevertheless, the idea that subducted oceanic crust undergoes melting to form arc magmas has persisted, not least because the expected melts would be relatively felsic, providing an explanation for the intermediate to felsic nature of many arc volcanic rocks. Experimental work by Rapp et al. (1991) and Rapp and Watson (1995) showed that silicic melts could indeed be produced by low-degree melting (<10%) of amphibolite at mantle temperatures and pressures (1,025°C and 0.8–1.6 GPa), and that in the presence of garnet (garnet amphibolite or eclogite), these melts would be HREE depleted. However, as shown most recently by Martin et al. (2005), these experimental melts are characterized by lower MgO contents than reported for adakites, necessitating the additional step of mantle hybridization of slab melts in models of adakite petrogenesis.

On the other hand, increasingly refined geophysical and petrological models of subduction zones show that, under normal circumstances, the subducting oceanic crust does not reach temperatures sufficient for melting before prograde metamorphic dehydration reactions render the slab infusible (e.g., Ringwood, 1977; Mysen, 1982; Davies and Stevenson, 1992; Peacock et al., 1994; Peacock, 1996; Schmidt and Poli, 1998; Poli and Schmidt, 2002; Gaetani and Grove, 2003; Arcay et al., 2007). Figure 2 shows a thermal model for a typical subduction zone, in which temperatures within the downgoing slab do not exceed 800°C to depths of at least 100 km. Poli and Schmidt (2002) noted that amphibole, which is thought to be a major host for water in the subducting oceanic crust, will have completely broken down by 800°C at 70-km depth, to leave a largely anhydrous assemblage dominated by olivine, orthopyroxene, clinopyroxene, and garnet (i.e., blueschist to eclogite facies transition at ~3 GPa; Ringwood, 1977; Peacock, 1993, 1996). Other hydrous minerals such as talc, chlorite, serpentine, lawsonite, and zoisite also dehydrate over a broad pressure-temperature range during subduction, and lawsonite and zoisite may persist to depths >200 km. Nevertheless, Forneris and Holloway (2003) showed experimentally that oceanic crust would be almost completely dehydrated by 90- to 110-km depth.

The near globally uniform depth to the Benioff zone beneath volcanic arcs of 100 to 110 km led to the early suggestion of a relationship between voluminous dehydration of the slab at this depth and partial melting in the overlying mantle wedge (e.g., Ringwood, 1977; Wyllie, 1978). Specifically, it is now suggested that convective corner-flow circulation of serpentinized peridotite (hydrated by slab-derived fluids) into higher temperature regions (~1,300°C) of the asthenospheric mantle wedge at depths ≤100 km results in partial melting to form basaltic magmas, the primary melts of normal subduction zones (Tatsumi, 1986, 1989; Peacock, 1993; Schmidt and Poli, 1998; Hattori and Guillot, 2003). Bourdon et al. (2003) and Grove et al. (2006) alternatively suggest that slab-derived fluids directly flux the hotter central part of the mantle wedge, where water-saturated melting of peridotite begins at temperatures >800°C at 3.2 GPa. Grove et al. (2006) confirmed experimental observations of Wyllie et al. (1989) that garnet (along with chlorite, ilmenite, olivine, clinopyroxene, and orthopyroxene) will be on the solidus during hydrous partial melting of peridotite at pressures >2.4 GPa, which casts further doubt on the unique identification of the subducting eclogitized slab as the origin of residual garnet trace element signatures (Pearce and Peate, 1995).

Because even the most primitive magmas erupted at the surface in island arcs have undergone some degree of fractionation and interaction with crustal rocks during ascent (Leeman, 1983; Thirlwall et al., 1996), the composition of primary subduction zone melts has not been determined directly. However, there is general agreement that primary melts from the peridotitic asthenospheric mantle wedge above subduction zones are highly magnesian basalts (≥10 wt % MgO) or even picrites (≥18 wt % MgO; DeBari and Sleep, 1991; Eggins, 1993; Thirlwall et al., 1996). These basalts are also significantly more hydrous and oxidized than normal midocean ridge basalts (MORB), with estimates varying from ~1 to as high as 16 wt percent H_2O, and up to FMQ + 3 (FMQ + 3 indicates an oxygen fugacity (f_{O_2}) 3 log units above that of the fayalite-magnetite-quartz buffer assemblage) in primary melts (Ballhaus, 1993; Brandon and Draper, 1996; Sobolev and Chaussidon, 1996; Parkinson and Arculus, 1999; Grove et al., 2003; Fischer and Marty, 2005). Arc basalts are also uniquely enriched in a suite of fluid mobile elements, including large ion lithophile elements (LILE: Rb, K, Cs, Ba, Sr), Li, B, Pb, As, Sb, and S, but depleted or not enriched in high field strength elements (HFSE: Nb, Ta, Zr, Hf), Ti, and P relative to MORB or mantle compositions. These chemical signatures are widely attributed to metasomatism of the mantle wedge (which has the depleted character of MORB-source peridotite) by aqueous fluids released from the subducting slab (e.g., Davidson, 1996; Noll et al., 1996; de Hoog et al., 2001). Under these conditions, HFSE are insoluble and are retained in residual titaniferous oxide or silicate phases either in the slab or mantle wedge (e.g., Brenan et al., 1994; Audétat and Keppler, 2005).

Partial melting of the subducted oceanic crust

As noted above, the temperature of the subducted oceanic lithosphere normally does not rise high enough for melting of

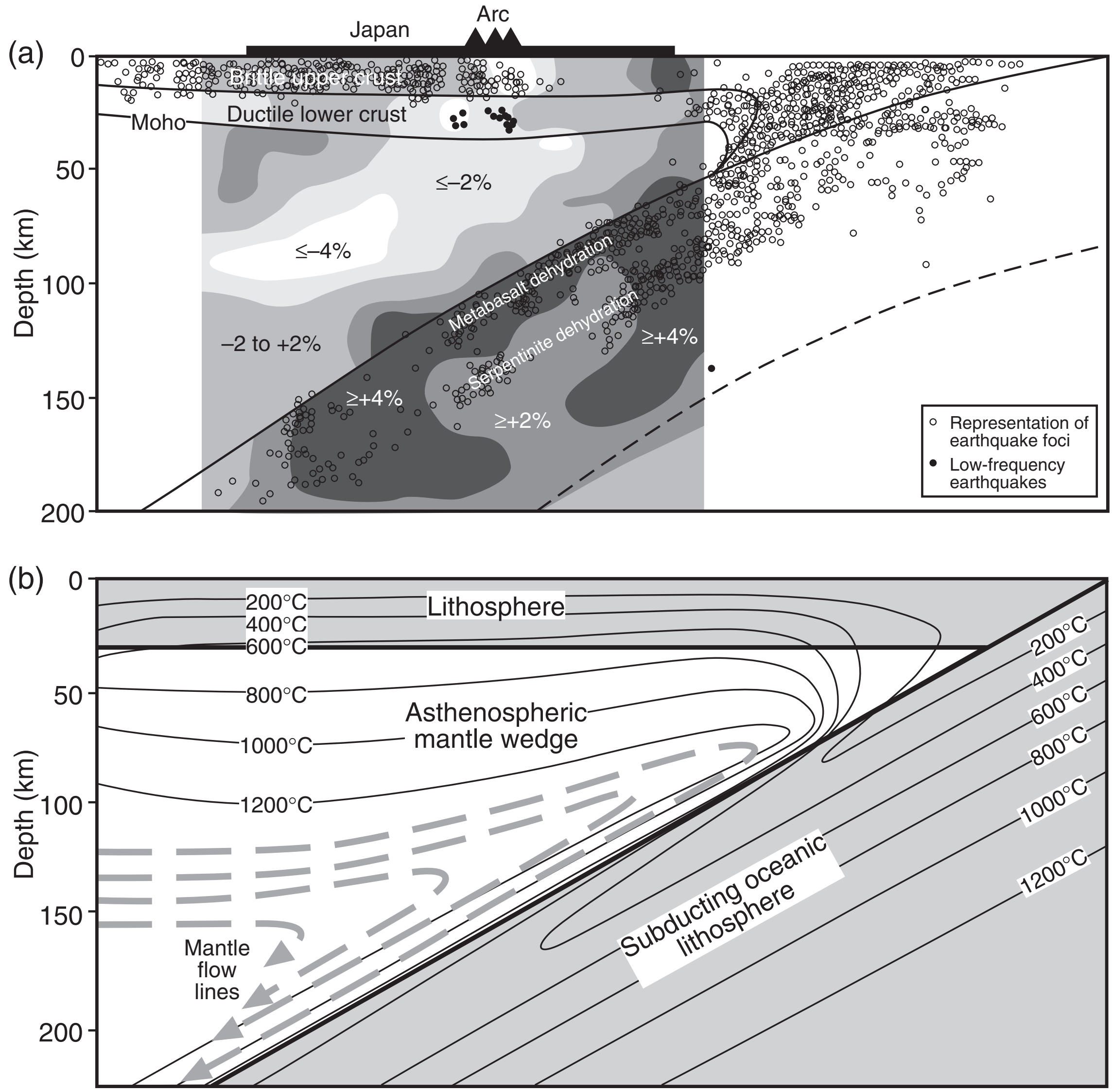

FIG. 2. (a). Seismic P-wave tomographic image, and (b) thermal numerical simulation sections across a typical arc. Tomographic section modified from Zhao et al. (1992) and Zhang et al. (2004). Thermal model from Furukawa (1993).

the basaltic crust before dehydration reactions render it infusible. However, the lower melting temperature of subducted pelagic sediments means that small amounts of melt from this source may contribute to the total flux of components from the slab in many subduction zone environments (e.g., Thirlwall et al., 1996; Plank, 2005; Kimura and Yoshida, 2006). Evidence for varying amounts of sedimentary input to arc magmas has been recognized primarily from isotopic signatures, especially of Pb, Sr, and O (e.g., Magaritz et al., 1978; McNutt et al., 1979; Hawkesworth, 1982; Barreiro, 1984; McMillan et al., 1993; Macfarlane, 1999), and Th/LREE ratios (Hawkesworth et al., 1997; Plank, 2005). Volumetrically, however, the amount of material contributed by sediments is likely to be small (e.g., <2–4%; Hawkesworth et al., 1994) relative to the fluid-transported flux from dehydration of the underlying metabasaltic oceanic crust (Poli and Schmidt, 2002).

Melting of hydrated basaltic oceanic crust can conceptually occur in situations where the slab is subducted at higher than normal temperatures, as in the case of subduction of young oceanic crust (≤25 m.y. old; Defant and Drummond, 1990), or in situations where the slab is abnormally heated at shallow depths, such as during shallow or stalled subduction (Peacock et al., 1994; Gutscher et al., 2000), slab detachment following arc collision (Gao et al., 2007; König et al., 2007), highly oblique subduction (Yogodzinski et al., 1995), ridge subduction (Kay et al., 1993; Guivel et al., 2003), or in slab windows where hot asthenosphere comes in direct contact with the plate edge (Yogodzinski et al., 2001; Thorkelson and Breitsprecher, 2005).

As noted above, partial melts of metabasalt will have intermediate to felsic compositions and, if generated at depths below the blueschist-eclogite transition where garnet is stable, will have characteristic HREE- and Y-depleted, Sr-enriched signatures. With the possible exception of some felsic glasses found in mantle xenoliths from suprasubduction zone settings (Schiano et al., 1995; Kilian and Stern, 2002), primary magmas with the expected composition of partial melts of hydrated basalt have not thus far been discovered, for the same reasons that unmodified primary melts from hydrated peridotite melting have not been observed at surface. Instead, adakitic slab melts are identified as evolved intermediate composition magmas that have hybridized with mantle peridotite during transit through the sub-arc mantle wedge en route to the surface (Kay, 1978; Sen and Dunn, 1994; Yogodzinski et al., 1995; Drummond et al., 1996; Kilian and Stern, 2002). Thus, adakites as defined in this sense are at least one step away from being primary slab melts.

Rare high Mg andesites and Nb-enriched basalts occur with adakite-like rocks in the Cenozoic arcs of Central America, the Northern Andes, Japan, and the Philippines (Defant et al., 1992; Sajona et al., 1996; Bourdon et al., 2002; Kamei et al., 2004). It has been suggested that this suite of rare volcanic rocks is related by the following scheme: adakites are slab melts that have undergone partial hybridization with the mantle wedge, high Mg andesites are more extensively hybridized, and Nb-enriched basalts form by melting of the residue of hybridization as it is dragged to greater depths in the mantle wedge by corner-flow convection (Kelemen, 1995; Kepezhinskas et al., 1996; Sajona et al., 1996; Tatsumi, 2006). Martin et al. (2005) described the same association, but referred to hybridized slab melts as high silica adakites, and partial melts of asthenosphere modified by reaction with these slab melts as low silica adakites. However, in a detailed study of high Mg andesites from Mount Shasta, California, Streck et al. (2007) concluded that these distinctive rocks were formed by mixing of normal arc basalts and evolved dacites and did not represent primitive mantle-derived magmas.

Fluid-melt miscibility?

There is increasing evidence for complete miscibility in the silicate melt-aqueous fluid system over a wide range of upper mantle pressure-temperature conditions, but at the shallowest mantle levels such fluids would separate into hydrous melts and solute-rich aqueous fluids (Bureau and Keppler, 1999; Audétat and Keppler, 2004; Manning, 2004; Kawamoto, 2006; Portnyagin et al., 2007). The exact pressure-temperature conditions for miscibility in subduction zone settings are poorly constrained and will vary with bulk composition, but the abovementioned authors suggest that it may occur near 100 km, the depth to the Benioff zone beneath volcanic arcs. Bureau and Keppler (1999) found that above this depth, amphibole dehydration would yield low-viscosity aqueous fluids, which could readily metasomatize the overlying mantle wedge and lead to arc magmatism. In contrast, at greater depths, more viscous silicate-rich supercritical fluids would likely remain trapped near their source. Audétat and Keppler (2004), however, came to exactly opposite conclusions and suggested that silicate-rich fluids in fact had low viscosities and good wetting properties and could therefore efficiently migrate into the mantle wedge, whereas silicate-poor aqueous fluids would remain trapped due to their higher wetting angles.

If supercritical fluids do indeed exist at shallow levels in subduction zones, then the distinction between slab dehydration and slab melting disappears. However, Kessel et al. (2005) reported that supercritical fluids generated at 6 GPa (~180-km depth) contained high concentrations of most trace elements and would not, therefore, impart the distinct aqueous-phase geochemical signatures characteristic of subduction zone magmas (e.g., high U/Th, Rb/Th); in fact, these supercritical fluids would more closely resemble the compositions of adakites, with high LREE/HREE and Sr/Y. Kessel et al. (2005) concluded that the distinctive fluid signatures characteristic of most arc magmas must therefore be generated by subcritical aqueous fluid metasomatism of the mantle wedge at depths less than 180 km.

Neoarchean magmatism and adakitic rocks

The preceding discussion has largely focused on Phanerozoic subduction zone magmas, where rocks with adakite-like compositions are relatively rare. In the Archean, however, volcanic and plutonic rocks with adakitic geochemical signatures were much more common. This observation has been explained by higher mantle temperatures, smaller, hotter, more numerous plates and ridge-convergent margin interactions, and thicker oceanic crust, leading to more widespread occurrence of oceanic crust melting during subduction (Polat and Kerrich, 2006, and references therein).

Neoarchean cratons, including the Superior and Slave (Canada), Yilgarn (Australia), and Dharwar (India) cratons, are particularly well exposed and extensively studied, as are their mineral deposits (e.g., Thurston, 1991; Poulsen et al., 1992; Ayer et al., 2002; Barley et al., 2005; Naqvi, 2005). There are also high-quality geochemical databases for diverse lithologic units in many terranes of these cratons. Consequently, we summarize the characteristics of magmatism, specifically adakitic, on these cratons to set the stage for evaluating the role of adakites in Archean mineral deposits (Table 2).

It is unwarranted to assign geodynamic settings of Precambrian magmatic units solely on the basis of geochemical comparisons with more recent counterparts. Accordingly, many workers have adopted the approach of spatially, stratigraphically, and temporally related lithological-geochemical associations. For example, interlayered komatiites and tholeiitic basalts with deep water shales and cherts, present in many Neoarchean greenstone belts, likely represent ocean plateaus erupted from mantle plumes (Campbell et al., 1989; Jackson and Fyon, 1991; Kerrich et al., 1999), although some komatiites were erupted onto rifted continental margins (Hollings et al., 1999). Bimodal basalt-dacite volcanic-intrusive sequences, with first cycle siliciclastic sediments plotting on mixing lines between the magmatic end members, are considered to have formed in intraoceanic arcs paired to trench turbidites (Taylor and McLennan, 1985).

The association of flows having boninitic compositions with low K, through medium K, to high K series basalts having arc-like compositions (synonymous with primitive tholeiitic to evolved calc-alkaline arc basalts: MacDonald et al., 2000), can reasonably be interpreted in terms of a convergent margin setting. Examples of this association have been reported from the 2.7 Ga Abitibi terrane of the Superior province (Kerrich et al., 1998; Wyman et al., 1999a, b) and the low to high K basalt association from several greenstone terranes of the Uchi subprovince (Hollings and Kerrich, 2006). In summary, these Neoarchean greenstone terranes have magmatic associations

TABLE 2. Characteristics of Granitoid Intrusions of the Abitibi and Pontiac Terranes and Mineral Deposits Where Present

Geodynamic stage	Magma series[1]	Intrusions dimensions	Composition (ppm)	Age (Ma)	$\delta^{18}O$ whole rock (‰)	Au (ppb) Cu (ppm)	Emplacement depth (km)	Petrogenesis	Mineral deposit(s)	Alteration	Comments
Abitibi											
Synvolcanic	low Al TTG	Lac Flavrian Bourlamaque subvolcanic plutons and sills	Sr = 131, Y = 55 Sr/Y = 2.4 Yb = 3.7 La/Yb = 4.7	2700	5.6 ± 0.5	1.8 ± 1.1 25 ± 29	~ 1	Wedge dehydration-slab melting; hydrous basalts in a convergent margin and fractionation products	VHMS of Rouyn-Noranda	+Fe, Mg	Supergiant (Kidd Creek) to ~1 Mt deposits formed on rifted arc or back-arc lithosphere
Syntectonic	high A1 TGGM	Round Lake, Lac Abitibi batholiths	Sr = 586, Y = 4 Sr/Y = 146 Yb = 0.38 La/Yb = 44	2690–2685	7.2 ± 0.5	0.42 ± 0.76 5.8 ± 3.9	~2 ~5	Slab melting and hybridization with mantle wedge	Stringer zones of Cu, Pb, Zn, Mo	Potassic	Rare uneconomic showings, likely magmatic-hydrothermal
Late- to post-tectonic	SMG	Watabeag batholith, Garrison stock	Sr = 998, Y = 6 Sr/Y = 166 Yb = 0.57 La/Yb = 42	2681–2676	8.2 ± 0.3	0.05 3.5 ± 1.2	~1	Slab melting and hybridization with mantle wedge	Stringer zones of Cu, Pb, Zn, Mo	Potassic	Rare uneconomic showings, likely magmatic-hydrothermal
Post-tectonic	SS	Matachewan batholith, Otto stock	Sr = 882, Y =10 Sr/Y = 88 Yb = 0.73 La/Yb = 48	2680–2675	8.8 ± 0.7	1.7 ± 4.0 25 ± 23	~1	Hydrous fluxing of depleted mantle wedge with hybridization	P, Ba, Cu, Zn	Potassic	Small showings
Pontiac											
Syn- to late-tectonic	MMGS	Lac Romigny, Lac Frichette, part of Lacorne	Sr = 1295, Y = 11 Sr/Y = 118 Yb = 0.84 La/Yb = 40	2685–2670	6.8 ± 0.7	1.2 ± 1.6 28 ± 41	~3–~10	Similar to Abitibi TGGM but greater wedge hybridization			
Post-tectonic	GMG	Throughout Pontiac, and Lacorne block	Sr = 73, Y = 9 Sr/Y = 8, Yb = 1.8, La/Yb = 9	~2645	8.2 ± 0.6	0.12 ± 0.11 2.1 ± 0.10	~3–~5	Intracrustal melts of metasedimentary sequence	Mo	Potassic	Pegmatitic Mo, Li, Ba with fluorite

Modified from Feng and Kerrich (1992) and Feng et al. (1993)

[1] Abbreviations: GMG = garnet-muscovite granite, MMGS = monzodiorite-monzonite-granite-syenite, SMG = syenite-monzonite-granite, SS = alkali feldspar syenite-quartz syenite, TGGM = tonalite–trondhjemite-granite-quartz monzonite, TTG = tonalite-trondhjemite-granodiorite

such as komatiite-basalt and bimodal basalt-dacite that are rare or absent in the Phanerozoic, as well as the boninite-low K basalt, and adakite-high Mg andesite-Nb-enriched basalt associations that are present in Cenozoic arcs (for a review see Polat and Kerrich, 2006).

Igneous units in Neoarchean greenstone terranes that meet many of the compositional criteria for adakite-like rocks occur in three magmatic associations:

1. Volumetrically small intrusive bodies or flows of adakitic composition that are synvolcanic. These rocks are of the adakite-high Mg andesite-Nb-enriched basalt association, with low to high K arc basalts and turbidites. They have been recorded from the Abitibi, Wawa, and Uchi subprovinces of the Superior province, and the eastern Dharwar craton, and appear to be more common than in Cenozoic arcs (Kerrich and Fryer, 1979; Hollings and Kerrich, 2000; Wyman et al., 2000; Polat and Kerrich, 2001; Naqvi et al., 2006; Manikyamba et al., 2007).
2. Syn- to late-tectonic batholiths of the high Al TTG magma series, such as the Lac Abitibi and Round Lake batholiths of the Abitibi greenstone belt (Feng and Kerrich, 1992).
3. Post-tectonic intrusive units variously termed sanukitoids or Mg diorites. These have been described from the western Superior province and Western Australia (Shirey and Hanson, 1986; Smithies and Champion, 2000).

The syn-arc adakite magmatic association is most consistent with slab melting and mantle wedge hybridization, because the associated basalts have all the geochemical characteristics of Cenozoic primitive interoceanic arc basalts such as on South Sandwich island (Hawkesworth et al., 1993; Hollings and Kerrich, 2006).

There is diversity of opinion on the source of Archean and younger TTG. In one model, TTG reflect melting of thick basaltic plateaus formed above mantle plumes (Condie, 2005; Bédard, 2006, and references therein). Alternatively, melting of thick basaltic crust has been proposed as a possible mechanism (Whalen et al., 2002). The original models involved slab melting at a convergent margin where it was understood that the subducted crust could be plateau or arc crust as well as MORB-like basalt (Tarney and Jones, 1994; Drummond et al., 1996; Martin et al., 2005, and references therein). Indirect evidence in support of slab melting for many high Al TTG includes: (1) the continuum of mafic element systematics between boninites (mantle wedge melts) and TTG (Drummond et al., 1996); (2) variable but subchondritic Nb/Ta ratios, most likely sourced in subcreted arc basalt (Rapp et al., 2003); (3) secular variation of MgO and Ni contents (Martin et al., 2005); and (4) the relatively low geothermal gradients (~20°C/km) of Archean subduction zones compared to plume environments, albeit higher than Phanerozoic subduction zones (Moyen and Stevens, 2006).

Tonalites of the TTG series extend to greater Th and LREE concentrations than syn-arc adakitic rocks. It is possible that these adakites are melts of subducted incompatible element-depleted MORB-like crust (Polat and Kerrich, 2002), whereas tonalites represent melting of incompatible element-undepleted ocean plateau crust (Tarney and Jones, 1994) or enriched arc crust (Rapp et al., 2003), in keeping with their voluminous character. According to Martin and Moyen (2002), there is a secular trend of increasing MgO and Ni contents in tonalites from 4.0 to 2.0 Ga; they interpret this trend to reflect a progressive decrease in the geothermal gradient and increase in depth of slab melting, such that Paleoproterozoic tonalitic slab melts traversed (and hybridized with) a deeper mantle wedge than Paleoarchean counterparts. The four Abitibi high Al TTG series and Superior province sanukitoids have high Cr and Ni contents, consistent with slab melts that have hybridized with mantle wedge peridotite.

There is a general secular step function change in compositions of granitoid batholiths at the Archean-Proterozoic boundary. Archean batholitic intrusions are prevalently Na-rich high Al TTG series magmas, with zero or positive Eu anomalies, whereas post-Archean granitoids belong to the K-rich calc-alkaline basalt-andesite-dacite-rhyolite magma series and have negative Eu anomalies. That transition is reflected in differences in the Eu anomalies of average Archean and Proterozoic upper continental crust (Taylor and McLennan, 1985; Drummond et al., 1996). One model to explain this relationship is that decreasing mantle temperatures resulted in a change in the locus of subduction zone melting from the slab to the sub-arc asthenospheric mantle wedge (Martin, 1986). However, there are exceptions. As noted above, rare adakite-like rocks thought to be derived by slab melting and wedge hybridization occur locally in Phanerozoic arc assemblages, as do tonalitic plutons (e.g., in the North American Cordillera: Gromet and Silver, 1987). Conversely, in the Archean, the basalt-andesite-dacite-rhyolite series has been documented in 3.2 Ga terranes of the Pilbara (Bickle et al., 1983; Vearncombe and Kerrich, 1999), and numerous post-tectonic (~2.68 Ga), K-rich, peraluminous granitoids occur in the Superior province (Feng and Kerrich, 1992). Thus, although the end of the Archean corresponds to a significant global change in the thermal structure of subduction zones, local variations in conditions and subduction kinematics may have permitted Phanerozoic-type petrogenetic processes to occur rarely in the Archean and Archean-type processes such as slab melting to persist in some Phanerozoic subduction zone settings.

Other geochemical differences between Archean high Al TTG adakites and Phanerozoic calc-alkaline basalt-andesite-dacite-rhyolite series rocks include major element trends in normative Ab-An-Or or Q'-ANOR diagrams (Gill and Stork, 1979; Streckeisen and Le Maitre, 1979), as well as higher Zr/Sm ratios in the former that increase with La/Sm (Drummond et al., 1996; Smithies and Champion, 2000; Condie, 2005; Martin et al., 2005), and Nb/Ta ratios that are variably lower than the primitive mantle value of 17 (Foley et al., 2002; Rapp et al., 2003). Moreover, Moyen and Stevens (2006) have conducted experiments generating these geochemical signatures under pressure-temperature conditions appropriate to geothermal gradients likely in Archean subduction zones. In contrast, modern island-arc basalts and calc-alkaline intermediate to felsic magmas have distinct major element compositions and extend to lower Zr/Sm and higher Nb/Ta ratios (Fig. 3). There are exceptions and overlaps between different magma series but, taken collectively, Archean high Al TTG adakites are compositionally distinct

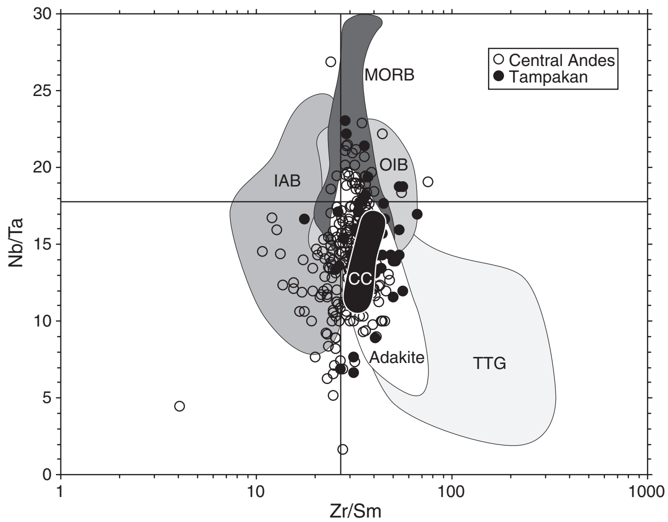

FIG. 3. Plot of Nb/Ta vs. Zr/Sm, showing fields for Archean TTG compared to bulk continental crust (CC) and modern midocean ridge basalts (MORB), ocean-island basalts (OIB), island-arc basalts (IAB), and calc-alkaline andesite-dacite-rhyolite suites from the Central Andes and Tampakan, Philippines (fields from Foley et al., 2002; for sources of data see captions to Figs. 9 and 16). The composition of the primitive mantle is shown by the intersection of the two lines.

from Phanerozoic tholeiitic and calc-alkaline rocks, and similar Eu anomalies and Zr/Sm and Nb/Ta ratios for adakites and TTG signify some common petrogenetic processes for this association (Fig. 3).

Alternative Mechanisms for Generating Adakite-Like Geochemical Signatures

Many of the geochemical characteristics of adakitic rocks listed in Table 1 are shared by normal andesitic and dacitic arc magmas and cannot be considered diagnostic of slab melting. Only the high Sr (≥400 ppm) and low Y (≤18 ppm) and Yb (≤1.9 ppm) concentrations, and resultant high Sr/Y (≥20) and La/Yb (≥20) ratios, are argued by proponents of slab melting to uniquely define adakites. These trace element signatures are interpreted to reflect source processes, specifically partial melting in the presence of garnet and absence of plagioclase (Martin, 1999).

Such conditions are satisfied by melting of garnet amphibolite or eclogite facies rocks, which may be found at the base of thickened (>40 km) continental crust or in eclogitized subducting oceanic crust. Garnet is also a stable phase in the subcontinental mantle lithosphere as well as the asthenosphere (Wyllie et al., 1989; Poli and Schmidt, 2002; Grove et al., 2006). If these are the only truly diagnostic geochemical characteristics for adakites, then a unique source in the subducting slab cannot be presumed because other potential sources exist. Thus, the first relationship to be tested, that slab melting plus mantle hybridization produces adakites, is found to be nonunique, as acknowledged by Defant and Kepezhinskas (2002, p. 256): "There is little way to differentiate a slab melt from a lower crustal melt."

Below, three alternative and arguably simpler ways to generate high Sr/Y, high La/Yb, intermediate-composition magmas are reviewed.

Partial melting of lower crustal garnet amphibolite

Garnet is a common metamorphic mineral in crustal rocks, increasing in abundance with depth from midcrustal levels in amphibolites to eclogite facies rocks in the lower crust. Thus, partial melting of the lower crust to yield intermediate-composition melts can be expected to occur in the presence of some amount of residual garnet (Green, 1982). In fact, dehydration melting of lower crustal amphibolites will result in progressive conversion to garnet granulite, according to the reaction (Rushmer, 1993; Wolf and Wyllie, 1994; Klepeis et al., 2003):

$$\text{hornblende} \pm \text{clinozoisite} \pm \text{quartz} + \text{plagioclase} \rightarrow \text{garnet} + \text{clinopyroxene} + \text{plagioclase} \pm \text{Fe oxides} + \text{melt.} \quad (1)$$

This melting relationship is spectacularly illustrated in Figure 4 by felsic leucosomes with garnet rims in mafic to intermediate rocks from the deeply eroded root of the Mesozoic southern New Zealand arc (Klepeis et al., 2003).

The increasing abundance of garnet with depth (absolute amounts are dependent on bulk composition) means that any geochemical signature reflecting the presence of garnet in the source, such as low Y and HREE concentrations, will be amplified with depth and degree of partial melting (e.g., Tuff and Gibson, 2007). Kay et al. (1991) and Haschke et al. (2002) calibrated plots of La/Yb versus La/Sm as a measure of garnet fractionation to estimate the depth and extent of crustal melting in the Central Andes. Many of the samples studied by these authors had La/Yb ratios and Sr concentrations well in excess of the minimum values for adakitic rocks (La/Yb ≥20, Sr ≥400 ppm), and yet their radiogenic isotope compositions clearly indicate significant degrees of crustal interaction. A continental crustal origin for these adakite-like geochemical signatures seems clear.

Other examples of rocks with adakite-like geochemical signatures formed by partial melting of lower crustal garnet amphibolites or eclogites have been documented on the basis of geochemical, isotopic, and geophysical evidence in Tibet (Chung et al., 2003; Hou et al., 2004), the Philippines (Yumul et al., 2000), the Cascades (Conrey et al., 2001), southern Sierra Nevada (Gromet and Silver, 1983; Saleeby et al., 2003), Baja California (Tulloch and Kimbrough, 2003), and New Zealand (Klepeis et al., 2003).

Interaction between asthenospheric melts and lower crust (MASH)

Few of the above cited papers for crustal amphibolite and/or eclogite melting propose that the resultant magmas are pure crustal melts. Instead, as shown by numerous authors, lower crustal partial melting is likely to be triggered by intrusion of hot, mantle-derived, mafic magmas, with subsequent fractionation and intermixing (e.g., Eichelberger, 1978; Hildreth, 1981; Hildreth and Moorbath, 1988; Huppert and Sparks, 1988; Fyfe, 1992; Snyder and Tait, 1998; Petford and Gallagher, 2001; Dufek and Bergantz, 2005). This process was termed MASH (melting, assimilation, storage, homogenization) by Hildreth and Moorbath (1988) and was based on an exhaustive study of the geochemical and isotopic compositions of Cenozoic Southern volcanic zone rocks in the Andes. Hildreth and Moorbath (1988) envisaged the entrapment of

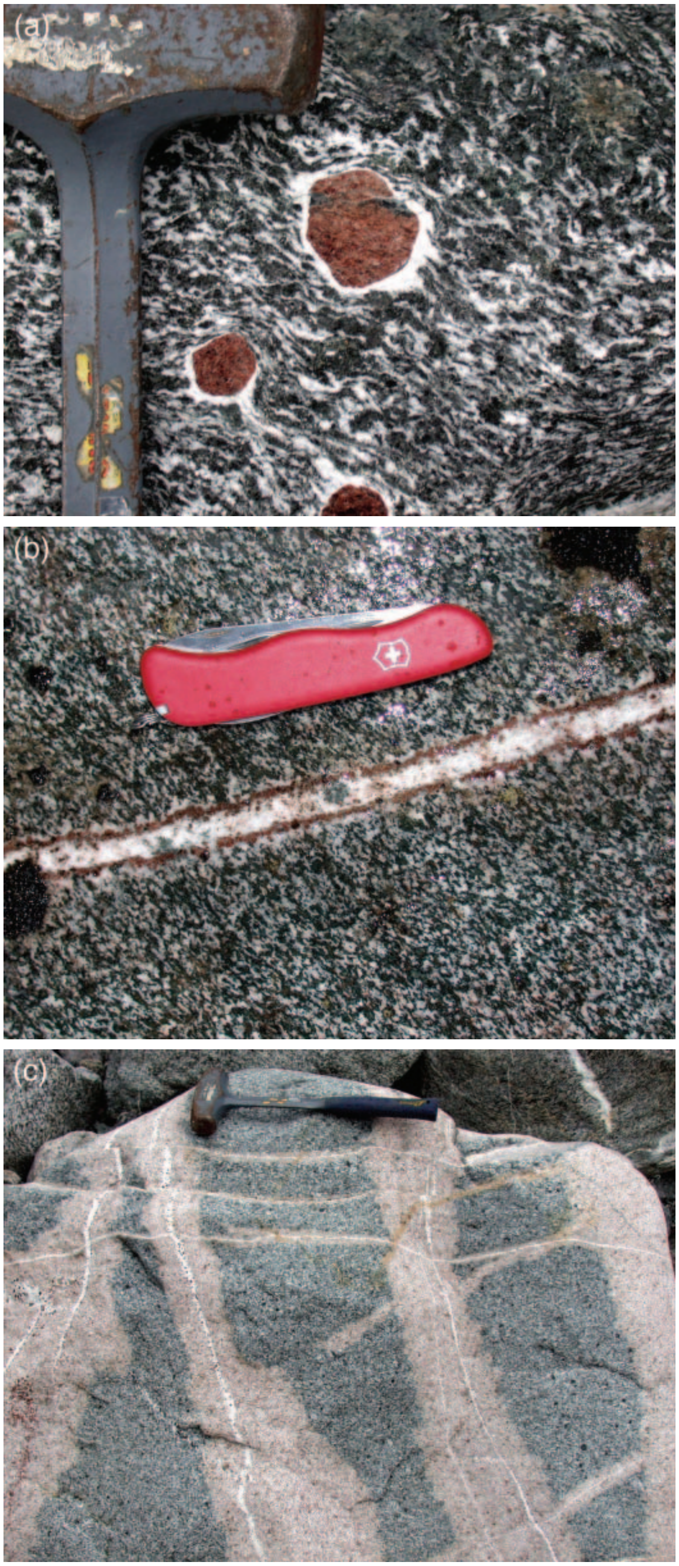

FIG. 4. Migmatitic dioritic and gabbroic gneisses from exposed lower crustal rocks in the Mesozoic southern New Zealand arc. (a). Melt leucosomes surrounding peritectic garnet formed from hornblende breakdown (eq. 1). (b). Garnet-lined leucosome (felsic dikelet). (c). Granulitic dehydration haloes of garnet and clinopyroxene replacing hornblende around leucosomes and fractures. Photographs reproduced from Klepeis et al. (2003, fig. 3), with kind permission of the authors and publisher (Geological Society of America).

dense asthenosphere-derived basaltic magmas at the base of the crust (the Moho density filter of Herzberg et al., 1983), where their high temperatures resulted in partial melting of crustal rocks and mixing with those melts to form hybrid evolved magmas of lower density, which could then rise through the crust. They suggested that the resultant magmas might contain tens of percent of lower crustal components, most evident in their evolved isotopic compositions (see also McBirney et al., 1987).

An important feature of the MASH model is the fate of the mafic magma influx. During the early stages of arc development, when crustal temperatures are still low, much of this basaltic flux may solidify at the base of the crust to form an underplated layer of basaltic composition. With continued and voluminous flux of hot magma, however, a partially molten MASH zone, "likely to be a plexus of dikes, sills, pods, small chambers, and mushy differentiated intrusions" (Hildreth and Moorbath, 1988, p. 483) is developed, perhaps after only 1 or 2 m.y. (Annen and Sparks, 2002; Richards et al., 2006). Loss of heat to the crust will result in fractional crystallization of this hydrous basalt, leaving a cumulate residue of mafic silicates including garnet, pyroxenes, and amphibole (Claeson and Meurer, 2004; Müntener and Ulmer, 2006). Early plagioclase crystallization, however, is suppressed by the high water content of the melt (Blatter and Carmichael, 1998; Müntener et al., 2001), and Müntener and Ulmer (2006, p. 1) have described the arc Moho as a "plagioclase saturation boundary." The resultant mafic cumulates will be of high density and, although formed at the base of the crust, would be identified seismically as mantle, with the top of the ultramafic cumulate zone representing the Moho (Hamilton, 1981; Griffin and O'Reilly, 1987; Müntener et al., 2001). Such deep arc structures have been recognized in the Talkeetna arc, Alaska (DeBari and Coleman, 1989; Greene et al., 2006), and the Kohistan arc, Pakistan (Miller and Christensen, 1994; Garrido et al., 2002). Subsequent cooling of these cumulates will result in conversion to even denser eclogite, with the potential for delamination along with the lithospheric mantle (e.g., Kay and Kay, 1993; Müntener et al., 2001; Behn and Kelemen, 2006). In fact, several models of crustal evolution require foundering of such cumulate materials to explain estimates of bulk crustal composition (e.g., Hawkesworth et al., 1993; Rudnick and Gao, 2003; Plank, 2005).

Dehydration melting of amphibolite in the lower crust, combined with direct crystallization of amphibole, garnet, and pyroxenes from intruding hydrous basalts, will tend to deplete the resulting intermediate-composition magma in Y and HREE, while enriching it in Sr due to the instability of plagioclase. Such processes have been invoked to explain adakite-like geochemical signatures (high Sr/Y, La/Yb) in upper crustal granitoids and volcanic rocks in a number of continental arcs (e.g., Gromet and Silver, 1987; Feeley and Hacker, 1995; Klepeis et al., 2003; Tulloch and Kimbrough, 2003).

Crystal fractionation

Perhaps the simplest mechanism for generating evolved magmas with strongly fractionated REE patterns and high Sr/Y ratios is fractional crystallization of minerals that preferentially partition Y and HREE in the absence of significant plagioclase fractionation (which preferentially partitions Sr; Castillo et al., 1999). The latter requirement (relatively high Sr concentrations in fractionated magma) is readily achieved in H_2O-rich (≥2 wt % H_2O) mafic to intermediate magmas due to the suppression of plagioclase on the liquidus until after the appearance of olivine, clinopyroxene, and hornblende (Moore and Carmichael, 1998; Kelemen et al., 2003). Indeed, DeBari and Coleman (1989) and Müntener et al. (2001) have shown that hydrous mafic magmas may crystallize up to 50 percent of their volume as ultramafic cumulates before plagioclase appears on the cotectic. Carmichael (2002) further suggested that only ~20 percent of the total arc magma flux reaches the surface as volcanic rocks, the rest crystallizes at depth as hornblende gabbros and cumulates (see also Anderson, 1980; Claeson and Meurer, 2004; Takahashi et al., 2005).

Both hornblende and clinopyroxene preferentially partition the HREE over LREE, although hornblende is more effective, having partition coefficients, D = [concentration of element in mineral]/[concentration of element in melt], that peak in the MREE at ~2 in andesitic melts (e.g., Green and Pearson, 1985; Rollinson, 1993; Klein et al., 1997) or up to 9.6 in more felsic melts (Sisson, 1994; Bachman et al., 2005). Fractionation of 16 percent of hornblende from an andesite (average medium K calk-alkaline andesite with 490 ppm Sr, 18 ppm Y, 11 ppm La, and 1.4 ppm Yb: Gill, 1981), or only 3 percent from a more felsic melt, can yield Sr/Y >40 (note this average andesite already has adakitic Sr/Y ≈ 27). Similarly, fractionation of 47 percent of hornblende from an andesite, or 11 percent from a more felsic melt, can yield La/Yb ratios >20 (Fig. 5a-b, Table 3). The fractionation of hornblende also imparts a characteristic listric-shaped REE profile on

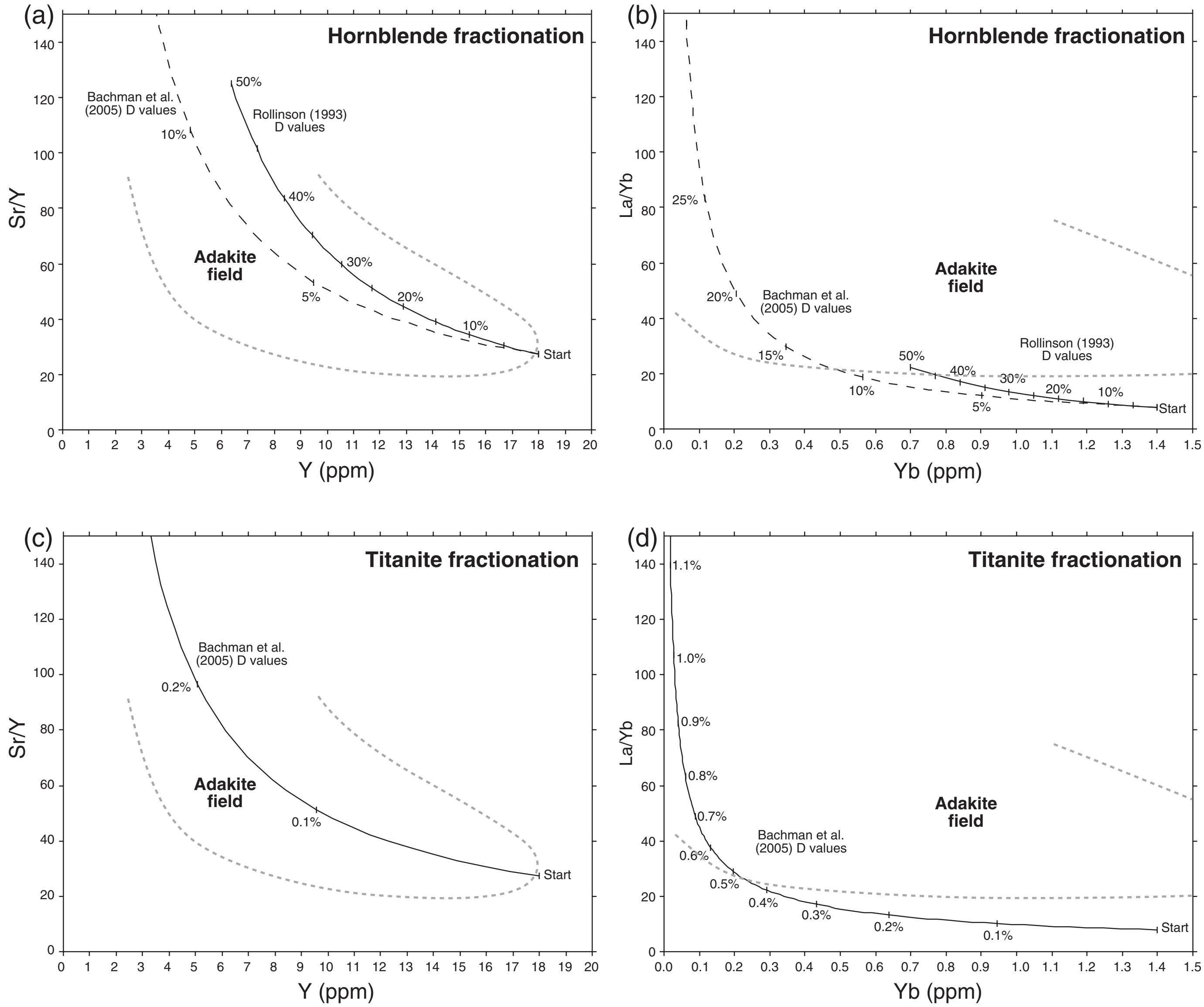

FIG. 5. Modeled Rayleigh fractionation of hornblende and titanite from a medium K calc-alkaline andesite (average composition from Gill, 1981) plotted on (a, c) Sr/Y vs. Y, and (b, d) La/Yb vs. Yb diagrams. Partition coefficients from Rollinson (1993) and Bachman et al. (2005) are listed in Table 3.

TABLE 3. Selected Partition Coefficients for Hornblende and Titanite in Andesitic Melt

	Rollinson (1993)		Bachman et al. (2005)	
Element	D(Hornblende)	D(Titanite)	D(Hornblende)	D(Titanite)
Sr	0.3	0.06	0.4	0.37
Y	2.5		13.5	633
La	0.5	2	1.4	133
Yb	2		9.6	393

Note: D = [concentration of element in mineral]/[concentration of element in melt]

chondrite-normalized diagrams, a pattern observed in many arc volcanic and plutonic suites (e.g., Lang and Titley, 1998; Castillo et al., 1999; Richards et al., 2001; Fig. 6). In contrast, garnet fractionation or restite separation should yield smoothly decreasing LREE to HREE patterns. Thus, the effects of garnet versus hornblende separation can be distinguished using plots of LREE/MREE (e.g., La/Sm) versus MREE/HREE (e.g., Sm/Yb or Dy/Yb: Kelemen et al., 2003). Kay et al. (1991, 1999), Richards and Villeneuve (2002), and Richards et al. (2006) used such plots to show that, although most Neogene volcanic rocks from the Central Andes are enriched in LREE relative to HREE, few in fact show strong MREE enrichments relative to HREE (i.e., high Sm/Yb or Dy/Yb) indicative of garnet control.

As noted by Baldwin and Pearce (1982) and Green (1982), fractionation of REE- and HFSE-rich accessory phases such as titanite, apatite, and zircon will have an even greater effect on trace element concentrations than common ferromagnesian silicate minerals. Titanite, in particular, shows strong preference for MREE and HREE over LREE (Prowatke and

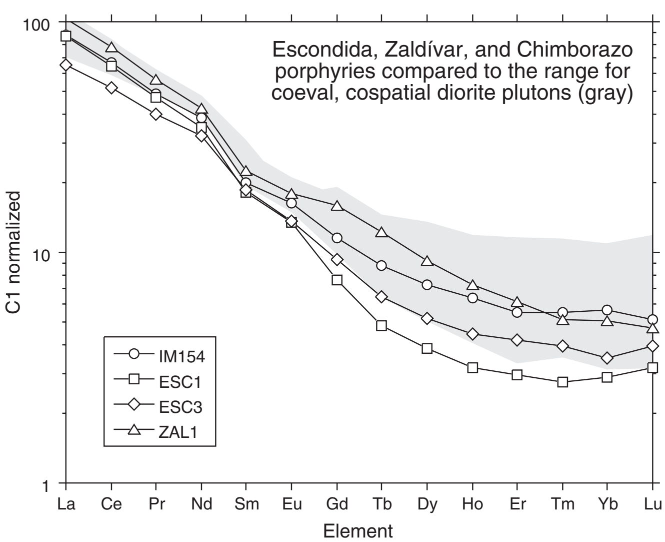

FIG. 6. C1 chondrite-normalized REE patterns for samples of porphyry intrusions from the Escondida (ESC1, ESC3), Zaldívar (ZAL1), and Chimborazo (IM154) porphyry Cu deposits, compared with the range of data from 19 samples of coeval (late Eocene to early Oligocene) diorite intrusions. All of these rocks display listric-shaped REE profiles, most strongly developed in the felsic porphyry samples, and indicate control by hornblende fractionation. Normalization values of Sun and McDonough (1989).

Klemme, 2006), with partition coefficients as high as 393 for Yb (133 for La) and 633 for Y in felsic magmas (Table 3; Bachman et al., 2005). Using these D values, fractionation of <0.1 or <0.4 percent of titanite is required to generate Sr/Y >40 and La/Yb >20, respectively (Fig. 5c-d). Hornblende, titanite, apatite, and zircon are very common phenocryst and microphenocryst phases in arc volcanic rocks with >54 wt percent SiO_2 (i.e., basaltic andesites and andesites: Anderson, 1980), and titanite and zircon increase in abundance in more fractionated rocks (i.e., dacites and rhyolites: Gromet and Silver, 1983, 1987; Richards et al., 2006). Thus, as proposed by Castillo et al. (1999), adakite-like geochemical compositions can be generated by fractionation of common phenocryst and accessory mineral phases from normal calc-alkaline rocks, especially where relatively high water contents suppress plagioclase crystallization. Importantly, because of the form of the Sr/Y versus Y and La/Yb versus Yb plots, adakitic Sr/Y and La/Yb values will inevitably be achieved in suites where Y or Yb are depleted by fractionation at roughly constant or even slightly decreasing Sr and La concentrations.

Assessment of Some Classic Phanerozoic Adakite Suites

In this section, published whole-rock geochemical data for several volcanic sequences from around the world that host adakite-like rocks, and have specifically been proposed as slab melts, are examined and evaluated in terms of the parameters outlined in Table 1; a summary of these comparisons is given in Table 4.

The obvious suite to examine first is that from the eponymous Adak Island in the Aleutians, first described by Kay (1978). However, Kay (1978), and later Defant and Drummond (1990), reported only one analysis of a singular magnesian adesite lava flow (actually a basaltic andesite with 55.5 wt % SiO_2) from the base of Moffett volcano, whereas most other Adak Island (and Aleutian) volcanic rocks range from high Mg and high Al basalts to normal calc-alkaline andesites (Kay and Kay, 1994). The trace element data for this single sample are incomplete, lacking data for Y so the Sr/Y ratio cannot be calculated (Sr = 1,783 ppm), although the La/Yb ratio (30.4; Yb = 0.948 ppm) is well within the adakitic range (La/Yb ≥20; Yb ≤1.9 ppm). Kay and Kay (1998) suggested that Adak Island was close to a subducting spreading ridge in the middle Miocene when the flow was erupted and that an origin by melting of a young, hot slab might apply, as argued by Defant and Drummond (1990). However, it seems remarkable that the origin of such a complex and contentious petrogenetic model can be traced to a single, incompletely characterized sample.

In the following subsections, figures are plotted using the adakitic field boundaries of Castillo et al. (1999) but extending the minimum Sr/Y ratio down to 20 (Defant and Drummond, 1993). As a general observation, data for Sr are commonly widely scattered, as might be expected for a fluid-mobile element in hydrous magmas. More reliable information about magmatic processes appears to be provided by REE, Y, and compatible elements such as Cr, Ni, and MgO, which are plotted against SiO_2 on Harker-type diagrams as an indication of variation with differentiation. Well-correlated trends are commonly observed in the plotted suites, suggesting a fractionation control for elemental

TABLE 4. High Sr/Y Volcanic Suites Tested

Locality	SiO_2 (≥56%)[1]	Na_2O (≥3.5%)	K_2O (≤3%)	Rb (≤65 ppm)	Sr (≥400 ppm)	Y (≤18 ppm)	Yb (≤1.9 ppm)
Arc volcanic rocks							
Adak Is. (Alaska)	No	No	Yes	Yes	Yes		Yes
Austral Andes (S Chile)	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Mindanao (Philippines)	Yes	Yes	Yes	Yes	Mostly	Yes	Yes
Negros (Philippines)	Yes	Mostly	Yes	Yes	Yes	No	Few
Batan (Philippines)	No	Mostly	Yes	Few	Yes	Mostly	Mostly
Parinacota (N Chile)	Yes	Yes	Few	No	Yes	Yes	Yes
Tata Sabaya (SW Bolivia)	Yes	Yes	Mostly	No	Yes	Yes	Yes
Llullaillaco (NW Argentina)	Yes	Yes	Yes	Mostly	Yes	Yes	Yes
Southern Central Andes	No	Mostly	Mostly	Many	Mostly		Many
Pichincha (Ecuador)	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Mineralization-related volcano-plutonic suites							
New Britain (Papua New Guinea)	No	Mostly	Mostly	Mostly	Some	Some	
Papua New Guinea–Solomon Is.	No	Mostly	Mostly	Mostly	Mostly	Some	
Western Luzon (Philippines)	No	Yes	Yes	Yes	Yes	Only >58% SiO_2	
Tampakan (Philippines)	No	Mostly	Mostly	Mostly	Mostly	Mostly	Mostly
Luzong (eastern China)	No	Yes	Few	Only Shaxi	Mostly	Only Shaxi	Only Shaxi
Dexing (southern China)	Yes	Mostly	Few	Few	Yes	Yes	Yes
Sierrita (Arizona)	Yes	Mostly	No	No	Only <70% SiO_2		Mostly
Mezcala (Mexico)	Yes	Yes	Few	No	Yes	Only >60% SiO_2	Yes
Central Chile	No	Mostly	Mostly	Mostly	Mostly	Some	Some
Los Pelambres (Central Chile)	Yes	Yes	Mostly	Mostly	Yes	Yes	Yes
Escondida (northern Chile)	Mostly	Mostly	Mostly	Some	Yes	Yes	Yes

[1] SiO_2 "No" if suite starts at more mafic compositions
[2] Mg # Average of suite
[3] I_{Sr} Average initial $^{87}Sr/^{86}Sr$ isotope ratio

abundances in many instances. In almost no cases do the magmas qualify as primitive (Ni, Cr, and Mg # are moderate to low except in basalts or basaltic andesites, which are mostly not adakites by definition because SiO_2 <56 wt %), and most suites show good fractionation trends that commonly start with nonadakitic mafic compositions and fractionate into the adakite fields. Only samples from the Austral Andes, and particularly from Cook Island and Cerro Pampa, appear to show arguably almost pristine slab-melting signatures.

Austral Andes

One of the better documented adakitic suites is found in the Austral volcanic zone of the southern Andes, where Holocene andesites and dacites are related to subduction of relatively young (<24 Ma) oceanic crust of the Nazca and Antarctic plates (Stern and Kilian, 1996). All of the rocks sampled by Stern and Kilian (1996) plot in the adakite Sr/Y versus Y field and satisfy many of the other parameters for adakitic rocks (Fig. 7, Table 4), although not all samples reach adakitic La/Yb values (Fig. 7d). Fractionation trends are not well developed by most trace elements or ratios in Harker diagrams (Fig. 7b-c, e-i), but smooth trends for MgO, FeO, Cr, and Ni (the latter to below adakitic values in dacites) suggest fractionation of ferromagnesian silicate minerals (pyroxenes, amphiboles, and plagioclase are noted as phenocryst phases by Stern and Kilian, 1996).

Against Adakite Geochemical Criteria (Table 1)

Ni (≥20 ppm)	Cr (≥30 ppm)	Sr/Y (≥20)	La/Yb (≥20)	Mg # (≈0.5)[2]	I_{Sr} (<0.7045)[3]	Age of subducted lithosphere	Figure	Reference
Yes			Yes	0.62		<15 Ma		Kay (1978), Kay and Kay (1998)
Only <65% SiO_2	Only <65% SiO_2	Yes	Some	0.50	0.7045	<24 Ma	7	Stern and Kilian (1996)
Some	Some	Yes	Few	0.47			8	Sajona et al. (1993)
		Few	No	0.46			8	Sajona et al. (2000)
		Mostly	Few	0.52			8	Sajona et al. (2000)
Yes	Yes	Yes		0.48	0.7067		9	Davidson et al. (1990)
No	No	Yes	Yes	0.46	0.7060		9	de Silva et al. (1993)
		Yes	Yes	0.45			9	Richards and Villeneuve (2001)
Few	Many		Few	0.43	0.7049		10	Kay et al. (1991)
Yes	Yes	Yes	Very few	0.51	0.7041	Carnegie Ridge?	11	Bourdon et al. (2002)
Only <56% SiO_2	Only <56% SiO_2	Some		0.45			13	Hine and Mason (1978)
Only <56% SiO_2		Mostly		0.48			14	Mason and Macdonald (1978)
Very few	Few	Mostly		0.44			15	Imai (2002)
Some	Many	Mostly	No	0.35			16	Rohrlach (2002)
Only Shaxi	Only Shaxi	Mainly Shaxi	Some	0.41	0.7057	No subduction		Wang et al. (2006a)
Some	Yes	Yes	Yes	0.49	0.7047	No subduction		Wang et al. (2006b)
No			Mostly	0.37	0.7081		17	Anthony and Titley (1988)
Some	Yes	Yes	Yes	0.53			18	González-Partida et al. (2003)
Only <56% SiO_2	Only <56% SiO_2	Some	Only rhyolite	0.42	0.7041	Juan Fernández ridge?	19	Hollings et al. (2005)
No	Few	Yes	Yes	0.47	0.7047	Juan Fernández ridge?		Reich et al. (2003)
Only <59% SiO_3	Only <59% SiO_4	Yes	Some	0.50			20	Richards et al. (2001)

On the basis of geochemical and isotopic data, Stern and Kilian (1996) proposed a complex, multistage petrogenetic model for the dacitic rocks, including variable proportions of subducted basalt (35–90%) and sediment (≤4%) melts, 10 to 15 percent contribution from the mantle wedge, 0 to 30 percent contribution from the upper plate continental crust, and fractional crystallization. However, the andesitic rocks from Cook Island show a clearer slab melting signature (≥90% basalt and ≤1% sediment melting, plus ≤10% mantle wedge). The Cook Island rocks are distinguished from the other more evolved dacites by high Sr/Y ratios (318–442; Fig. 7b), mainly reflecting very high Sr concentrations (1,660– 2,003 ppm; Fig. 7i). Their high Mg number (~0.65), high Cr and Ni concentrations, and primitive Sr isotope ratios (~0.7027) make them good candidates for partial melts of isotopically depleted, subducted oceanic (MORB) crust, modified by reaction with peridotitic mantle wedge. A similar origin was proposed by Kay et al. (1993) for late Miocene volcanic rocks with adakite-like geochemical characteristics from Cerro Pampa, just north of the Austral volcanic zone.

Philippines

The Philippines archipelago has been claimed to be a classic slab-melting adakite locality and has been the focus of a number of papers by Sajona and coworkers (e.g., Sajona and

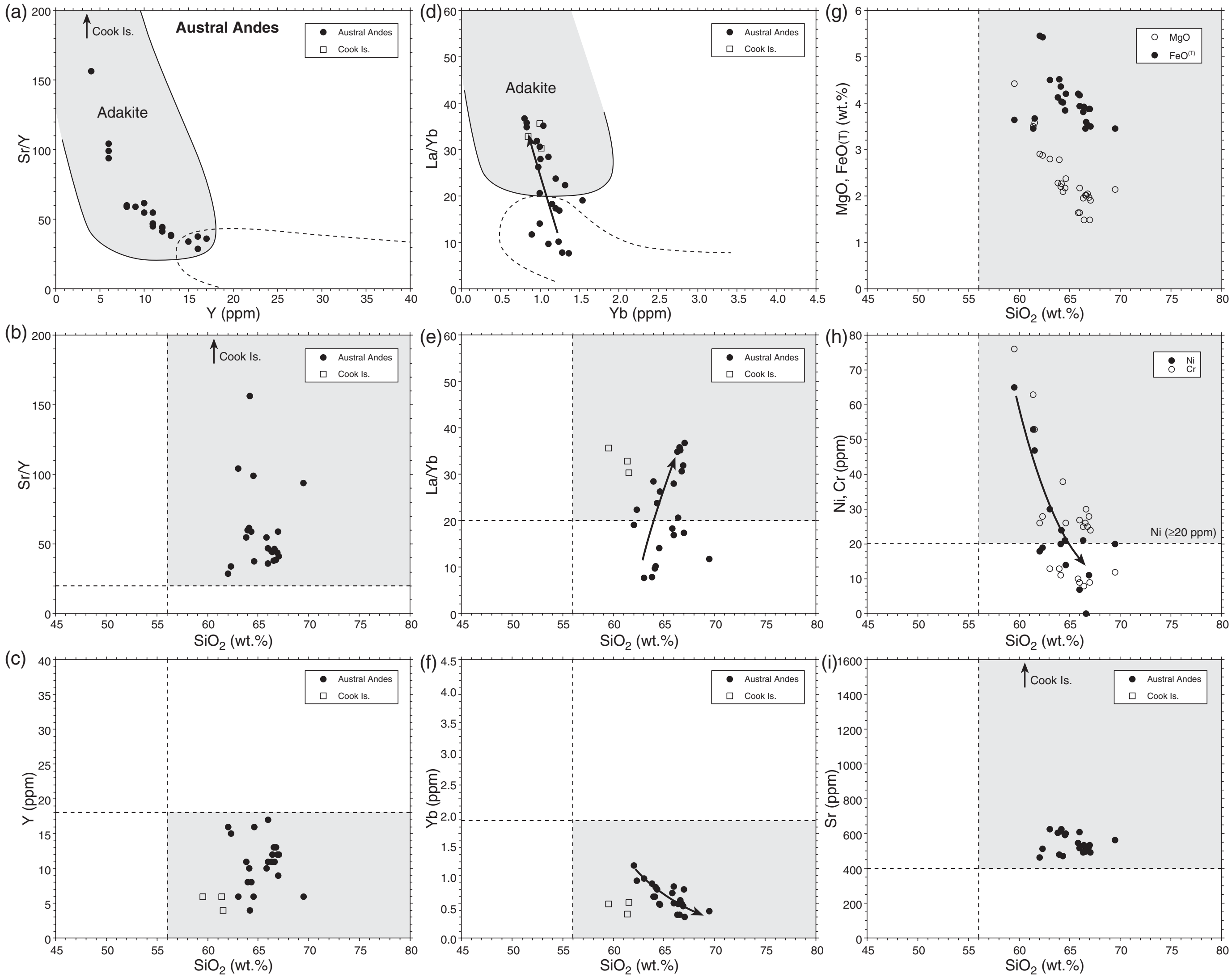

FIG. 7. Geochemical data for volcanic rocks from the Andean Austral volcanic zone (data from Stern and Kilian, 1996). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

Maury, 1998; Sajona et al., 1993, 1996, 2000), as well as others who have claimed a link (or otherwise) to porphyry deposits (discussed separately below). The Neogene tectonic evolution of the Philippines is highly complex, featuring multiple subduction events including opposing subduction on the east and west sides of the archipelago, subduction of oceanic crust of various ages, arc collisions, and cessation of subduction (reviewed by Rohrlach, 2002, and Rohrlach and Loucks, 2005). In this context, it is difficult to ascribe a given volcanic suite to any particular subduction or tectonic event. Nevertheless, Sajona et al. (1993) suggested that rocks of adakitic composition from western Mindanao are related to subduction and melting of the Miocene Sulu Sea plate and proposed that adakites in general might be related to the onset of subduction. Similarly, Sajona et al. (2000) proposed that adakite-like rocks from Batan island in the northern Philippines are derived from partial melting of the middle Miocene South China Sea basin along the Manila trench, whereas those from Negros island in the central Philippines are derived from melting of the Miocene Sulu Sea plate along the Negros trench, as in Mindanao.

Key data from the Mindanao, Batan, and Negros adakite-like suites (Sajona et al., 1993, 2000) are plotted in Figure 8 and summarized in Table 4. Although the Mindanao and most of the Batan samples plot in the adakitic Sr/Y versus Y field, the Negros suite does not (Fig. 8a). Using the La/Yb $\geq$20 and Yb $\leq$1.9 ppm criteria, only a few of the Mindanao and Batan samples plot in the La/Yb versus Yb adakitic field (Fig. 8d). Harker diagrams in Figure 8b-c and e-i reveal several important features of these suites. Firstly, most of the Batan samples have SiO_2 <56 wt percent and are, therefore, not adakitic by this definition. Secondly, smooth fractionation trends for MgO and Fe_2O_3 against SiO_2 (Fig. 8g) suggest that, although these suites are obviously not comagmatic (they are from different locations in the Philippines), they share similar and common magmatic differentiation histories.

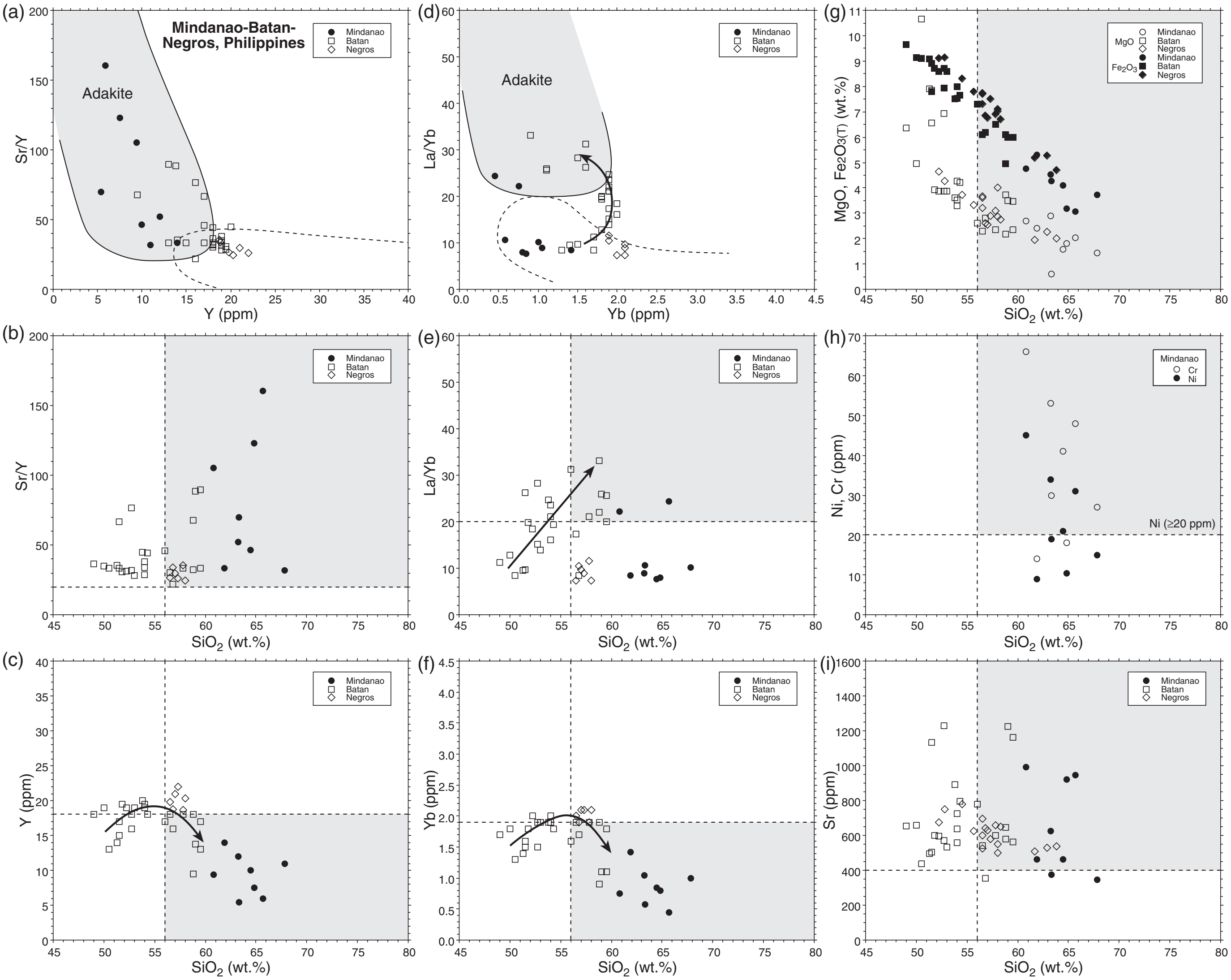

FIG. 8. Geochemical data for volcanic rocks from Mindanao, Batan, and Negros in the Philippines (data from Sajona et al., 1993, 2000). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

The plots of Y and Yb concentrations against SiO_2 show particularly revealing trends, with increasing concentrations of these elements in the Batan suite up to ~56 wt percent SiO_2 and thereafter decreasing trends (Fig. 8c,f). In both cases, the mafic rocks increase up to or above the respective adakitic minimum values at the minimum SiO_2 contents for adakites and then decrease again to adakitic values with fractionation. The Batan suite, which covers a compositional range from basalt to andesite, shows a particularly clear evolution in the La/Yb versus Yb diagram (Fig. 8d), describing a curved path from subadakitic La/Yb values into the adakite field with fractionation (Fig. 8e). According to Sajona et al. (2000), the mineralogy of the Batan basaltic rocks is dominated by olivine and clinopyroxene (with minor plagioclase, titanomagnetite, and hornblende), whereas the andesites are described as "hornblende andesite" (the mineralogy of the Negros dacites is not reported). Strontium shows no systematic variation with SiO_2 but scatters widely, consistent with the minor reported plagioclase (Fig. 8i). The simplest explanation for these geochemical trends, therefore, is increasing magmatic concentrations of Y and Yb to supra-adakitic values in hornblende-poor basalts in which these elements are incompatible, followed by rapid decrease in concentration once hornblende appears as a major phenocryst phase in andesites. If this interpretation is correct, then the high Sr/Y and La/Yb values of some of these andesitic and dacitic samples reflect upper plate fractionation processes and cannot be used to infer source compositions. A similar conclusion was reached by Dreher et al. (2005) and Macpherson et al. (2006) for adakite-like volcanic rocks from eastern Mindanao. Notably, Macpherson et al. (2006, p. 581) suggested that "any subduction zone has the potential to produce adakitic magma if basalt crystallizes at sufficient depth."

Assessment of Some Adakite-like Suites From Normal Calc-Alkaline Arcs

The geochemical criteria for adakitic rocks are so broad that many, even most, normal calc-alkaline volcanic arc suites contain some samples that might be classified by some parameters as adakitic. Most commonly, these rocks can be shown to be products of upper-plate crustal contamination, interaction with garnetiferous lower crust, and/or fractional crystallization under hydrous conditions (i.e., MASH or AFC processes). For example, Neogene thickening of the Central Andean crust, locally up to 75 km (James, 1971; Beck and Zandt, 2002; Yuan et al., 2002), makes it particularly likely that a garnet signature will be developed in magmas that have interacted to any degree with the lower crust in this region, as noted by Kay et al. (1987), Hildreth and Moorbath (1988), and several others cited below. To illustrate these trends, three datasets from different parts of the Neogene Andes are discussed below.

Northern Central Andes (18°–26°S)

A compilation of 340 geochemical analyses of Neogene volcanic rocks from the northern Central Andes is presented in Figure 9. These data have been compiled from 18 publications (sources of data are listed in the caption to Fig. 9) from volcanoes ranging in age from middle Miocene to Quaternary, with no particular selectivity other than completeness of data. Despite this wide geographic and moderate age range, the data define remarkably coherent trends in Harker diagrams (Fig. 9b-c, e-i), especially for the major elements (Fig. 9g), suggesting broadly common petrogenetic histories and

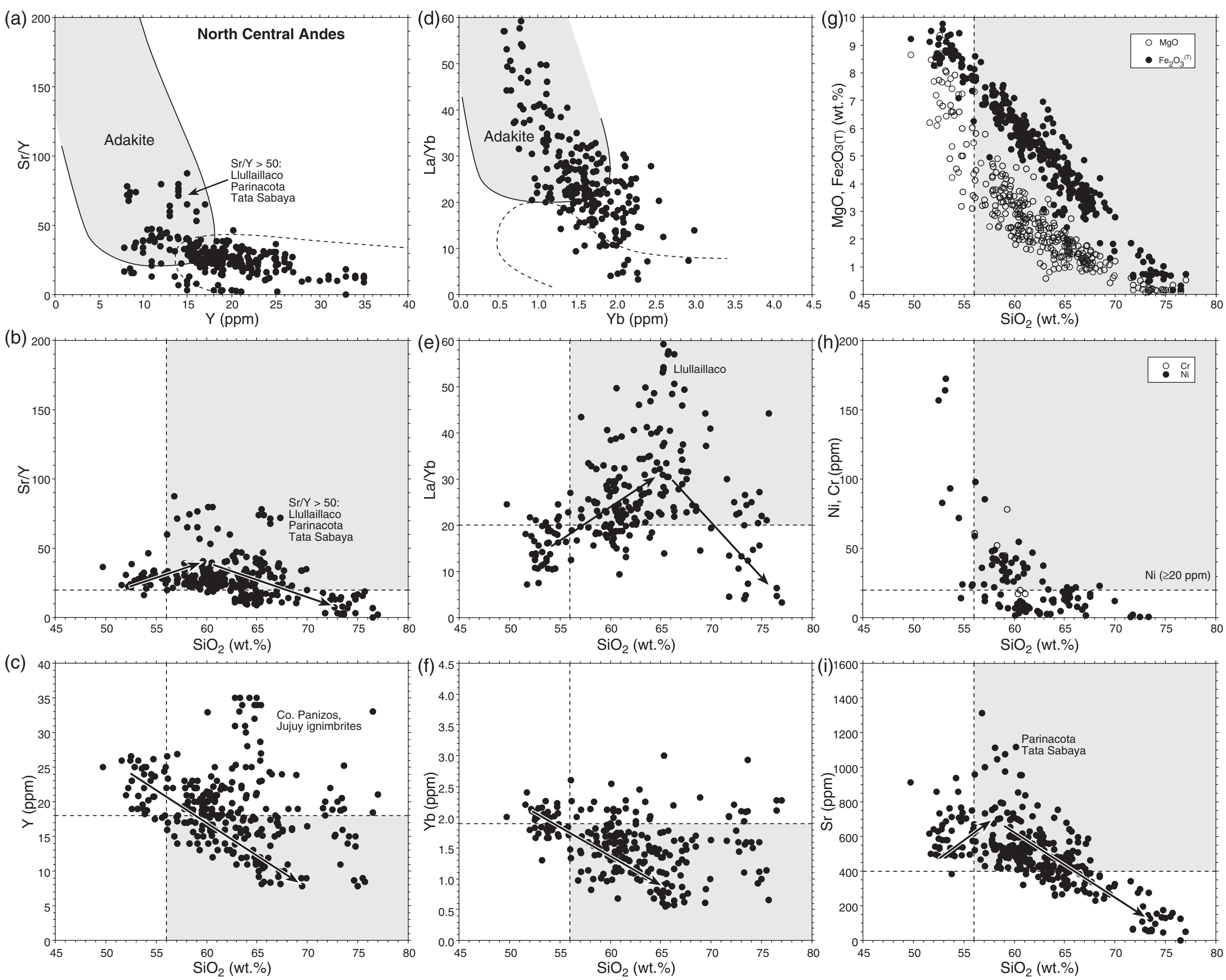

FIG. 9. Geochemical data for volcanic rocks from the northern Central Andes (18°–26°S; data from Déruelle, 1982; Gardeweg and Ramirez, 1987; Koukharsky et al., 1987; Seggiaro et al., 1987; Francis et al., 1989; Ort et al., 1989; Davidson et al., 1990; de Silva et al., 1993; Feeley and Davidson, 1994; Coira et al., 1996; Wittenbrink, 1997; Kay et al., 1999; Kraemer, 1999; Matthews et al., 1999; Richards and Villeneuve, 2001, 2002; Siebel et al., 2001; Richards et al., 2006). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

fractionation-controlled compositions in evolved rocks. As can be seen from panels (a) and (d) in Figure 9, many of these rocks plot in the adakitic fields in terms of Sr/Y versus Y and La/Yb versus Yb, and yet none of the 18 papers cited concluded that these rocks were formed by slab melting. Instead, such compositions are unanimously ascribed to interaction with thickened continental crust, for which strong support is indicated by variably enriched crustal isotopic signatures (see Davidson et al., 1991, Wörner et al., 1992, Feeley and Davidson, 1994, and Feeley and Hacker, 1995, for particularly cogent arguments).

When examined in detail, a similar pattern emerges for the evolution of high Sr/Y and La/Yb ratios as observed in the Philippines. Basaltic andesites and andesites show a general trend of increasing Sr/Y up to ~59 wt percent SiO_2, followed by a steady decrease to values below the adakitic minimum (Sr/Y ≥20) in most dacites and rhyolites (Fig. 9b). Yttrium concentrations show a steady decline throughout this compositional range (excepting some high values in the Jujuy and Co. Panizos felsic ignimbrites, which likely reflect crustal contamination) from supra-adakitic values in basaltic andesites and most andesites to below 18 ppm in most dacites and rhyolites (Fig. 9c). Strontium, on the other hand, mirrors the Sr/Y trend, with initially increasing values up to ~59 wt percent SiO_2, then decreasing to below 400 ppm in most dacites and rhyolites (Fig. 9i). A similar pattern is shown by the La/Yb ratio, but here the increase is from sub-adakitic values (La/Yb <20) to a maximum near 65 wt percent SiO_2, and then a steep decline to subadakitic values again in rhyolites (Fig. 9e). The variation of Yb with SiO_2 is rather scattered (La, not shown, is also very scattered), but minimum concentrations show an inverse variation from ~2 ppm in basaltic andesites to ~0.5 ppm in dacites (i.e., basaltic andesites mostly have supra-adakitic Yb concentrations, but more evolved rocks show a range from ~3 to ~0.5 ppm; Fig. 9f). Included in this dataset are samples from individual volcanoes with particularly high Sr/Y ratios (>50 at Llullaillaco, Parinacota, Tata Sabaya; Table 4), high La/Yb ratios (>50 at Llullaillaco), and high Sr concentrations (>800 ppm at Parinacota, Tata Sabaya), whereas other high Sr/Y samples represent individual lava flows among otherwise "normal" volcanic sequences (e.g., Richards et al., 2006).

The trends shown in Figure 9 are clearly related to magmatic fractionation and contamination processes (i.e., AFC) and start from basaltic andesitic compositions outside the permissible silica range for adakitic rocks. The maxima for the Sr/Y ratio and Sr concentrations at ~59 wt percent SiO_2 likely reflect the onset of significant plagioclase fractionation in andesites (plagioclase phenocrysts are sparse in basaltic andesites and mafic andesites), whereas the generally decreasing Y and Yb concentrations likely reflect a combination of hornblende and titanite fractionation (both are commonly observed phenocryst and accessory phases in andesites and dacites). Divergence from these trends in rhyolites (which are commonly ignimbrites) likely reflects significant crustal contamination or even wholesale crustal melting (e.g., Francis et al., 1989; de Silva, 1989; Lucassen et al., 1999; Richards and Villeneuve, 2002; Richards et al., 2006).

The supra-adakitic concentrations of Y and Yb in the most mafic samples are perhaps the strongest evidence that these rocks are not derived by partial melting of a subducting slab but are instead consistent with a partial melting origin within the hydrated mantle wedge and subsequent magmatic evolution by MASH and AFC processes. Individual volcanoes and flows within volcanic sequences indicate garnet control on trace element compositions, yielding locally high Sr/Y and La/Yb values. However, these very localized variations in both space and time preclude any fundamental change in magma source and instead imply tapping of discrete batches of magma that have evolved at different crustal depths (e.g., Hildreth and Moorbath, 1988; Richards and Villeneuve, 2002).

Southern Central Andes (28°–38°S)

A smaller dataset of Neogene volcanic rocks from the southern Central Andes (southern part of the Central volcanic zone and northern part of the Southern volcanic zone; Kay et al., 1991; summarized in Table 4) reveals similar relationships to those described above, with increasing La/Yb ratios and decreasing minimum Yb concentrations with SiO_2, extending into the adakitic La/Yb versus Yb field for some evolved dacitic rocks (Fig. 10a-c). In detail, however, the dataset includes samples from two distinct evolutionary trends: one as described above, and a second group in which La/Yb increases only slightly with SiO_2, and Yb concentrations either remain constant or scatter to higher values. Kay et al. (1991) attributed these differences to the effect of increasing crustal thickness from the Oligocene to Miocene, resulting in higher La/Yb ratios in younger rocks. The most felsic dacites and rhyolites show the greatest divergence from these trends, as noted in the northern Central Andean suite, likely reflecting crustal contamination processes. Smooth fractionation trends for major elements (Fig. 10d) and generally low Ni concentrations (avg = 13 ppm) confirm the evolved nature of these suites, and moderately radiogenic Sr isotopic compositions (avg $^{87}Sr/^{86}Sr = 0.7049$) attest to crustal interaction.

The 28° to 38°S segment of the Central Andes is a region of shallow to flat subduction and thickened continental crust (55–65 km; Hildreth and Moorbath, 1988), with significantly less volcanism than in the region to the north. Gutscher et al. (2000) suggested that such a tectonic configuration could lead to slab melting and eruption of small volumes of adakitic magma due to anomalous heating of the leading edge of the slab during the early stages of flat-slab subduction. However, a much simpler explanation for the garnet signature in some of the volcanic rocks from the southern Central Andes is thickening of the continental crust through which subduction zone magmas must pass (Kay and Mpodozis, 2002; Kay et al., 2005). Kay et al. (1991, 1999) inferred that the lower crust in this region varied from garnet amphibolite to garnet granulite with progressive partial melting during the Neogene, thus yielding progressively more Yb-depleted (high La/Yb) and isotopically contaminated magmas. Because it is hard to imagine how a mantle- or lower plate-derived magma could pass through 55 to 65 km of felsic continental crust without interaction and differentiation (Pearce and Peate, 1995), the geochemical characteristics of these evolved magmas almost certainly resulted from such crustal process, rendering inferences about source processes untenable (Davidson, 1996).

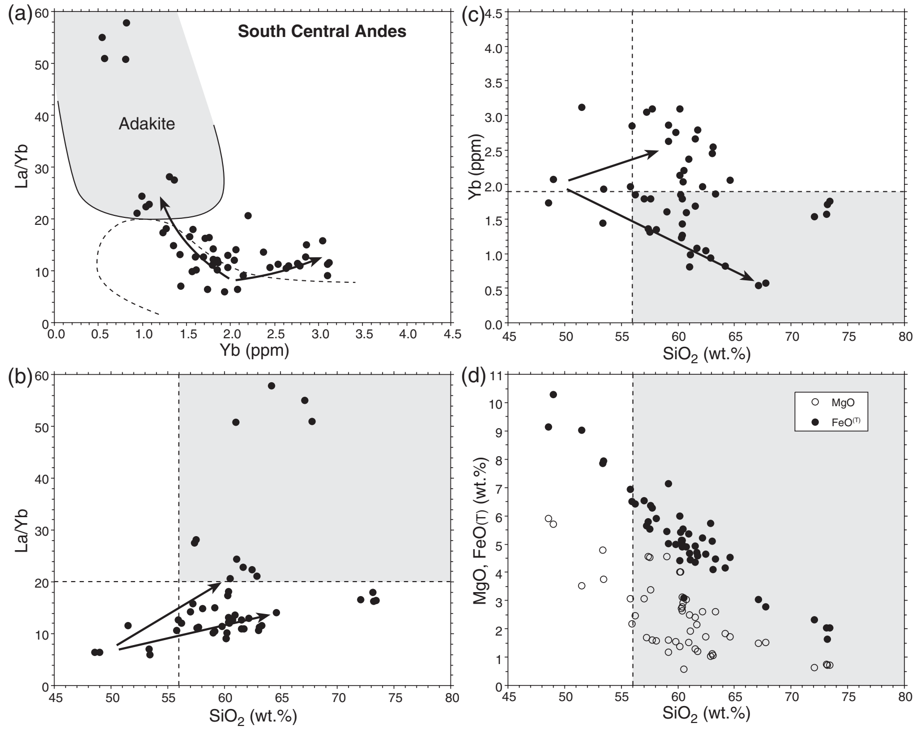

FIG. 10. Geochemical data for volcanic rocks from the southern Central Andes (28°–38°S; data from Kay et al., 1991). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

Northern Andes: Pichincha, Ecuador

There is considerable disagreement in the literature regarding the origin of high Sr/Y volcanic rocks in the Northern Andes of Ecuador. Beate et al. (2001), Bourdon et al. (2002), and Samaniego et al. (2005) favor a slab-melting model related to shallow subduction of the Carnegie Ridge, whereas Garrison and Davidson (2003), Chiaradia et al. (2004), and Bryant et al. (2006) favor MASH or AFC models acting on wedge-derived magmas passing through thickened continental crust. Data from the Pichincha volcano are illustrative of the problem (Fig. 11, Table 4; Bourdon et al., 2002). The suite does indeed plot within the adakitic Sr/Y versus Y field (Fig. 11a) but shows a well-defined trend of increasing Sr/Y (decreasing Y and weakly increasing Sr) with increasing SiO_2 (Fig. 11b-c, i). Moreover, most samples plot well below the adakitic La/Yb versus Yb field (Fig. 11d) and fractionate barely into the field for two dacites, with steadily decreasing Yb concentrations (Fig. 11e-f). These and other fractionation trends shown in Figure 11g-h suggest that the parental magma to this suite was not adakitic: a projection of the Sr/Y fractionation trend to more mafic compositions suggests that had rocks of only a few percent lower silica content been available for sampling (~54 wt % SiO_2) they would likely have had subadakitic Sr/Y ratios, and almost all of the samples have subadakitic La/Yb ratios. The well-defined trends of decreasing Y and Yb, and weakly increasing Sr concentrations with increasing SiO_2 are strongly suggestive of a fractionation control, likely by amphibole with limited plagioclase segregation (both recorded as phenocryst phases by Bourdon et al., 2002).

Nevertheless, this example is not clear-cut, and other features of the suite, such as relatively unradiogenic Sr isotope compositions (avg $^{87}Sr/^{86}Sr$ = 0.7041) and high Mg number and Cr and Ni concentrations (Table 4; Bourdon et al., 2002), would be consistent with a model of mantle wedge-modified slab melts, were it not for the inconsistencies noted above.

REE fractionation in volcanic suites from normal calc-alkaline arcs

As noted above, fractionation of garnet or hornblende from intermediate-composition magmas will yield distinctive chondrite-normalized (CN) REE patterns because of the strong affinity of garnet for HREE and moderate affinity of hornblende for MREE. Garnet fractionation or separation from melt in a restite should therefore yield increasing LREE/MREE and MREE/HREE ratios, whereas hornblende fractionation should yield increasing LREE/MREE but steady or decreasing MREE/HREE ratios ≈ or <1 (i.e., listric patterns; Fig. 6). When $(La/Sm)_{CN}$ (representing LREE/MREE) and $(Dy/Yb)_{CN}$ (representing MREE/HREE) ratios from the normal calc-alkaline arcs examined above are plotted against SiO_2 as a measure of fractionation (Fig. 12), it is observed that $(La/Sm)_{CN}$ increases from ~2 in mafic rocks to a maximum of ~7 at ~70 wt percent SiO_2 and then declines sharply, whereas $(Dy/Yb)_{CN}$ shows a steady but slight decline from values ≈1 throughout the fractionation range. These trends are consistent with hornblende fractionation from basaltic andesite through dacite, likely followed by fractionation of strongly LREE enriched accessory minerals such as monazite or

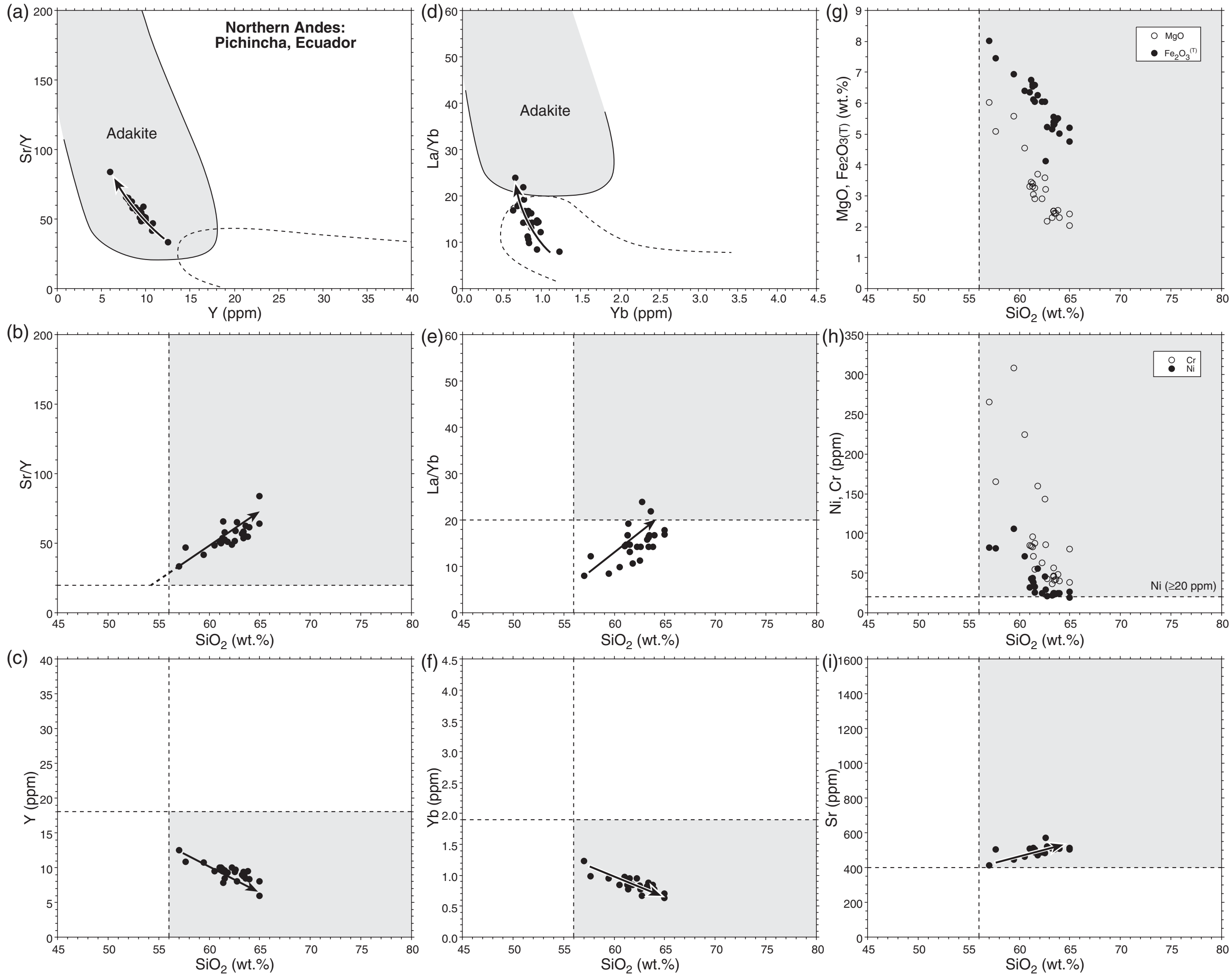

FIG. 11. Geochemical data for volcanic rocks from the Pichincha volcano in the northern Andes of Ecuador (data from Bourdon et al., 2002, with additional illustrated but unlisted data kindly supplied by E. Bourdon, pers. commun., 2006). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

allanite, and to a lesser extent apatite and titanite, from felsic magmas (e.g., Miller and Mittlefehldt, 1982; Gromet and Silver, 1983). Thus, despite including samples that fit some of the adakitic compositional criteria listed in Table 1, the detailed behavior of REE (especially MREE and HREE) in these suites is inconsistent with a significant involvement of garnet fractionation or, therefore, a slab-melting origin, as concluded by most of the authors cited above.

Assessment of Some Adakite-like Suites Related to Porphyry Systems

Since publication of papers by Thiéblemont et al. (1997) and Sajona and Maury (1998) that argued for an adakitic affinity for some volcanoplutonic rocks associated with some porphyry and epithermal Cu-Au deposits in the Philippines, rocks with some adakitic characteristics (most commonly, high Sr/Y) have been identified, or reinterpreted, as adakites from numerous metallogenic regions around the world, including other parts of the southwest Pacific, China, Tibet, Chile, Péru, Ecuador, Mexico, and the southwestern United States. Several authors have inferred from these compositions a direct relationship between slab melting and mineralization, pointing to a paper by Mungall (2002) which argued that slab melts might be uniquely associated with Au and Au-rich Cu deposits. Mungall (2002) proposed that slab melts should be highly oxidized (high in Fe^{3+}, due to sea-floor oxidation) in comparison to moderately oxidizing slab-dehydration fluids, and that reaction of these slab melts with the mantle wedge would cause extensive oxidation. Note, however, that Wang et al. (2007) have recently reported that if subducted organic-rich trench sediments also melt, which is perhaps a more likely process, then the resultant mixed slab melts might in fact be reduced rather than oxidized. If oxidation does take place, sulfide minerals that host chalcophile and siderophile

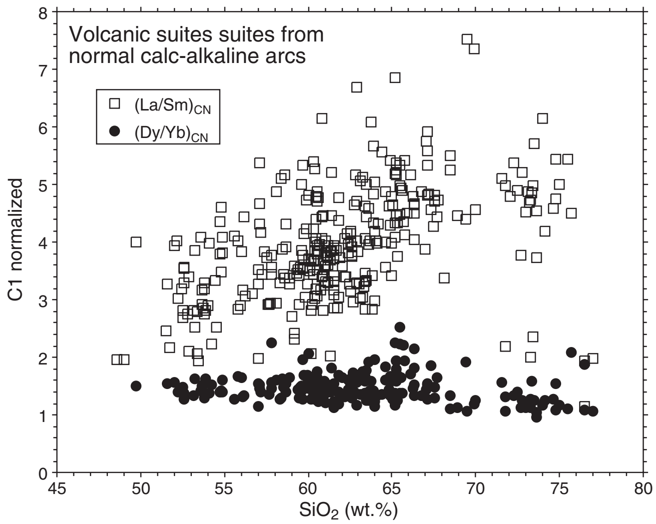

FIG. 12. C1 chondrite-normalized $(La/Sm)_{CN}$ and $(Dy/Yb)_{CN}$ ratios vs. SiO_2 for normal arc volcanic rocks from the Central Andes and Ecuador (sources of data as for Figs. 9–11). Normalization values of Sun and McDonough (1989).

elements in the mantle wedge would break down, releasing these metals to subsequent partial melts (i.e., mantle wedge-hybridized adakites, or high Mg andesites). Although this theory has conceptual merit (the importance of a high oxidation state in arc metallogeny is widely recognized because of its effect on sulfur speciation and metal solubilities in magmas; e.g., Hamlyn et al., 1985; Candela, 1992; Wyborn and Sun, 1994; Richards, 2003; Jugo et al., 2005), it is based on many untested assumptions about the exact nature of slab melts, their interaction with the mantle wedge, and the subsequent behavior of metals during partial melting, magma ascent, and hydrothermal fluid evolution. It also assumes that normal calc-alkaline petrogenetic processes cannot achieve the same results, contrary to the models of Cline and Bodnar (1991) and Cline (1995).

Below, seven examples of arc volcanoplutonic suites associated with porphyry and epithermal mineralization from around the world in which adakite-like rocks can be recognized are reviewed. It should be emphasized that, except where noted, the papers cited do not claim an adakitic or slab-melting relationship for these suites. A common theme emerges, as noted in previous sections, of differentiation from nonadakitic mafic parental magmas into the adakite range of some parameters for evolved felsic rocks, which can most simply be explained by hydrous fractionation of hornblende and/or titanite, while plagioclase fractionation is suppressed.

Papua New Guinea and the Solomon Islands

The southwest Pacific region is one of complex microplate tectonics, involving interactions between numerous small oceanic plates, continental fragments, and island arcs, caught up between the northward-migrating Australasian plate, the westward-migrating Pacific Ocean plate, and Eurasia. Numerous porphyry Cu-Au and epithermal Au deposits occur in the region associated with arc volcanoplutonic rocks, and these magmatic suites commonly contain some rocks that display one or more adakitic geochemical characteristics. Data for porphyry-associated intrusive rocks from the island of New Britain are shown in Figure 13 (Hine and Mason, 1978), and data from other mineralized suites in Papua New Guinea and the Solomon Islands are shown in Figure 14 (Mason and Macdonald, 1978; summarized in Table 4). Rare earth element data were not published for these suites, but some samples plot within the adakitic Sr/Y versus Y field, with particularly high Sr/Y values occurring in plagioclase-quartz porphyries from Kulu and Plesyumi in New Britain (Fig. 13a-b; Hine and Mason, 1978). High Sr concentrations in these porphyries (Fig. 13f) might be explained by accumulation of the 15 to 20 percent of plagioclase phenocrysts reported in these rocks, whereas low Y concentrations might reflect fractionation of hornblende and titanite, both of which were also reported to be present. Furthermore, Hine and Mason (1978) noted that the porphyry deposits were formed relatively late in the development of the arc, after the crust had thickened to 20 to 30 km. The remaining samples are characterized by supra-adakitic Y concentrations at 56 wt percent SiO_2 (Figs. 13c, 14c), with clear fractionation trends to lower Y values in felsic rocks in the Papua New Guinea-Solomons suite (Fig. 14c). Both suites also display smooth fractionation trends for major and other trace elements from basaltic to rhyolitic compositions in Harker diagrams (Figs. 13d-e, 14d-e), with sub-adakitic concentrations of Cr and Ni in most felsic samples (>56 wt % SiO_2). These suites therefore appear to be normal calc-alkaline island-arc magmas derived from basaltic parents, with high Sr/Y values locally being developed in some late porphyry-related instrusions by crystal fractionation and accumulation processes.

Philippines

Volcanic rocks from the Philippines that have been termed adakites by some authors have already been discussed above. Two other suites of intrusive rocks associated with porphyry Cu-Au deposits are examined in Figure 15 (from the western Luzon arc: Imai, 2002) and Figure 16 (from Tampakan in Mindanao: Rohrlach, 2002; Rohrlach and Loucks, 2005; data are summarized in Table 4). Both suites contain samples that plot in the adakitic Sr/Y versus Y field (Figs. 15a, 16a), but the Tampakan suite has La/Yb ratios well below the adakitic minimum (Fig. 16d; no Yb data were available for the western Luzon suite). Sr/Y values increase from ~20 in basalts and basaltic andesites to >160 in some dacites, with a smooth decrease in Y and increase in Sr concentrations (Figs. 15b-c, f, 16b-c, i). Smooth fractionation trends are also shown for major elements (Figs. 15d, 16g), and Cr and Ni concentrations are mostly low (Figs. 15e, 16h). As in the case of the volcanic rocks from the Philippines discussed above, it is concluded that these data are consistent with magmatic AFC processes under hydrous conditions, most likely involving hornblende ± titanite fractionation in the absence of significant plagioclase separation. Rohrlach (2002) specifically related the Tampakan suite to the terminal stages of subduction, with mantle wedge-derived magmas undergoing lower crustal fractionation in the presence of up to 5 wt percent H_2O. Imai (2002) further noted that porphyry Cu deposits in western Luzon

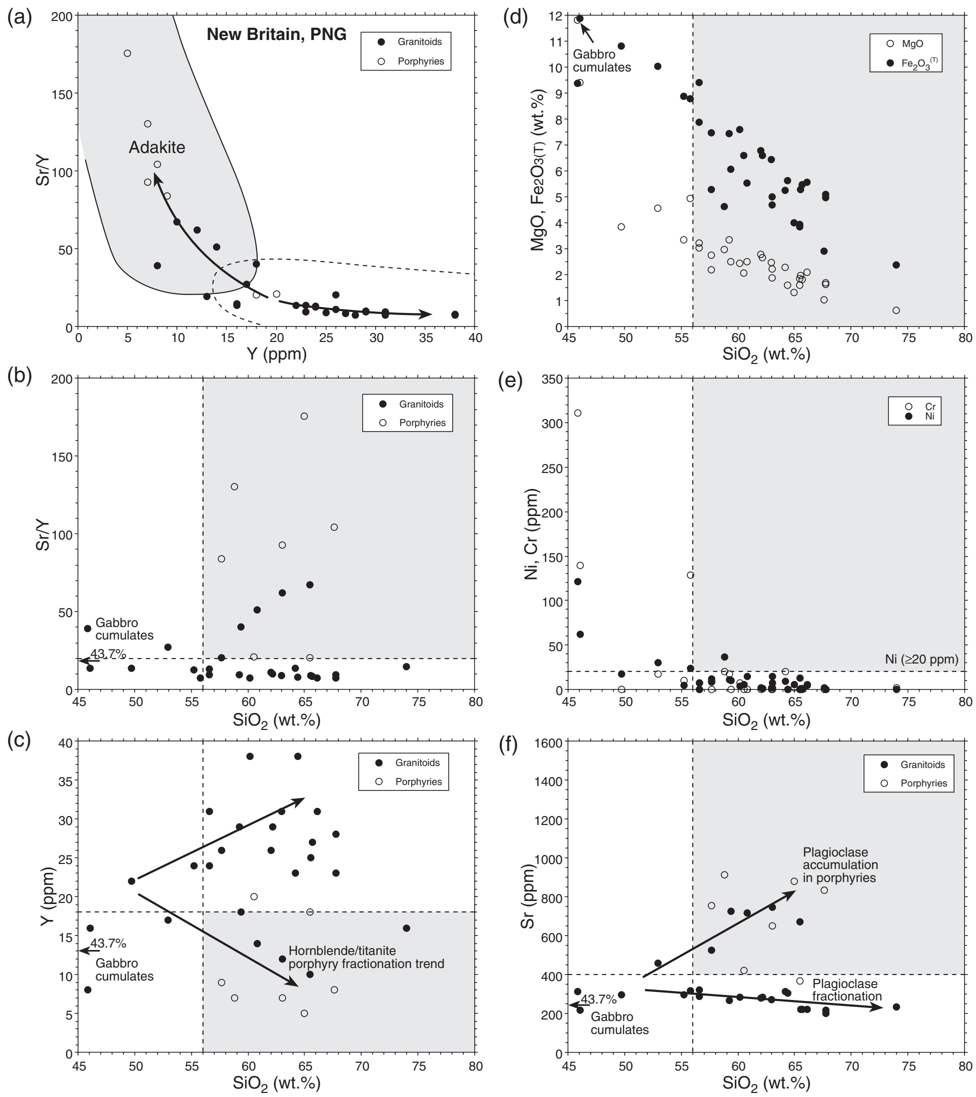

FIG. 13. Geochemical data for porphyry copper-associated intrusive rocks in New Britain, Papua New Guinea (data from Hine and Mason, 1978). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

are not necessarily related to intrusive rocks with high Sr/Y, thus undermining any unique link even to adakite-like rocks, regardless of origin.

China

Wang et al. (2006a, b) presented analyses of igneous rocks associated with porphyry Cu and volcanic-hosted Cu-Au deposits from the Dexing area of southern China and the Luzong area of eastern China, respectively, which include samples that plot in the adakitic Sr/Y versus Y and La/Yb versus Yb fields (summarized in Table 4). However, these rocks have relatively radiogenic Sr isotope ratios (avg $^{87}Sr/^{86}Sr$ = 0.7057 and 0.7047, respectively) and evolved from basaltic or andesitic compositions. Wang et al. (2006a, b) ruled out a slab-melting origin for these suites largely on geodynamic grounds, because they were emplaced during a period of crustal extension, not subduction. They suggested that these magmas might have been formed by partial melting of delaminated lower crust below depths of 50 km.

Sierrita, Arizona

Data from the Sierrita porphyry copper deposit (Anthony and Titley, 1988) are shown in Figure 17 and summarized in Table 4. Most of the samples, except two highly fractionated rhyolites and a diorite, plot within the adakitic La/Yb versus Yb field (Fig. 17a) but define a trend of increasing La/Yb and decreasing Yb with increasing SiO_2 (excluding the two low La/Yb rhyolites: Fig. 17b-c). Sr concentrations also decrease with increasing SiO_2 (Fig. 17f). Major elements define rough fractionation trends from diorite to aplite and rhyolite (Fig. 17d), and Ni concentrations are low (<15 ppm; Fig. 17e). Strontium and neodymium isotope compositions are also highly evolved (avg $^{87}Sr/^{86}Sr$ = 0.7081 and ε_{Nd} = –7.1: Anthony and Titley, 1988). As concluded by these authors, these

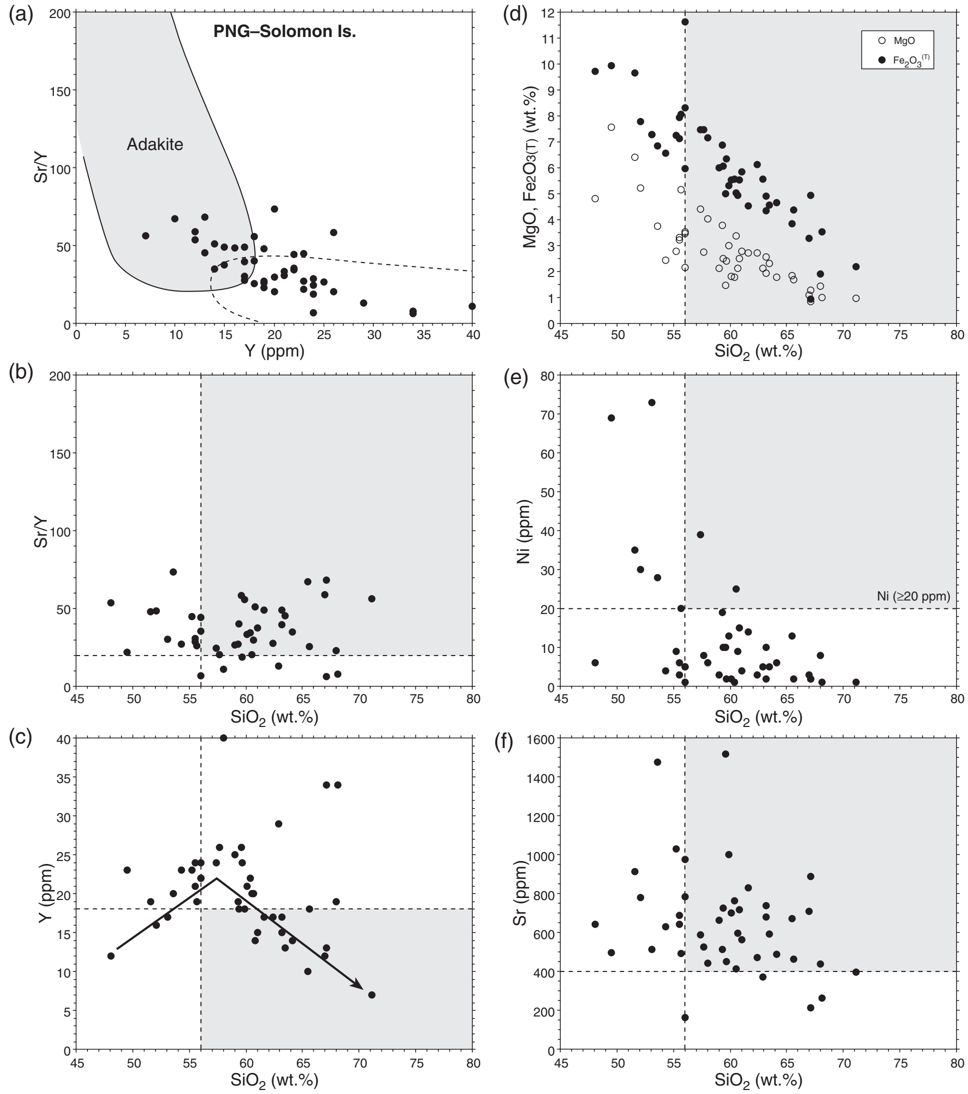

FIG. 14. Geochemical data for other porphyry copper-associated intrusive rocks in Papua New Guinea and the Solomon Islands (data from Mason and Macdonald, 1978). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

geochemical characteristics are consistent with amphibole and plagioclase fractionation combined with progressive assimilation of continental crustal materials (AFC processes), a conclusion supported by Lang and Titley (1998). The adakite-like La/Yb ratios appear to have no source significance but instead are products of amphibole fractionation from hydrous magmas, as also suggested by listric-shaped REE patterns (fig. 6 of Anthony and Titley, 1988; figs. 6, 7, and 16 of Lang and Titley, 1998).

Mezcala, Mexico

González-Partida et al. (2003) presented data for Paleocene granitoids from the Mezcala district, which are regionally associated with porphyry Cu and local Au-Fe skarn deposits, and suggested that the rocks were adakites formed by slab melting. Most of the data plot within the adakitic Sr/Y versus Y and La/Yb versus Yb fields in Figure 18a and d but define trends of increasing Sr/Y and La/Yb and decreasing Y and Yb with increasing SiO_2 (Fig. 18b-c, e-f). In particular, the least evolved samples (~59 wt % SiO_2) contain 19 ppm Y, and therefore this fractionation trend starts outside the adakite Sr/Y versus Y field and fractionates into it. Major elements also define normal fractionation trends (Fig. 18g-h), and normalized REE data display listric patterns (fig. 5 of González-Partida et al., 2003), characteristic of amphibole fractionation. The authors reported that biotite and amphibole are abundant in these rocks, including hornblende autoliths (cognate xenoliths) in some intrusions, and that apatite, zircon, titanite, and titanomagnetite are common as accessory phases. González-Partida et al. (2003) also reported that prior to the time of intrusion, the Laramide orogeny had caused thickening of the continental crust to ~40 km (>50 km in their abstract). In combination, the evidence of extensive hornblende fractionation (hornblende autoliths and phenocrysts, listric REE patterns), the presence of apatite, zircon, and titanite as accessory phases, and the evolved compositions of the rocks

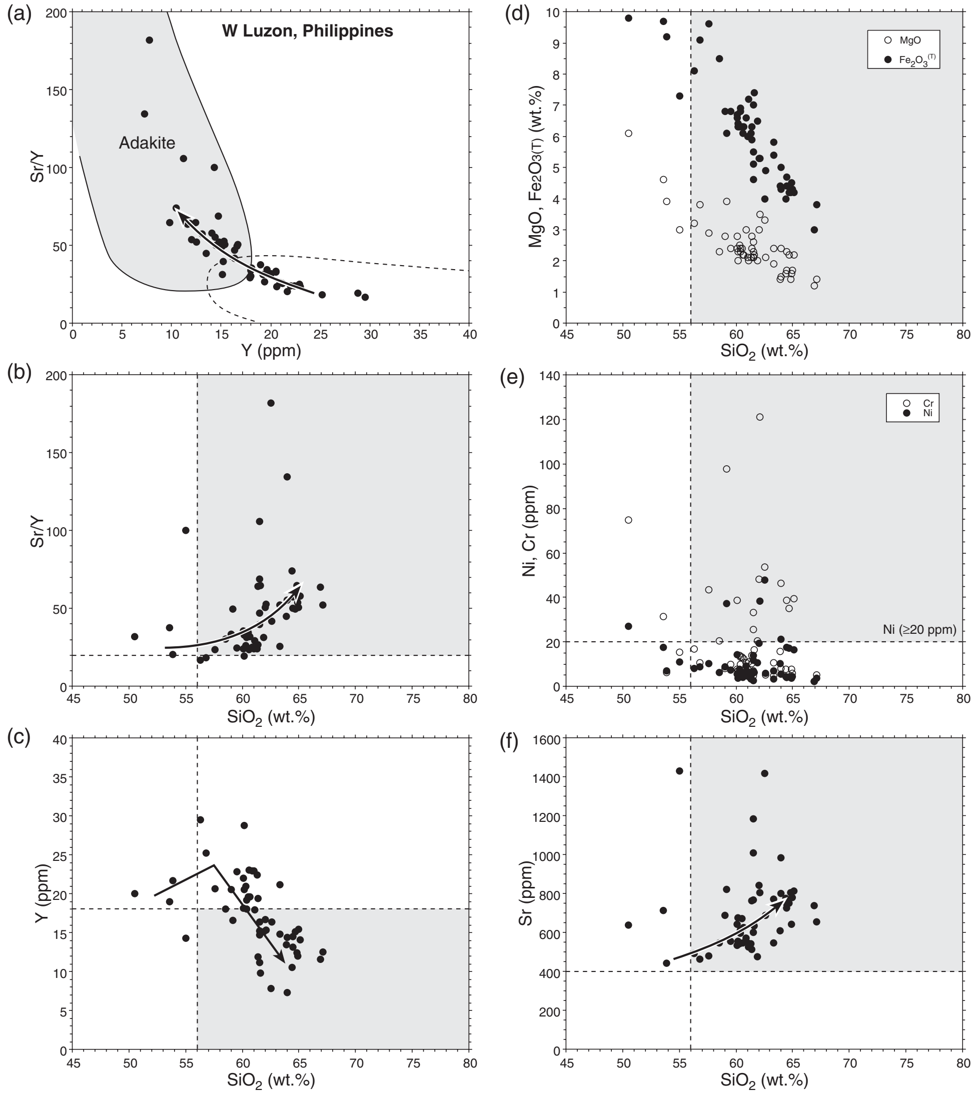

FIG. 15. Geochemical data for intrusive rocks associated with porphyry Cu-Au deposits from the western Luzon arc, Philippines (data from Imai, 2002). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

(to 66.6 wt % SiO_2) strongly suggest a fractional crystallization origin for the adakite-like characteristics of these rocks, which were likely developed during ascent through a thickened continental crustal column.

Central Chile

Hollings et al. (2005) reported data from Oligocene-Pliocene volcanic rocks associated with porphyry Cu and epithermal Au deposits in Central Chile and suggested that high Sr/Y and La/Yb values in the Pliocene La Copa rhyolite reflected a sudden geodynamic transition related to subduction of the Juan Fernández ridge. Data for this suite are shown in Figure 19, where it can be seen that the Pliocene rhyolites and some Oligocene-Miocene basalts and basaltic andesites plot in the Sr/Y versus Y adakite field (Fig. 19a), but that the Oligocene-Miocene rocks define a trend of roughly decreasing Sr/Y and Sr with increasing SiO_2, and many have >18 ppm Y (Fig. 19b-c, i). All of the Oligocene-Miocene rocks fall below the La/Yb versus Yb adakite field (Fig. 19d) and most have >1.9 ppm Yb (Fig. 19f) and <20 ppm Ni (for compositions >56 wt % SiO_2; Fig. 19h). These data are not dissimilar to those reported from the Central Andes (Figs. 9, 10) and can be explained simply in terms of magmatic differentiation. Only the La Copa rhyolite warrants further consideration as a possible adakite, but its extremely evolved chemical composition (~71 wt % SiO_2) and relatively evolved isotopic signatures ($^{87}Sr/^{86}Sr$ = 0.7043 and ε_{Nd} = 1.7) are indicative of significant crustal contamination via AFC processes, as is the case for most Andean rhyolites. In particular, fractionation of small amounts of titanite or other Y- and HREE-rich accessory minerals such as zircon or xenotime, common in highly fractionated rocks, could quickly deplete these magmas in Y and Yb (Förster, 1998; Bachman et al., 2005).

A similar argument can be made for samples with high Sr/Y and La/Yb ratios from the Los Pelambres porphyry Cu deposit (Reich et al., 2003), where highly evolved samples range

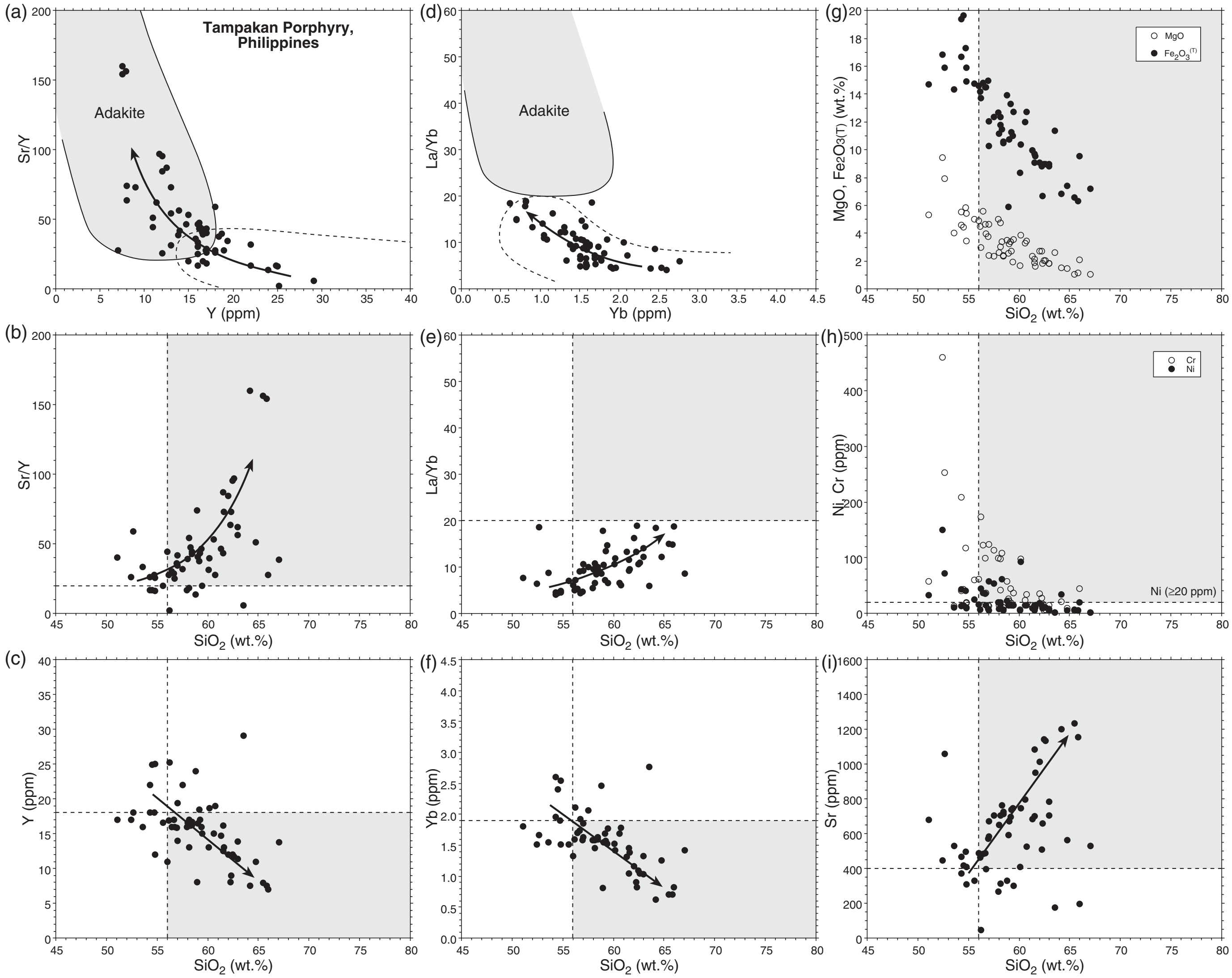

FIG. 16. Geochemical data for intrusive rocks associated with the Tampakan porphyry copper deposit, Mindanao, Philippines (data from Rohrlach, 2002). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

from 63 to 72 wt percent SiO_2, Y and Yb (both within the adakitic range) show decreasing concentrations with increasing SiO_2, Sr/Y and La/Yb increase with SiO_2, Ni and Cr are both below 20 ppm, Rb exceeds 65 ppm, and Sr and Nd isotope compositions are relatively evolved (avg $^{87}Sr/^{86}Sr$ = 0.7047 and $\varepsilon_{Nd} = -0.1$).

La Escondida, northern Chile

La Escondida is the world's largest porphyry Cu mine in terms of production and is located in the main Eocene-Oligocene porphyry belt of northern Chile. Richards et al. (2001) presented geochemical data for the porphyries, related dioritic intrusions, and volcanic rocks, and concluded from evidence of progressive MREE-HREE depletion and accentuation of listric-shaped REE profiles with increasing silica content (Fig. 6) that the magmas had evolved principally by hornblende fractionation during crustal differentiation. These data are illustrated in Figure 20, where it can be seen that the samples mostly fall within the adakitic Sr/Y versus Y field, but only the most evolved rocks plot in the adakitic La/Yb versus Yb field (Fig. 20a, d). The suite displays steadily decreasing Y, Yb, and Sr concentrations (Fig. 20c, f, i), and roughly increasing Sr/Y and La/Yb ratios with differentiation (Fig. 20b, e), consistent with hornblende, titanite, and plagioclase fractionation from a nonadakitic basaltic andesitic parental magma.

REE fractionation

A plot of $(La/Sm)_{CN}$ and $(Dy/Yb)_{CN}$ ratios versus SiO_2 for samples from the Tampakan, Mezcala, Central Chilean, and Escondida porphyry systems (Fig. 21) reveals similar trends to those observed for other calc-alkaline arc rocks (Fig. 12). The $(La/Sm)_{CN}$ ratios generally increase with fractionation until rhyolitic compositions are reached, whereas $(Dy/Yb)_{CN}$ ratios show a flat (≈1) or slightly decreasing trend. As in the case of the unmineralized arc rocks, these trends are

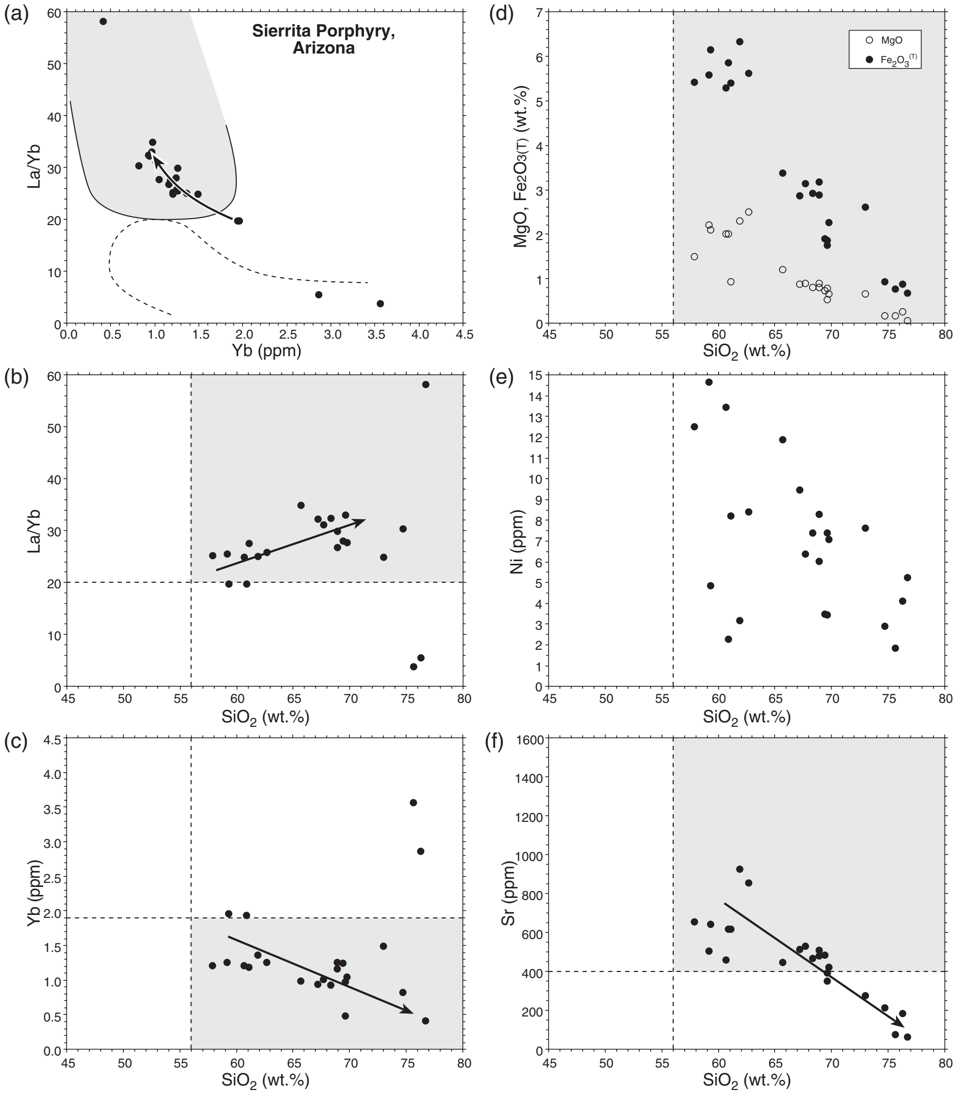

FIG. 17. Geochemical data for intrusive rocks from the Sierrita porphyry copper deposit, Arizona, United States (data from Anthony and Titley, 1988). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

consistent with crustal-level fractionation of hornblende and other minerals from intermediate-composition magmas but not with significant amounts of residual or fractionating garnet as required by a slab-melting origin.

Discussion

Are adakites slab melts?

The theory that subducting oceanic crust will melt under some conditions is not contested here, and slab melting may have been a common occurrence in the Archean, if less common or rare in the Phanerozoic. However, whether the products of such melting can be recognized in igneous rocks erupted at the surface, and what the characteristics of such rocks should be, is much less clear and is widely debated in the petrology literature. Pure slab melts are probably never erupted at surface, and the consensus definition of an adakite seems to be an evolved slab melt that has interacted extensively with the asthenospheric mantle wedge during ascent, leading to anomalously high Mg number and Ni and Cr concentrations as well as anomalous Nb/Ta and Zr/Sm ratios when compared to normal calc-alkaline arc rocks of similar SiO_2 content (Rapp et al., 2003). Adakites so defined are at least one step, and likely two or more steps, away from being pristine slab melts, those steps being: (1) interaction with the mantle wedge and possible freezing; (2) if frozen, remelting of the modified mantle wedge; and (3) in continental arcs and mature oceanic arcs, differentiation and possible crustal interaction (AFC processes) upon ascent. However, Leeman (1983, p. 561) warned that such processes render inferences about original partial melting processes very difficult to constrain: "Studies of arc volcanic rocks may yield misleading conclusions concerning processes of magma generation related to subduction unless evolutionary processes are defined and their effects considered." Davidson (1996, p. 259) similarly noted that "Protracted differentiation at arcs, commonly

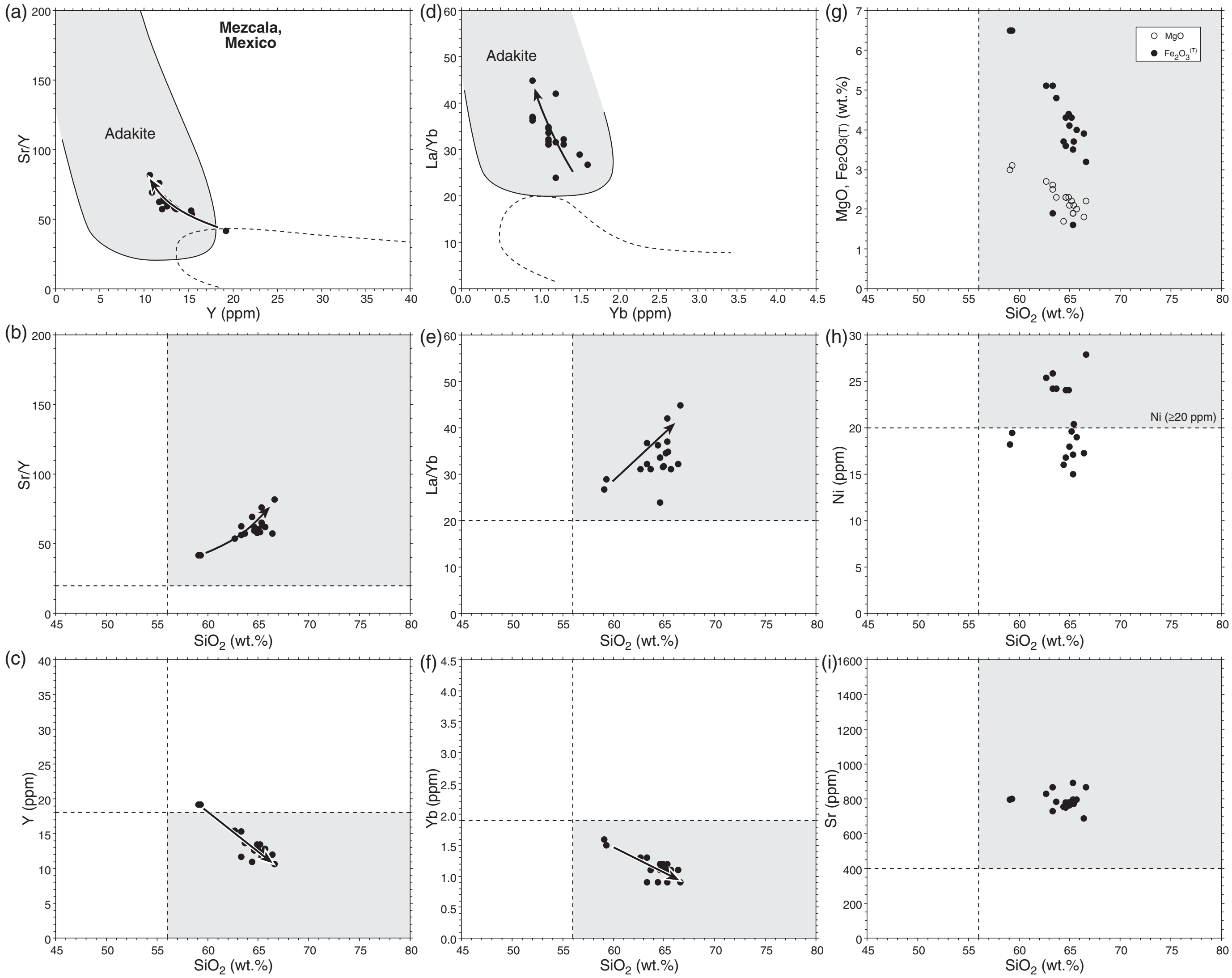

FIG. 18. Geochemical data for Paleocene granitoids from the Mezcala district, Mexico (data from González-Partida et al., 2003). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

open system, can invalidate the inversion of geochemical data to constrain source contributions."

Adakites pose a particular problem, because the criteria for their recognition are a mixture of the expected characteristics of primary felsic (dacitic) slab melts and the actually more mafic (high Mg andesitic) products of interaction of those melts with depleted mantle peridotite (Table 1). The result is a set of ambiguous criteria, individual components of which can fit a wide range of rock types formed by other more common processes.

Thus, none of the Phanerozoic suites examined here (Table 4), including the type suite from Adak Island, fit all of the proposed criteria for classification as adakites, the closest fits being the Pichincha suite from Ecuador, and Cook Island, Austral Andes. This has led some advocates of the slab-melting theory, such as Defant and Kepezhinskas (2002, p. 256), in reply to a discussion of their 2001 paper by Conrey (2002), to propose that "adakite should be a general term used for those rocks with adakitic geochemical characteristics and should have no 'process' implications." Nevertheless, these authors maintained that adakites were "probably predominantly slab melts, because most of the time the crust is not thick enough to produce garnet stability (>40 km) in the lower crust" (Defant and Kepezhinskas, 2002, p. 256). As shown above, however, garnet is not uniquely required for development of the moderately high Sr/Y and La/Yb signatures found in many arc suites, which can also be achieved through hydrous fractionation of common phenocrysts phases such as hornblende and titanite.

Are slab melts required for porphyry Cu formation?

The global occurrence of porphyry Cu deposits in both oceanic and continental volcanic arcs and their remarkably uniform gross characteristics seem to require common and reproducible metallogenic processes. Thus, it appears that unusual tectonic or magmatic processes are not critical for the formation of porphyry Cu deposits.

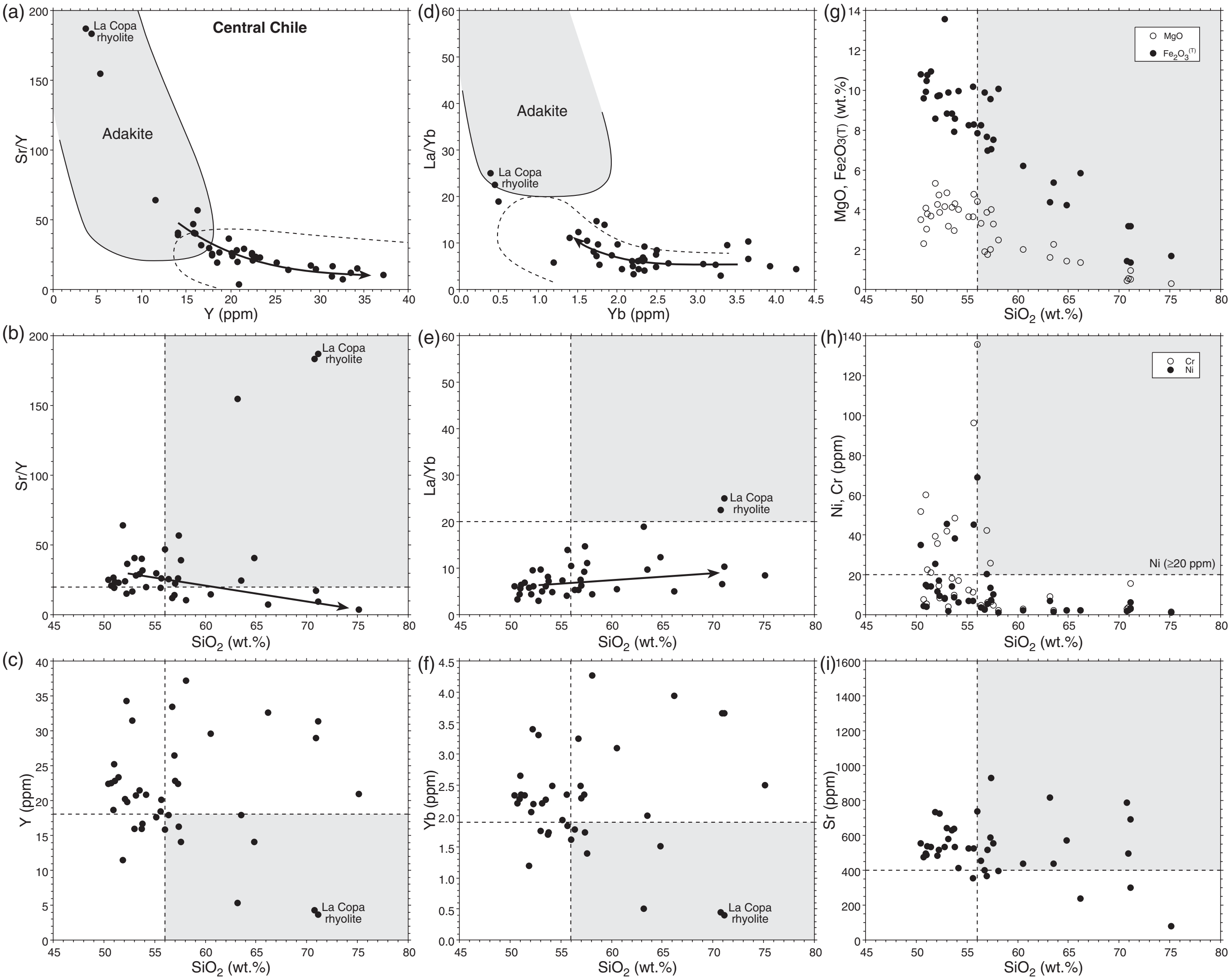

FIG. 19. Geochemical data for Oligocene-Pliocene volcanic rocks associated with porphyry Cu and epithermal Au deposits in Central Chile (data from Hollings et al., 2005). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

Porphyry Cu deposits have been explored for and studied in detail for several decades, and a unique geochemical fingerprint that differentiates fertile from infertile magmatic suites has so far proved elusive (e.g., Gustafson, 1979). Nevertheless, a subtle relative depletion of Y and HREE in fertile suites has been noted in several instances (e.g., Baldwin and Pearce, 1982; López, 1982). Oyarzun et al. (2001) suggested on the basis of previously published Sr and Y data that such high Sr/Y, low Y rocks from northern Chile were adakitic slab melts, and that slab melting was a critical process in the origin of magmas that form giant porphyry Cu deposits.

A more thorough examination of these and other magmatic suites associated with porphyry Cu deposits from around the world confirms that some deposits are associated with intrusive and volcanic suites in which some samples fit some of the adakitic criteria, but that in all cases they can be shown to be highly differentiated rocks, commonly with evolved isotopic compositions reflecting crustal interaction processes. The most primitive members of these suites are commonly more mafic than the minimum silica content for adakites (56 wt % SiO_2), which have then evolved to more felsic compositions by MASH and/or AFC processes, in some cases attaining one or more adakitic characteristics (most commonly, high Sr/Y).

None of the mineralized suites illustrated above fit all of the criteria for definition as adakites (Table 4) but can instead readily be shown to have derived what adakite-like signatures they have from crustal differentiation processes. Thus, it is concluded that the proposed connection between adakites formed by slab melting plus mantle hybridization and the formation of porphyry deposits does not hold.

Nevertheless, some of the geochemical characteristics of adakite-like rocks may indeed have metallogenic significance. In particular, the high Sr/Y and La/Yb characteristics of some porphyry-related magmas probably reflect the fundamentally hydrous and evolved nature of those lithologic units, which favor amphibole over plagioclase fractionation, as noted

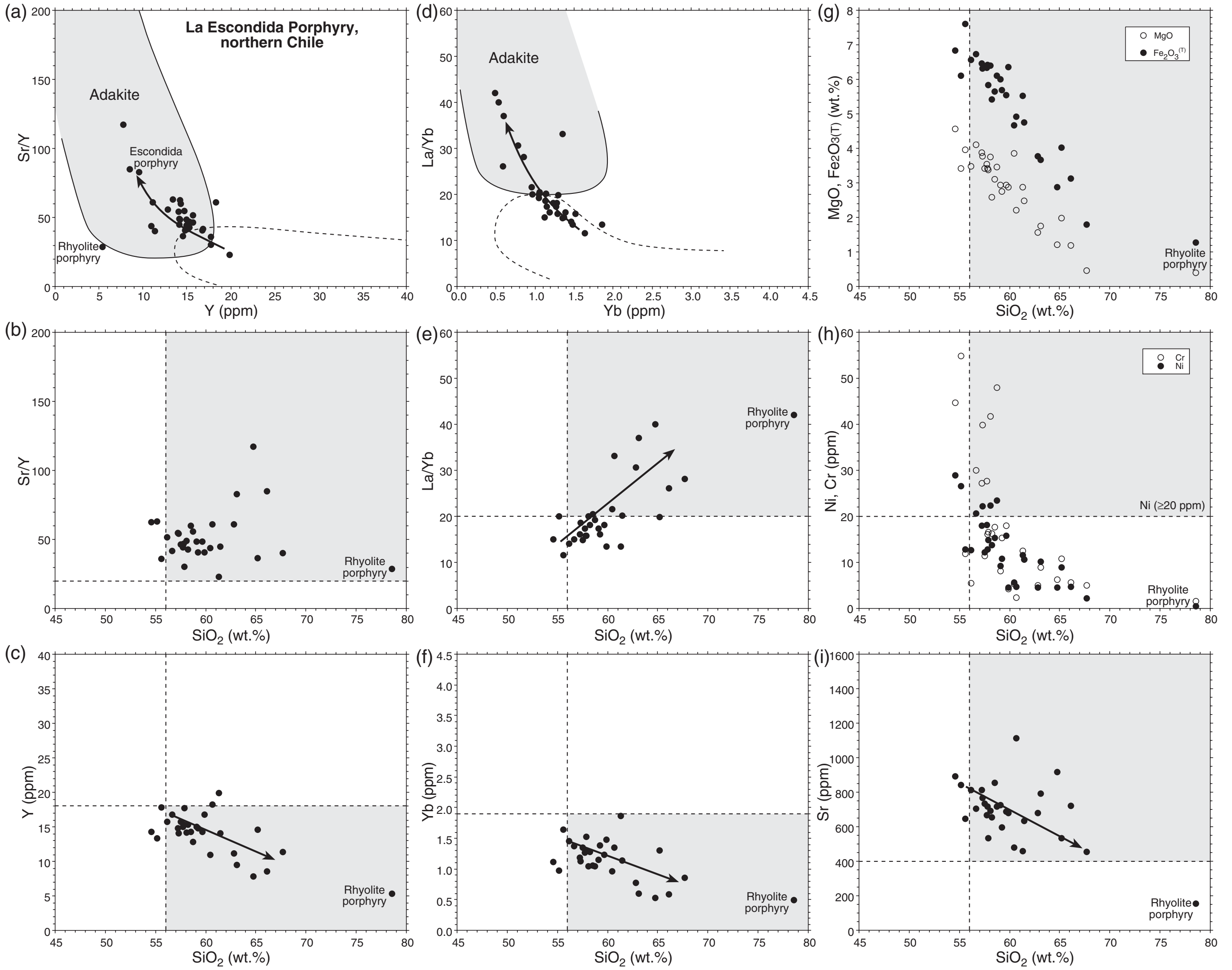

FIG. 20. Geochemical data for porphyry and related intrusions, and volcanic rocks from the Escondida area, northern Chile (data from Richards et al., 2001). Plots show fields and limits for adakitic compositions in gray; arrows show fractionation trends defined by variations with increasing silica content. See text for discussion.

above. High magmatic volatile contents and extensive magmatic differentiation processes are well understood to be key to the formation of metalliferous magmatic hydrothermal fluids, which are exsolved at relatively late stages of magmatic evolution after emplacement in the middle to upper crust (e.g., Burnham, 1979; Hedenquist and Lowenstern, 1994; Candela and Piccoli, 2005). Kay et al. (1999) and Richards (2003) noted that many large porphyry belts form at late stages in arc development, commonly after significant crustal thickening (see also Haschke et al., 2002). It may therefore be that maturation of MASH- and AFC-type magma-processing systems is required before a sufficient flux of heat and evolved, volatile-rich magmas can extend into the upper crust, where porphyry deposits form. Such late-stage, fertile magmas would be more likely to display deep crustal fractionation signatures, perhaps even involving garnet, than earlier, less evolved compositions.

Might slab melts be involved in Au-rich porphyry and related deposits?

Mungall (2002) proposed that slab melts might be specifically involved in the evolution of Au-rich porphyry systems because of their hypothesized potential to oxidize the mantle wedge (but see Wang et al., 2007) to the point of complete destruction of accessory sulfide phases, resulting in the release of highly siderophile elements such as Au and platinum group elements to the melt phase. The second part of this theory is attractive and has been proposed by others to result from normal mantle-wedge oxidation plus multistage partial melting, such as occurs during arc collisions and subduction reversals (e.g., Hamlyn et al., 1985; Solomon, 1990; Wyborn and Sun, 1994; Richards, 1995, 2005). However, the products of such transitory melting events are normally small-volume, mafic alkalic magmas, which do not resemble adakitic rocks

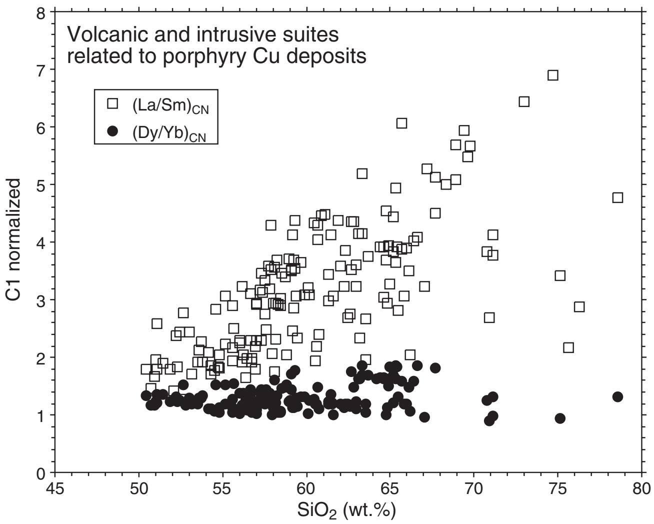

FIG. 21. C1 chondrite-normalized $(La/Sm)_{CN}$ and $(Dy/Yb)_{CN}$ ratios vs. SiO_2 for volcanic and intrusive rocks associated with the Tampakan, Mezcala, Central Chilean, and Escondida porphyry Cu deposits (sources of data as for Figs. 16–20). Normalization values of Sun and McDonough (1989).

(Richards, 1995). For example, volcanic and intrusive rocks associated with the Porgera, Lihir, and Emperor alkalic-type gold deposits in Papua New Guinea and Fiji are, with few exceptions, considerably more mafic than 56 wt percent SiO_2 (alkali basaltic or shoshonitic parental magma compositions), and mostly have higher Y and Yb than adakitic rocks (Richards, 1990; Rogers and Setterfield, 1994; Müller et al., 2001).

Other Au-rich porphyry Cu deposits, such as Bingham Canyon, Utah (Waite et al., 1997) and Bajo de la Alumbrera, Argentina (Halter et al., 2004) have nonadakitic Sr/Y compositions (Y >18 ppm), radiogenic Sr isotope compositions, and evidence for the involvement of parental magmas more mafic than andesite.

Thus, there seems to be no obvious role for adakitic magmas or slab melts in the genesis of either alkalic-type Au deposits or Au-rich porphyry Cu deposits.

Mineralization in Archean granitoids, and Archean porphyry Cu deposits

This section focuses on Neoarchean terranes for the same reasons set out for summarizing Archean magmatism and adakitic rocks. The best documented areas for these purposes are the Abitibi and Pontiac accreted terranes of the Superior province, Canada, which are areally extensive, well mapped, and have a large endowment of mineral deposits. Erosional level is not a significant issue for the geologic record of Archean porphyry Cu deposits, because shallow crustal levels are variably preserved in these Archean terranes. Volcanic-intrusive-turbidite complexes, submarine volcanic-hosted massive sulfide deposits, some porphyry-type deposits, and fluviatile siliciclastic sedimentary rocks collectively record surface to shallow crustal environments. This preservation is a result of the 250- to 350-km-thick, refractory, buoyant, subcontinental lithospheric mantle root beneath all Archean cratons, which prevented the reworking characteristic of many younger (Proterozoic) terranes (Kerrich et al., 2005). These considerations bear on the empirical observation that there are few Archean porphyry Cu deposits (Lambert and Groves, 1981). However, the fact that a few porphyry Cu deposits, hosted by syn-arc calc-alkaline intrusions, do occur in Neoarchean terranes means that the issue of preservation is not a constraint and that the putative role of adakites in porphyry Cu deposits can be tested.

Phanerozoic granitoids of both the basalt-andesite-dacite-rhyolite and high Al TTG magma series occur in convergent margin settings. Similarly, granitoids of the Abitibi-Pontiac terranes have arc-volcanic associations and/or compositions consistent with a convergent margin environment (Feng and Kerrich, 1992; Sutcliffe et al., 1993). These granitoids have been characterized in terms of (1) major and trace element compositions; (2) age; (3) emplacement pressures; (4) Au, platinum group element, and transition metal contents; and (5) quartz and whole-rock oxygen isotope compositions. For samples with primary $\delta^{18}O_{quartz\text{-}whole\ rock}$ fractionations, the primary metal contents and compositions (e.g., Sr, Y, REE contents, and Sr/Y and La/Yb ratios) are well constrained (Feng et al., 1993; Table 2).

Four of the six granitoid series, each encompassing many intrusions, in the Abitibi-Pontiac terranes meet all of the criteria of adakitic-tonalite suites (Tables 1, 2). None have primary Au or Cu contents greater than the Neoarchean upper crustal average, and three of the four series have crystallization pressures less than 20 MPa, implying shallow depths of emplacement, so erosion level should not be a limiting factor for the preservation of porphyry-style deposits. A few plutons of each of the three granitoid series have uneconomic stringer zones of Cu mineralization, yet the Cu-Pb-Zn-Mo or P-Ba-Cu budgets differ from Phanerozoic porphyry Cu deposits (Table 2).

In their review of Superior province mineral deposits, Poulsen et al. (1992) identified three classes of granitoid-hosted Cu and/or Mo low-grade deposits or subeconomic prospects: (1) Cu-Mo deposits in syn-arc subvolcanic sills, such as the Don Rouyn deposit, Noranda; (2) Mo-Cu-Au deposits hosted in late-tectonic granitoid stocks, exemplified by the McIntyre mine and Setting Net Lake showings; and (3) quartz Mo-(Cu) veinlet deposits, including the post-tectonic Preissac batholith, Quebec.

In the Quebec sector of the Abitibi greenstone belt, the small Don Rouyn deposit near Noranda has been described as an Archean porphyry-type deposit (Goldie, 1979). A copper-bearing siliceous zone is hosted by tonalites, which were likely subvolcanic sills of the synvolcanic stage. Only major element data are available: Al_2O_3 contents are too low to qualify as adakites or high Al TTG but instead likely belong to the quartz diorite-low Al TTG magma series (Tables 1, 2). Similarly, the Devlin Cu deposit, hosted by leucotonalites of the Chibougamau pluton, has been cited by Guha et al. (1984) as an Archean porphyry Cu-type deposit. However, no REE data are available, and the mineralization does not have the characteristic potassic and propylitic alteration styles of classic porphyry Cu deposits. Furthermore, fluid inclusion homogenization temperatures mostly less than 150°C are lower than is typical for veins in porphyry deposits (Guha et al., 1984).

In the Bousquet district of the Abitibi greenstone terrane, the Doyon deposit, hosted by the Mooshla intrusive complex, has stringer Cu-Au mineralization. A range of intrusive rock types is present, including low Al trondhjemite and tonalites, quartz diorite, and gabbros with Al_2O_3 >15 wt percent; however, the high Al lithologic units possess Fe and Ti contents too high, and La/Yb too low to qualify as adakitic (Galley and Lafrance, 2007). The Cu-Au mineralization cannot be definitively linked to magmatism, but may be a telescoped epithermal system (A. Galley, pers. commun., 2007).

The Lac Troilus Au-Cu deposit in the Evans-Frotet greenstone belt, Quebec, is another possible candidate for an arc-related Archean porphyry-type deposit, containing 2.5 Moz Au, 3 Moz Ag, and 60,000 t Cu (Fraser, 1993). Disseminated mineralization occurs at the boundary between mafic and intermediate volcanic units; the latter have >16 wt percent Al_2O_3, consistent with adakitic compositions, but there are no REE data for these rocks. The mineralization is not intrusion hosted and there are no annular zones of potassic and propylitic alteration, so a porphyry classification is not clear.

In relation to the second class of Mo-Cu-Au deposits of Poulsen et al. (1992), such as McIntyre, numerous volcanic units and intrusive bodies, spanning 2700 to 2680 Ma, of trondhjemitic composition occur in the Timmins district. These rocks possess the high Al_2O_3 but low Yb contents and high La/Yb ratios characteristic of adakites and high Al TTG (Kerrich and Fryer, 1979; Ayer et al., 2005). A disseminated Cu-Au-Mo deposit occurs in felsic schists, probably originally fragmental units, in the McIntyre mine. The felsic quartz-feldspar porphyry flows are adakitic in terms of the criteria set out in Table 1 (Kerrich and Fryer, 1979). However, there are significant differences to Phanerozoic porphyry Cu deposits: mineralization was post-, not synvolcanic; the porphyritic texture is metasomatic; and the ore is hosted by previously metamorphosed schists (Davies and Luhta, 1978).

In relation to the third class of quartz Mo-(Cu) veinlet deposits of Poulsen et al. (1992), such as in the Preissac-Lacorne batholith, the host potassic peraluminous granitoids were emplaced in the Superior province from ~2680 to ~2640 Ma (Ayres and Černý, 1982; Feng et al., 1993; Table 2). These are second stage, intracrustal melts of metasedimentary sequences, which postdate the termination of arc-related magmatism by 10 to 50 m.y.

A low-grade Mo occurrence is hosted by the 2643 Ma Setting Net Lake epizonal porphyritic granodiorite to quartz monzonite stock, in northwestern Ontario near Red Lake. Grades are 0.06 wt percent MoS_2 with trace Cu. The conjunction of intrusion-hosted mineralization, porphyritic texture, metal budget, and potassic-propylitic alteration was interpreted in terms of porphyry-type mineralization by Ayres et al. (1982) and Ayres and Černý (1982). However, although no major or trace element data were reported, high modal K-feldspar contents are consistent with a peraluminous composition, and the post-arc timing of magmatism casts doubts on the applicability of Phanerozoic-style porphyry Cu models.

The Boddington Au-(Cu-Pb-Mo-W) mine in Western Australia has also been proposed as an Archean analogue of Phanerozoic porphyry Cu-type deposits (e.g., Roth et al., 1991). Located in the 2714 to 2675 Ma supracrustal sequence of the Saddleback greenstone belt, southwestern Yilgarn craton, this world-class volcanic- to intrusion-hosted Au deposit (~400 t Au) consists of late (D_4) veins introduced after the end of volcanism at 2675 Ma and prior to late, unaltered, granitoid plutonism at ~2611 Ma. Given the post-arc setting and intrusive host rocks, Boddington has been compared to other post-tectonic, structurally hosted Au deposits of the Yilgarn craton such as Mount Magnet, Mount Charlotte, and Wiluna, rather than syn-arc deposits (Allibone et al., 1998).

Perhaps the best-documented Archean porphyry-type deposit is at Malanjkhand, in the Central Indian tectonic zone. This Cu-Mo-Au deposit (470 Mt avg 0.9% Cu at a 0.2% cutoff, 0.025% Mo, and 0.14 g/t Au) is hosted by calc-alkaline granites dated at 2490 ± 80 Ma by Re-Os (Stein et al., 2004). The geology of the Malanjkhand terrane is unlike that of neighboring Archean terranes typical of Neoarchean greenstone TTG belts and is interpreted to be a microplate accreted during amalgamation of part of the Indian craton (Stein et al., 2004).

Other close porphyry analogues are the Fe-Cu-Mo deposits of the 3.3 Ga McPhee dome in the Pilbara craton. This breccia-fracture mineralization, with potassic alteration, is hosted by composite calc alkaline granodiorite-quartz monzonite porphyry intrusions. Four low-grade occurrences include the Coppins Gap and Gobbos prospects (grades of <0.2 wt % Cu and <0.01 wt % Mo; Barley, 1982).

A review of Precambrian porphyry Cu deposits by Sikka and Nehru (1997) confirms a calc-alkaline to alkaline magmatic association for Proterozoic examples.

In summary, many Neoarchean greenstone-granitoid terranes are at erosional levels where volcanic and subvolcanic units are preserved, but credible examples of porphyry Cu deposits in these terranes are rare, and those that do occur are hosted by normal calc-alkaline intrusions. Synvolcanic adakitic rocks and high Al TTG intrusions are present in these terranes, but these rocks are not associated with porphyry Cu deposits. Nor are porphyry deposits associated with sanukitoids, either in Archean or Phanerozoic terranes (Feng et al., 1993; Polat and Kerrich, 2006). In contrast, small porphyry Mo deposits, commonly with fluorite, are present in many Neoarchean terranes, hosted by peraluminous S-type granitoids; these post-arc, second-stage melts of metasedimentary sequences are compositionally and genetically distinct from adakites (Ayres and Černý (1982; Table 2).

Conclusions

Our purpose in writing this paper has been to examine critically the link proposed by some authors between porphyry Cu deposits, especially giant porphyry Cu deposits, and adakitic magmas ultimately derived by melting of subducting oceanic crust. To do this, we first reviewed the various chemical definitions of adakites and considered the evidence for their formation by slab melting, as well as alternative mechanisms for producing such geochemical signatures by deep crustal melting and/or fractionation (MASH and AFC processes). It was shown that a case can be made for slab melting in restricted tectonic environments that lead to unusually high slab temperatures at shallow depths in the Phanerozoic and more widely in the Archean when mantle geotherms were higher. This evidence is clearest in immature island-arc settings, where interactions with the upper plate are least and primitive magma compositions are most closely approached (e.g., Defant and Drummond, 1990). However, even in these settings, erupted adakitic magmas are not primary slab melts but instead are interpreted to have variably hybridized with the peridotitic mantle wedge during passage to the surface. Another subclass of subduction-related magmas, high Mg andesites, has been interpreted to form by partial melting of the asthenospheric mantle wedge previously contaminated by slab melts, although an alternative and simpler origin involving mixing and contamination of normal arc magmas has recently been proposed by Streck et al. (2007).

In mature island- or continental-arc settings, more proximal and more likely causes of the subtle trace element signatures that are used to identify adakites, such as high Sr/Y and La/Yb ratios, are found to be interactions of normal tholeiitic to calc-alkaline arc magmas with lower crustal rocks, especially where garnet or amphibole are present (e.g., garnet amphibolites) and/or normal crystal fractionation processes involving amphibole ± titanite ± minor plagioclase segregation (plagioclase crystallization is suppressed by the high water contents of arc magmas). Hornblende fractionation, in particular, leads to characteristic listric-shaped chondrite-normalized REE patterns in evolved magmas, due to its preferential partitioning of MREE. Such patterns are characteristic of calc-alkaline basalt-andesite-dacite-rhyolite suites, including those associated with porphyry Cu deposits. These magmas are also commonly isotopically evolved, reflecting MASH or AFC crustal interactions. Thus, we conclude that normal and inevitable magmatic processes affecting arc magmas as they ascend through the upper plate lithosphere can generate many of the characteristic geochemical signatures used to identify adakites. Consequently, any attempt to see through such extensive and complex open-system processes, operating in both the asthenosphere and upper plate lithosphere, to determine a unique source signature in the subducting plate will be exceedingly difficult to constrain.

We reviewed published geochemical data for a number of arc volcanic suites from around the world in which adakite-like compositions have been reported. Many of these claims are based on only a few of the geochemical criteria proposed for the definition of adakites, commonly only high Sr/Y ratios (≥20)—many papers contained incomplete geochemical analyses, especially for REE. Almost without exception (the main exception being Cook Island in the Austral Andes), these suites display simple fractionation trends in Harker-type diagrams of element concentrations or ratios versus SiO_2. These trends commonly start at compositions outside the accepted ranges for adakitic rocks and then fractionate into some but rarely all of those fields. In some cases, such as in the Central Andes, the most primitive basaltic andesitic compositions have supra-adakitic concentrations of Y (>18 ppm) and Yb (>1.9 ppm), and subadakitic La/Yb ratios (<20). Yttrium and Yb concentrations decrease and La/Yb and Sr/Y ratios increase into adakitic ranges with fractionation to andesitic and dacitic compositions, whereafter these trends reverse in felsic rocks. These trends are simply interpreted in terms of amphibole ± titanite and late plagioclase fractionation in intermediate rocks and extensive crustal interaction and/or fractionation of accessory minerals in felsic rocks.

Assessment of suites associated with some porphyry Cu deposits that include rare adakite-like compositions using the same approach reveals similar fractionation trends, most clearly illustrated by the Tampakan and Escondida suites (for which full geochemical data are available). Fractionation trends for both suites start outside the range of adakitic compositions for several parameters and then evolve by fractionation into these ranges, showing that these adakite-like signatures are not primary and do not reflect source compositions.

If slab melts were critical ingredients in porphyry-related magmas, then it might be expected that porphyry Cu deposits should be particularly common in the Archean, where adakitic rocks and high Al TTG suites are more abundant, and the case for widespread slab melting is strongest. However, not only are porphyry Cu deposits uncommon, but those few that occur are associated with normal calc-alkaline rocks and not adakites or high Al TTG. Poor preservation of Archean upper crustal rocks is commonly cited to explain the rarity of Archean porphyry deposits, but this argument fails to recognize the supracrustal nature of greenstone belts and the common preservation of Archean volcanic rocks and associated massive sulfide deposits. If porphyry Cu deposits were common in the Archean due to the widespread occurrence of slab melting, then they should be abundantly preserved and clearly related to adakites, neither of which is the case.

We conclude that adakite-like compositions in most Phanerozoic arc volcanic suites and porphyry-related intrusive suites are the products of upper-plate crustal interaction and fractionation processes affecting normal tholeiitic to calc-alkaline arc magmas, predominantly sourced by partial melting of the hydrated asthenospheric mantle wedge. It may be impossible to prove or disprove a contribution of slab melts to asthenosphere-derived arc magmas, but proximal and demonstrable explanations for the subtle geochemical signatures of adakite-like magmas, such as crystal fractionation and upper plate crustal interaction, must be considered most likely until clearly proven otherwise. A unique role for slab melts in the formation of porphyry Cu deposits, large or small, is likewise considered unproven and unlikely.

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