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Geochemical differences between subduction- and collision-related copper-bearing porphyries and implications for metallogenesis

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Abstract Porphyry Cu (–Mo–Au) deposits occur not only in continental margin–arc settings (subduction-related porphyry Cu deposits, such as those along the eastern Pacific Rim (EPRIM)), but also in continent–continent collisional orogenic belts (collision-related porphyry Cu deposits, such as those in southern Tibet). These Cu-mineralized porphyries, which develop in contrasting tectonic settings, are characterized by some different trace element (e.g., Th, and Y) concentrations and their ratios (e.g., Sr/Y, and La/Yb), suggesting that their source magmas probably developed by different processes. Subduction-related porphyry Cu mineralization on the EPRIM is associated with intermediate to felsic calc-alkaline magmas derived from primitive basaltic magmas that pooled beneath the lower crust and underwent melting, assimilation, storage, and homogenization (MASH), whereas K-enriched collision-related porphyry Cu mineralization was associated with underplating of subduction-modified basaltic materials beneath the lower crust (with subsequent transformation into amphibolites and eclogite amphibolites), and resulted from partial melting of the newly formed thickened lower crust. These different processes led to the collision-related porphyry Cu deposits associated with adakitic magmas enriched by the addition of melts, and the subduction-related porphyry Cu deposits associated with magmas comprising all compositions between normal arc rocks and adakitic rocks, all of which were associated with fluid-dominated enrichment process.

In subduction-related Cu porphyry magmas, the oxidation state (fO_2), the concentrations of chalcophile metals, and other volatiles (e.g., S and Cl), and the abundance of water were directly controlled by the composition of the primary arc basaltic magma. In contrast, the high Cu concentrations and fO_2 values of collision-related Cu porphyry magmas were indirectly derived from subduction modified magmas, and the large amount of water and other volatiles in these magmas were controlled in part by partial melting of amphibolite derived from arc basalts that were underplated beneath the lower crust, and in part by the contribution from the rising potassic and ultrapotassic magmas. Both subduction- and collision-related porphyries are enriched in potassium, and were associated with crustal thickening. Their high K_2O contents were primarily as a result of the inheritance of enriched mantle components and/or mixing with contemporaneous ultrapotassic magmas.

Key words: Geochemistry; subduction- and collision-related; Cu-bearing porphyry; eastern

Pacific Rim; southern Tibet.

1 Introduction

Porphyry Cu deposits are the world's main source of Cu as well as a source of significant amounts of Mo and Au; as such, these deposits have been the focus of a large amount of research, both theoretical and applied (e.g., Sillitoe, 1972, 1973, 1998, 2000, 2005, 2010; Richards, 2003, 2009, 2011a, b, 2013; Hou et al., 2004, 2009, 2011; Richards and Kerrich, 2007; Sun et al., 2013). Typical porphyry Cu deposits occur in subduction-related continental and island arc settings, such as those of the Pacific Rim, which are closely associated with the subduction of oceanic crust (e.g., Kelser et al., 1975; Skewes and Stern, 1995; Kirkham, 1998; Kay et al., 1999; Kerrich et al., 2000; Richards et al., 2001). The classic model of porphyry Cu mineralization (e.g., Sillitoe, 1972), which is based on porphyry deposits formed in arc settings, has been the basis of successful exploration and discovery of porphyry deposits in the circum-Pacific metallogenic belt (Fig. 1a; e.g., Mitchell and Garson, 1972; Jorhan et al., 1983; Bektas et al., 1990; Solomon, 1990; Rui et al., 2004). More recent discoveries have highlighted the occurrence and formation of porphyry Cu (–Mo–Au) deposits in continent–continent collisional settings, such as in southern Tibet, Iran, and western Pakistan (e.g., Rui et al., 1984; Hou et al., 2001, 2003, 2004, 2009, 2011; Qu et al., 2001; Richards, 2009, 2011a, b; Shafiei et al., 2009; Pettke et al., 2010; Richards et al., 2012; Ayati et al., 2013; Asadi et al., 2014; Fig. 1a, b). Research on deposits in these collisional environments has led to the establishment of a model of collisional orogenic porphyry mineralization (e.g., Rui et al., 2006; Hou et al., 2007, 2009, 2011; Hou and Cook, 2009; Lu et al., 2013; Yang et al., 2014; Wang et al., 2014a, b). The development of porphyry Cu deposits in different tectonic settings, such as those of subduction-related continental margin–arcs (referred to as 'subduction-related porphyry Cu deposits' in this study) and continent–continent collisional (referred to as 'collision-related porphyry Cu deposits' in this study) settings, suggests that the magmas associated with these deposits were derived either from sources with different compositions and/or formed through different mechanisms.

Although a few studies have compared subduction- and collision-related porphyry Cu deposits (e.g., Hou et al., 2009, 2011), most of this previous research has concentrated on the genetic association between adakitic rocks and porphyry Cu deposits (e.g., Richards and Kerrich,

2007; Richards, 2009; Sun et al., 2011, 2012). Thus, it is unclear whether there are systematic geochemical differences between subduction- and collision-related copper-bearing porphyries. Here, we use published geochemical data for typical patterns of Cu-bearing porphyries to identify differences in geochemical characteristics of subduction- and collision-related Cu-bearing porphyries. The data are from continental margin arc settings along the eastern Pacific Rim (EPRIM; based on two stages of formation, during the Late Cretaceous–Paleogene and the Neogene), and from a continent–continent collision zone in southern Tibet (which formed during the Miocene), and we discuss variations in the source compositions and formation mechanisms of the deposits, thereby providing a basis for further exploration of other areas with tectonic settings suitable for porphyry Cu mineralization.

2 Temporal and spatial distribution of porphyry deposits

Globally, porphyry Cu (–Mo–Au) deposits occur mainly in the circum-Pacific, Tethys–Himalaya, and ancient Asia (Central Asia) metallogenic belts (e.g., Cooke et al., 2005; Sinclair, 2007; Richards, 2013; Sun et al., 2014). The circum-Pacific and Tethys–Himalaya belts formed mainly in the Mesozoic and Cenozoic, and, relatively complete geological data have allowed research into the mechanisms and processes involved in porphyry mineralization. Approximately 97% of large to giant porphyry Cu deposits have formed in magmatic arc settings (e.g., Kerrich et al., 2000; Cooke et al., 2005; Sillitoe, 2010), including the classic metallogenic provinces in island arc settings, such as those of the western Pacific in Indonesia and the Philippines (e.g., Hedenquist and Richards, 1998; Cooke et al., 2005). However, metallogenic porphyry Cu provinces in continental margin–arc environments are generally located in the eastern Pacific, including in the Chile–Peru, Panama–Colombia, southwestern United States–Mexico, and western United States–Canada metallogenic provinces (e.g., Sillitoe, 2010). Large porphyry Cu deposits of the Pacific Rim, which are generally located in the eastern Pacific, developed in the late Mesozoic and Cenozoic (e.g., Cooke et al., 2005). Here, we focus on geochemical data for Cu-bearing porphyries associated with the subduction of oceanic crust that formed during two major phases of metallogenesis in the eastern Pacific. The first phase, in the Late Cretaceous–Paleogene, was associated with the formation of the Laramide porphyry province in Arizona (e.g., Lang and Titley, 1998), the Mezcala porphyry province in Mexico (e.g.,

González-Partida et al., 2003), the El Salvador deposit in the Chilean Porphyry Cu belt (e.g., Baldwin and Pearce, 1982), and the Bingham mining district in Utah (e.g., Stavast et al., 2006). The second phase of metallogenesis occurred during the Miocene, and was associated with the formation of the Bajo de la Alumbrera porphyry Cu-Au deposit in Argentina (e.g., Müller and Forrestal, 1998; Ulrich and Heinrich, 2001), the giant El Teniente Cu-Mo deposit (e.g., Cannell et al., 2005; Stern et al., 2007, 2010; Vry et al., 2010) and the giant Los Pelambres porphyry Cu deposits in central Chile (e.g., Reich et al., 2003), the porphyry Cu-Au deposits of the Refugio District in northern Chile (e.g., Muntean and Einaudi, 2000), and porphyry Cu-Mo deposits in Ecuador (e.g., Chiaradia et al., 2004; Schutte et al., 2010; Fig. 1a).

The majority of the porphyry Cu mineralization in continent–continent collisional settings is located in the central and eastern part of the Tethys–Himalaya metallogenic belt, including the Cenozoic Sungun-Dalli-Sar cheshmeh porphyry Cu belts in Iran, the Gangdese and Yulong porphyry Cu belts in southern and eastern Tibet, respectively. The Cenozoic Sungun-Dalli- Sar cheshmeh porphyry Cu belt mainly occurred during Miocene times (e.g., Shafiei et al., 2009; Haschke et al., 2010; Richards et al., 2012; Ayati et al., 2013; Asadi et al., 2014; Richards, 2014). The Yulong porphyry Cu belt formed during 40 – 35 Ma (e.g., Rui et al., 1984; Ma, 1990; Tang and Luo, 1995; Hou et al., 2006, 2009, 2011; Yang et al., 2009, 2014; Lu et al., 2013), and the Gangdese porphyry Cu belt is an E–W trending ~350 km-long belt located in the Indo-Asian collisional zone and that contains several large and a series of intermediate to small porphyry Cu deposits (e.g., Hou et al., 2004, 2009, 2011; Qu et al., 2004; Wang et al., 2014a, b; Fig. 1b). The majority of fault-controlled porphyry Cu mineralization in the Gangdese belt is hosted in graben controlled by N–S faults (e.g., Hou et al., 2004, 2009, 2011) and formed between 19.7 and 11.5 Ma (e.g., Hou et al., 2003, 2004, 2009, 2011; Qu et al., 2003, 2007, 2009; Rui et al., 2004). These deposits formed as a result of the 65–55 Ma collision between India and Eurasia (e.g., Mo et al., 2007, 2008) and as such developed in a typical continent–continent collision setting. The majority of geochemical data for collision-related porphyry Cu mineralization are from the Gangdese porphyry Cu belt in southern Tibet (Fig. 1b; e.g., Hou et al., 2004; Qu et al., 2004; Guo et al., 2007; Gao et al., 2007a; Wang et al., 2014a, b).

3 Geochemistry

Data was gathered from a variety of studies on ore-bearing porphyry rocks which are mainly from eastern Pacific Rim (EPRIM) and Gangdese belt in southern Tibet, because their geodynamic settings is well constrained. Several data filters were employed to ensure inclusion of only the highest quality data in this study. Samples not meeting the following criteria were excluded from discussion: (1) whole rock SiO_2 concentrations of less than 56 wt.% or greater than 75 wt.%; (2) sample suggested in article texts to be substantially altered, or crustal contamination, or assimilation; (3) data published before or in 1980; (4) major elements plus loss on ignition totals greater than 102% or less than 98 wt.%; (5) total volatile content greater than 3 wt.%.

3.1 Major and trace element geochemistry

Porphyry Cu mineralization on the EPRIM is divided into deposits that formed during the Late Cretaceous–Paleogene (herein CPEPR) and deposits that formed during the Miocene (herein MPEPR). The CPEPR deposits are generally associated with diorite, granodiorite, quartz diorite, quartz monzonites, and granite (e.g., Baldwin and Pearce, 1982; Lang and Titley, 1998; González-Partida et al., 2003). In contrast, the majority of the MPEPR deposits are associated with andesite, monzodiorite, granodiorite, quartz diorites, monzonite and dacite (e.g., Müller and Forrestal, 1998; Reich et al., 2003; Cannell et al., 2005; Schutte et al., 2010; Stern et al., 2010; Vry et al., 2010). Miocene porphyry Cu deposits in the continent–continent collisional setting of the Gangdese porphyry Cu belt in southern Tibet (herein MPST) are associated with diorite, granodiorite, quartz monzonite, dacite, monzonitic granite and granite (e.g., Hou et al., 2004; Wang et al., 2014b). The majority of the MPEPR samples are classified as calc-alkaline in K_2O vs. SiO_2 diagram (Fig. 2a), with some high-K calc-alkaline and tholeiitic samples and a small number of alkaline samples. In comparison, the majority of the CPEPR samples (Fig. 2a) are classified as high-K calc-alkaline, with minor calc-alkaline samples. The MPST samples (Fig. 2b) are generally high-K calc-alkaline, with some samples classified as calc-alkaline and alkaline series.

In Harker diagrams (Fig. 3), Al_2O_3, CaO, Fe_2O_3, TiO_2, and MgO concentrations of Cu-bearing porphyries are negatively correlated with SiO_2 concentrations, whereas no clear correlations are observed between Na_2O and SiO_2 concentrations. Although the P_2O_5 concentrations of MPST and CPEPR are negatively correlated with SiO_2, those of MPEPR have not see this trend (Fig. 3f). In the majority of the porphyries discussed here, Mg# values

(Mg#=100 × Mg^{2+}/(Fe^{2+} + Mg^{2+}) are relatively high (≥40), and K_2O concentrations and K_2O/Na_2O ratios are generally higher in collision-related porphyry samples than in subduction-related porphyry samples (Table 1).

Variations in trace element vs. SiO_2 concentrations (Fig. 4) indicate that Sr concentrations are negatively correlated with SiO_2 concentrations in MPST and CPEPR, whereas Th and Zr concentrations in MPST and MPEPR samples show no correlation SiO_2. All samples from the EPRIM and southern Tibet show similar ranges of concentrations of trace elements (e.g., Zr, Ba, and Sr), although Th concentrations are much higher in the MPST samples than in the EPRIM samples (Fig. 4). Moreover, the Th concentrations of most samples in MPST and some of CPEPR are higher than those of the upper and lower crust (Fig. 4d).

Chondrite-normalized rare earth element (REE) patterns (Fig. 5a–c) indicate clear fractionation between light REEs (LREE) and heavy REEs (HREE) with the latter generally showing flat patterns, and with no significant negative Eu anomalies; the CPEPR and MPST samples show higher LREE concentrations than do the MPEPR samples.

Primitive-mantle-normalized multi-element variation diagrams (Fig. 5d–f) indicate that all samples are significantly enriched in the large ion lithophile elements (LILE; e.g., Rb and U) relative to the high field strength elements (HFSE), and have pronounced negative Nb–Ta–Ti anomalies, with the vast majority of samples also having negative P anomalies. The majority of the MPST samples exhibit HREE concentrations lower than those of the EPRIM samples, and also exhibit negative Ba anomalies. In addition, trace element concentrations in the MPEPR samples are more variable than those in the CPEPR and MPST samples.

3.2 Sr–Nd isotope geochemistry

The MPEPR samples exhibit higher $\varepsilon Nd_{(t)}$ values (−2.18 to 6.79) and lower $^{87}Sr/^{86}Sr_{(i)}$ ratios (0.7037–0.7071) than the CPEPR samples ($\varepsilon Nd_{(t)}$ of –12.1 to –3.19; $^{87}Sr/^{86}Sr_{(i)}$ of 0.7054–0.7145) (Fig. 6; Table 1). Meanwhile, MPST samples exhibit a wide range of $\varepsilon Nd_{(t)}$ (-6.83 to 5.70) and $^{87}Sr/^{86}Sr_{(i)}$ (0.7034–0.7091) isotope ratios (Table 1; Fig. 6). All of the samples plot between Mid-Ocean Ridge Basalt (MORB) and mantle-derived ultrapotassic rocks on a Sr vs. Nd isotope diagram (Fig. 6).

3.3 Adakitic characteristics of Cu-bearing porphyry intrusions

Adakites formed from magmas generated by partial melting of a subducted slab in the garnet stability field (Defant and Drummond, 1990; Defant et al., 1992). These rocks have high concentrations of SiO_2 (>56 wt.%) and Al_2O_3 (>15 wt.%), low concentrations of MgO (<3 wt.%), Y, and HREE (Y and Yb concentrations of <18 and <1.9 ppm, respectively), high LILE concentrations, and Sr concentrations of >400 ppm. Those rocks with adakite-like compositions is referred to as adakitic rocks (e.g., Chung et al., 2003; Hou et al., 2004; Castillo, 2012), which can be produced by assimilation and fractional crystallization (AFC), the melting of delaminated lower crust, partial melting of the lower crust and other model. It is an intense debate topic whether there is a link between adakitic magmas and porphyry mineralization in continental margin–arc and post-subduction settings (e.g., Thiéblemont et al., 1997; Sajona and Maury, 1998; Oyarzun et al., 2001, 2002; Rabbia et al., 2002; Richards, 2002, 2009, 2011a, b; Richards and Kerrich, 2007; Wang et al., 2008; Castillo, 2012; Sun et al., 2011, 2012). Nevertheless, all of the MPST samples are classified as adakitic rocks in the Sr/Y vs. Y (Fig. 7a, b) and $(La/Yb)_N$ vs. $(La)_N$ diagrams (Fig. 7c, d) that are typically used to distinguish adakitic rocks from normal arc andesites, dacites, and rhyolites (ADR). In comparison, some of the EPRIM samples are classified as adakitic rocks, with the rest plotting in the ADR field. The published data for Cu-bearing porphyries on the EPRIM and in southern Tibet indicate that the former have generally higher Y concentrations and lower Sr/Y and $(La/Yb)_N$ values than the latter (Table 1), indicating a temporal–spatial relationship between adakitic rocks and porphyry Cu deposits in the EPRIM and southern Tibet (e.g., Thiéblemont et al., 1997; Sajona and Maury, 1998; Defant and Kepezhinskas, 2001; Oyarzun et al., 2001, Mungall, 2002; Hou et al., 2004), although not all mineralized porphyries are adakitic (e.g., Hou et al., 2011).

4 Discussion

4.1 Origin of porphyry Cu deposits in collisional orogenic settings

Porphyry Cu deposits that formed in continental arc settings, such as the porphyry Cu mineralization on the EPRIM, have been intensively studied (e.g., Sillitoe, 1972; Richards, 2003, 2009, 2011a, b, 2013; Cooke et al., 2005). However, the processes involved in the formation of porphyry Cu deposits in collisional orogenic settings remain, and these processes are considered in

this section.

The formation of porphyry Cu mineralization is associated with high oxygen-fugacity (fO_2) magmas that contain high concentrations of H_2O and Cu (Sillitoe, 1997; Parkinson and Arculus, 1999; Mungall, 2002; Sun et al., 2004, 2010, 2012, 2013; Hou et al., 2009, 2011; Richards, 2009, 2011a, b). A certain high-fO_2 conditions can cause Cu concentrations to increase in the magma at the sulphide-sulphate transition, thus promoting mineralization (e.g., Ballard et al., 2002; Mungall, 2002; Richards, 2003; Sillitoe, 2010; Botcharnikov et al., 2011). In comparison, high H_2O concentrations are essential to the efficient removal of ore metals from silicate melts during emplacement in the upper crust (e.g., Burnham, 1979; Richards, 2009; Richards et al., 2012). Furthermore, arc basalts and MORB have higher Cu concentrations than the continental crust, the lower continental crust, and the primitive upper mantle (e.g., Sun, 1982; Rudnick and Gao, 2003; Sun et al., 2011, 2013). Consequently, porphyry Cu deposits are generally thought to form from hydrothermal fluids exsolved from hydrous, high-fO_2, sulfur-rich arc magmas derived from a metasomatized mantle wedge that formed during slab subduction (e.g., Arculus, 1994; Noll et al., 1996; De Hoog et al., 2001; McInnes et al., 2001; Sun et al., 2003, 2004, 2013; Mungall et al., 2006; Richards, 2009, 2011a, b; Wallace and Edmonds, 2011).

It is thought that the crust beneath southern Tibet is twice as thick as the thickness of normal crust as a result of collision between the Asian and Indian plates (e.g., Zhao and Nelson, 1993; Owens and Zandt, 1997). However, extensive Andean-type calc-alkaline magmatism in the southern part of the Lhasa Terrane (Linzizong volcanics and Gangdese batholiths, ~195 to 45 Ma; e.g., Mo et al., 2007, 2008; Chung et al., 2009; Kang et al., 2014) involved magmas derived from a metasomatized mantle wedge with normal crustal thickness (30–40 km; Chung et al., 2003, 2009). The whole rock geochemistry, Sr–Nd isotope compositions, and zircon Hf isotopic data of ~38–9 Ma adakitic rocks in southern Tibet suggest that the crust in this area underwent a major phase of tectonic thickening (by up to 50 km) between ~45 and 30 Ma (e.g., Chung et al., 2003, 2009; Hou et al., 2004; Guan et al., 2012; Zheng et al., 2012) that was not caused by the impingement of Indian continental crust (e.g., Chung et al., 2009; Hou et al., 2009, 2011; Zheng et al., 2012). This finding, combined with the absence of significant folding in the Tertiary Linzizong volcanics, suggests that the crustal thickening in southern Tibet resulted from large-scale underplating of mantle-derived basaltic magmas (e.g., Mo et al., 2007, 2008; Chung et al., 2009;

Hou et al., 2009; Zheng et al., 2012), rather than from shortening of the upper crust (e.g., Tapponnier et al., 2001).

Miocene porphyry Cu deposits are located in the southern Lhasa subterrane (Fig. 1b), a section of juvenile crust associated with the Late Triassic to early Tertiary 220–40 Ma subduction and accretionary of Tethyan Ocean crust (e.g., Mo et al., 2007, 2008; Chung et al., 2009; Ji et al., 2009; Zhu et al., 2009, 2011). In addition, the fact that the volcanism that formed the Paleogene Linzizong volcanics only occurred in the southern part of the Lhasa Terrane is thought to be a result of breakoff of the subducted Neotethyan slab (e.g., Chung et al., 2009; Lee et al., 2009). The Miocene MPST porphyries that host Cu mineralization exhibit lower Nd and higher Sr isotope ratios than MORB (Fig. 6), similar to the Linzizong volcanics (e.g., Mo et al., 2007; Chung et al., 2009; Chen et al., 2011). This result, combined with the regional evolution of southern Tibet during the Cenozoic and the fact that the Miocene MPST porphyries have adakitic compositional affinities and were sourced from a thickened region of the lower crust (e.g., Chung et al., 2003, 2005, 2009; Hou et al., 2004), suggests that Miocene collisional orogenic porphyry Cu mineralization in southern Tibet formed as a result of the following: slab-breakoff of the northward-subducting Neotethyan oceanic lithosphere from Indian continental lithosphere at ac. ~50 Ma in the early stage of the India-Asia collision (e.g., Chung et al., 2003, 2009; Lee et al., 2009) induced partial melting of metasomatised mantle wedge material that had interacted with fluids and subducted sediment melts, including slab-derived melts generated during and after the breakoff. These high-fO_2 arc-like basaltic melts contained elevated concentrations of chalcophile elements (such as Cu) and volatiles (such as H_2O and Cl), and they ascended and underplated the lower crust in southern Tibet after the termination of Gangdese/Linzizong magmatism and generation of an orogenic root created (~45–30 Ma; e.g., Chung et al., 2003, 2009). Unlike in continental arc settings, these underplated basaltic magmas probably did not mainly undergo a process of melting, assimilation, storage, and homogenization (MASH) to form volatile-rich, high-fO_2, Cu-bearing intermediate–felsic magmas (e.g., Hou and Cook, 2009; Hou et al., 2009, 2011). Instead, these underplated magmas gradually cooled and transformed to amphibolites and eclogitic amphibolites, and crustal thickness increased (e.g., Chung et al., 2003, 2009; Hou et al., 2004, 2009, 2011) during continuous N–S compression associated with India–Asia continental collision.

Widespread 24–12 Ma magmatism and the formation of 24–10 Ma porphyry Cu mineralization in N–S graben in southern Tibet suggests that this area underwent a transition from tectonic compression to extension during the Miocene (e.g., Coleman and Hodges, 1995; Blisniuk et al., 2001; Williams et al., 2001; Spicer et al., 2003; Hou et al., 2004; Guo et al., 2007). Either this regional tectonic regime, the breakoff of northward-subducting Indian lithosphere (e.g., Mahéo et al., 2002; Williams et al., 2004; Wang et al., 2014a, b), or the foundering/delamination/ convective removal of thickening subcontinental lithospheric mantle beneath southern Tibet (e.g., Turner et al., 1993, 1996; Chung et al., 2009; Zhao et al., 2009) caused the asthenospheric mantle beneath southern Tibet to ascend. This rising asthenosphere caused not only the formation of widespread N–S striking extension faults (e.g., Coleman and Hodges 1995; Blisniuk et al., 2001; Williams et al., 2001), but also partial melting of a region of enriched mantle (e.g., Turner et al., 1996; Miller et al., 1999; Williams et al., 2004; Zhao et al., 2009), generating parental magmas that formed ultrapotassic and potassic rocks in southern Tibet. The high geothermal gradient in the area (e.g., Liu et al., 2011), along with decompression associated with E–W extension, underplating, and the uprising of hot mantle-derived magmas, triggered partial melting of the newly formed Cu-bearing amphibolite or eclogitic amphibolite lower crust, generating adakitic melts in southern Tibet. Considered the relatively water poor amphibole–eclogite or garnet–amphibolite in collisional orogens (average estimated maximum H_2O contents: 1.2 wt.%; Leech, 2001) is not efficiently produce adakitic melts having the high H_2O contents ($>$5 wt.%) of the porphyry Cu-Mo (-Au) ore-forming magma (Wolf and Wyllie, 1991; Skjerlie and Patino Douce, 2002; Yang et al., 2014), the mantle-derived potassic and ultrapotassic magmas that contained abundant volatiles (e.g., H_2O and Cl) (e.g., Rock, 1987; Rock et al., 1990; Foley et al., 1992; Behrens et al., 2009) probably mixed with high-fO_2 crustal-derived adakitic melts that contained high concentrations of chalcophile elements (such as Cu), H_2O, and other volatile components released during the partial melting of amphibolite, before these mixed magmas ascended into the upper crust along extensional structures and structural weaknesses, most likely producing Cu-bearing porphyries in southern Tibet.

4.2 Potassium-rich characteristics of mineralized Cu porphyries

The high K_2O and some LILEs (e.g., Ba and Rb) concentrations in the porphyry can be

related to the potassic alteration and/or crustal assimilation. However, the low loss on ignition (LOI $\leqslant$ 3 wt.%) of samples in this study suggests that the potassic alteration is not important. Meanwhile, obviously higher K_2O, Rb, and Ba concentrations of most samples than the upper continental crust (Figs. 4a, 8a, b, c), combined with the relationship between Mg# and K_2O, Rb, and Ba (Figs. 4a, 8a, b, c), is inconsistent with the crustal assimilation. In addition, the high Ce/Yb ratios ($>$20) of most ore-bearing porphyries in this study can represent their primary magma (Müller and Forrestal, 2000; Fig. 8d). Therefore, the intermediate to felsic calc-alkaline mineralized Cu porphyries contain elevated concentrations of K as compared with normal arc magmas (e.g., Richards, 2009), and are commonly closely related to alkalic or potassic magmas (e.g., Sillitoe, 1991, 1997, 2002; Sillitoe and Camus, 1991; Vila and Sillitoe, 1991; Barrie, 1993; Kirkham and Margolis, 1995; Lang et al., 1995; Kirkham and Sinclair, 1996; Keith et al., 1997; Müller and Forrestal, 1998; Holliday et al., 2002; Yang et al., 2014; Fig. 1). In addition, Sillitoe (2002) considered that some porphyry Cu-Au deposits are related to alkalic magmatism in arc terranes; and Müller and Groves (1993) suggested that the presence of potassic rocks could be used as an exploration tool and may suggest that an area is highly prospective for porphyry Cu–Au deposits. The majority of samples discussed here have high Mg# values (>40; Fig. 3h), suggesting that magmas associated with porphyry Cu deposits contain mantle-derived components (Rapp and Watson, 1995). For example, the high-grade Bingham porphyry Cu (–Mo–Au) deposit on the EPRIM is the product of mixing between an evolving magmatic system and injections of mafic alkaline magmas (e.g., Keith et al., 1997; Hattori and Keith, 2001; Maughan et al., 2002; Pettke et al., 2010). In addition, the presence of porphyry mineralization and both alkalic and adakitic rocks in post-collisional settings are considered to be related with mafic alkalic magmatism (e.g., Richards, 1995; Shafiei et al., 2009; Yang et al., 2014). Furthermore, the essential H_2O contents of porphyry Cu ore-forming magmas ($>$5 wt. %; Wolf and Wyllie, 1991; Skjerlie and Patino Douce, 2002) developed in post-collisional settings cannot be satisfied by only partial melting amphibolite or elclogite (Leech, 2001) as above discussion and need additional water (Yang et al., 2014). Therefore, the Miocene Cu-bearing porphyry in southern Tibet involves both alkaline and high-K calc-alkaline series magmatism (e.g., Hou et al., 2004, 2009, 2011; Fig. 2b) and is thought to have resulted from the mixing of lower-crust-derived melts and mantle-derived potassic–ultrapotassic magmas (e.g., Guo et al., 2007).

Although ultrapotassic rocks are widespread globally and are related to some porphyry deposits (Fig. 1), the majority of samples in this study (with the exception of a few ultrapotassic samples in the Bingham district; Maughan et al., 2002), including limited data for Miocene ultrapotassic rocks of the EPRIM (Kay et al., 1994; Redwood and Rice, 1997; Sandeman and Clark, 2004; Maria and Luhe, 2008; Gómez-Tuena et al., 2011) and southern Tibet (Miller et al., 1999; Ding et al., 2003, 2006; Williams et al., 2004; Gao et al., 2007b; Zhao et al., 2009; Chen et al., 2012), do not contain high concentrations of Cu (<130 ppm). However, these mantle-derived potassic and ultrapotassic magmas are typically enriched in the LILE, LREE, and volatiles such as H_2O, CO_2, F, and Cl (e.g., Rock, 1987; Rock et al., 1990; Behrens et al., 2009), all of which likely enhance the solubility of chalcophile elements, such as Cu and Au, in high-temperature aqueous fluids (e.g., Heinrich et al., 1992; Pokrovski et al., 2005, 2008; Simon et al., 2005, 2006; Zajacz et al., 2008, 2011; Seo et al., 2009). This indicates that the generally high K_2O concentrations (K_2O/Na_2O > 0.5) in magmas associated with porphyry Cu mineralization are most likely produced by mixing between melts derived from the underplated basaltic lower crust and ascending mantle-derived potassic and ultrapotassic magmas (e.g., Pettke et al., 2010; Yang et al., 2014). This interpretation is consistent with the Sr–Nd isotope compositions of the samples discussed here, all of which plot between MORB and ultrapotassic magma compositions in a Sr vs. Nd isotope diagram (Fig. 6).

4.3 Comparison of between subduction- and collision-related Cu porphyries

As discussed above, the formation of subduction- and collision-related porphyry Cu ore-forming magmas derived from sources with different processes and/or compositions. Here, we use the geochemical data described above to compare subduction- and collision-related porphyry Cu mineralization.

4.3.1 Similarities

4.3.1.1. Components related to arc magmatism

Although the arc magmatism is clearly linked to the development of porphyry Cu deposits on the EPRIM in spatial, the geochemistry of Cu porphyries in collisional zones, such as LILE enrichment (e.g., Rb, K, Th, U and Sr), HFSE depletion (e.g., Nb, Ta and Ti), and depletions in

HREE and Y, are also similar to those observed in typical subduction-related magmas (Fig. 5d–f; e.g., Wilson, 1989), suggesting that these subduction signature in collision-related porphyries is probably resulted from the reactivation of subduction-modified material of arc magma before continental collisions (e.g., Hou et al., 2004, 2009, 2011; Richards et al., 2009, 2011a, b).

4.3.1.2. Thickened crust

Recent studies indicate that porphyry Cu deposits are located in thick mature continental arcs (e.g., Cook et al., 2005; Sillitoe, 2010; Lee et al., 2012) and collisional orogenic belts (e.g., Hou et al., 2004, 2009, 2011; Yang et al., 2014). Compressional tectonics, caused by the subduction of oceanic crust or continent–continent collision, lead to localized deformation and crustal thickening immediately prior to emplacement of mineralized intrusions in continental arc settings (e.g., Sillitoe, 1998; Kay et al., 1999) and orogenic collisional zones (e.g., Hou et al., 2009, 2011). This thickening of the crust favors MASH-type underplating of primitive metasomatized mantle-wedge-derived magmas beneath the lower crust. This process can yield evolved, volatile-rich, metalliferous hybrid intermediate (andesitic–dacitic) melts (e.g., Richards, 2003; Hou et al., 2009; Wang et al., 2014b). By comparison, thickened crust (>50–45 km) can cause the underplated basaltic material to transform to amphibolites and eclogitic amphibolites (e.g., Defant and Drummond, 1990; Rapp et al., 1999), thus affecting the concentration of water in the magma. Contrast to the mass water carried by the subducted oceanic slab in the continental arc, the water content for porphyry Cu (Mo-Au) formation in the collisional settings is likely storage in amphibole-bearing mineral assemblages that were stable during earlier stages of crustal thickening and break down to release water during late stage magma activity (Kay and Mpodozis, 2001; Richards, 2009).

4.3.2 Differences

4.3.2.1. Depth of generation of Cu-bearing porphyry magmas

Thickened regions of the crust are characteristically associated with porphyry Cu deposits, as discussed above. However, most samples of MPST exhibit higher $(La/Yb)_N$ (11.7–63.0, average of 31.1) ratios than do MPEPR (1.67–53.1, average of 13.0) and CPEPR (7.95–34.7, average of 18.6) samples (Table 1; Figs. 5, 7), implying that the MPST samples formed from magmas sourced

deeper than those associated with the EPRIM samples (e.g., Haschke et al., 2002; Haschke and Günther, 2003; Chung et al., 2009). The magma source depths of MPST is probably related with the underplated mafic magmas and increasing crustal thickness during Eocene and Oligocene (e.g., Chung et al., 2009). In contrast, the formation of MPEPR are related with the shallowing subduction zone or during the initial steepening of a formerly flat subduction zone (Kay and Mpodozis, 2001). In addition, some EPRIM samples are exhibit high La/Yb values, which probably caused by residual garnet in their source and formed in a mature continental arc setting (Müller and Forrestal, 1998).

4.3.2.2. Enrichment mechanisms

Porphyry Cu mineralization is associated with magmas that contain abundant fluids (e.g., H_2O) and other volatile components (e.g., Cl and F), suggesting that these magmas underwent some sort of enrichment process. Although some LILEs (e.g., Rb, and Ba) and Th concentrations can caused by the crustal contamination, the obviously higher Rb, Ba, and Th concentrations of most samples in this study than the upper continental crust imply that the crustal assimilation is not important as above discussion (Figs. 4, 8). So, the differences in LILE (such as Ba) and HFSE (such as Th) abundances and LILE/HFSE ratios (such as Ba/Yb, Sr/Yb, Nb/Yb, and Th/Yb) between porphyry Cu mineralization in southern Tibet and on the EPRIM suggest that the former have been enriched by interactions with melts, whereas the latter have been enriched by interaction with fluids (Fig. 9a, b, c). This inference is consistent with the formation of these deposits in different tectonic regimes (continent–continent collision and continental margin–arc settings, respectively) and different formation processes, as discussed above.

Two different evolutionary trends of samples from southern Tibet and the EPRIM are evident in a Th/La vs. Sm/La diagram (Fig. 9d). Tommasini et al. (2011) suggested that significantly high Th concentrations in mantle-derived ultrapotassic magmas are associated with components derived from a high Sm/La and Th/La source. In addition, the high Th/La values of porphyry Cu mineralization in southern Tibet, which are similar to those of coexisting ultrapotassic magmas, combined with similar to variable high Th/Yb and Nb/Y trends in both magmas, and the presence of newly formed crust in southern Tibet (as discussed above), suggest a link between porphyry Cu mineralization and coexisting Miocene potassic and ultrapotassic magmas in southern Tibet as above discussion.

5 Conclusions

1. Porphyry Cu (–Mo–Au) deposits occur not only in continental margin settings (such as the EPRIM) but also in continent–continent collisional orogenic belts (such as southern Tibet). These deposits developed in different tectonic regimes and show some differences in some trace element (e.g., Th, and Y) concentrations and ratios (e.g., Sr/Y, and La/Yb), implying that they underwent different formation processes and/or were derived from sources with different compositions.

2. Subduction-related porphyry Cu mineralization is probably associated with magmas generated by underplated mafic material that underwent a MASH process, whereas collision-related porphyry Cu mineralization is produced by a process in which underplated arc-like basaltic magma beneath the lower crust is gradually cooling and transformed into amphibolites and eclogitic amphibolites, which then undergo partial melting and interaction with underplated potassic and ultrapotassic melts from an enriched mantle. These differences in the formation processes cause some differences in geochemistry, such as the adakitic affinity and melt-enriched compositions recorded in collision-related Cu porphyries, and the contrasting evolution of subduction-related Cu porphyries which record an evolution from normal arc rocks to adakitic rocks, and which are characterized by fluid-dominated enrichment.

3. Magmas associated with both subduction- and collision-related porphyry Cu mineralization are generated during crustal thickening and compressional tectonism. In addition, their high K_2O contents are probably derived from (1) the inheritance of enriched mantle components and/or (2) mixing with contemporary mantle-derived ultrapotassic magmas.

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Figure captions

Fig. 1. (a) Worldwide distribution of porphyry Cu deposits and Cenozoic potassic and ultrapotassic rocks on the Eastern Pacific Rim (EPRIM) and in the world (modified from Müller et al. (1992), and Sillitoe (2010)) and (b) Miocene porphyry Cu mineralization and ultrapotassic rocks in the Gangdese porphyry Cu belt of southern Tibet (modified from Hou et al. (2004, 2009), and Zhao et al. (2009)). Distribution of Cenozoic potassic and ultrapotassic rocks on EPRIM and in the world based on Wallace and Carmichael (1989), Müller et al. (1992), Kay et al. (1994), Carlier et al. (1997), Redwood and Rice (1997), Haschke et al. (2002), Maughan et al. (2002), Carlier and Lorand (2003), Sandeman and Clark (2004), Conticelli et al. (2007), Jiménez and López-Velásquez (2008), Mamani et al. (2010), Gómez-Tuena et al. (2011), Prelević et al. (2014), and Saadat et al. (2014).

Fig. 2. Diagrams showing variations in SiO_2 vs. K_2O (a, b) for mineralized porphyries around the world; CPEPR (Late Cretaceous–Paleogene mineralized porphyries on the eastern Pacific Rim) data from Baldwin and Pearch (1982), Lang and Titley (1998), González-Partida et al. (2003), and Stavast et al. (2006); MPEPR (Miocene mineralized porphyries on the eastern Pacific Rim) data from Müller and Forrestal (1998), Muntean and Einaudi (2000), Ulrich and Heinrich (2001), Reich et al. (2003), Chiaradia et al. (2004), Cannell et al. (2005); Stern et al. (2007, 2010), Vry et al. (2010), and Schutte et al. (2010); MPST (Miocene mineralized porphyries in southern Tibet) data from Hou et al. (2004), Lin et al. (2004), Qu et al. (2004), Zheng et al. (2004), Wang et al. (2006, 2010, 2012), Gao et al. (2007a), Xia et al. (2007, 2010), Li et al. (2011), and Qin et al. (2011); data for late Cretaceous–Paleogene ultrapotassic rocks on the eastern Pacific Rim from Haschke et al. (2002), Maughan et al. (2002), Jiménez and López-Velásquez (2008), and Mamani et al. (2010); data for Miocene ultrapotassic rocks on the eastern Pacific Rim from Wallace and Carmichael (1989), Kay et al. (1994), Carlier et al. (1997), Redwood and Rice (1997), Carlier and Lorand (2003), Maria and Luhe (2008), Sandeman and Clark (2004), and Gómez-Tuena et al. (2011); and data for Miocene ultrapotassic rocks in southern Tibet from Miller et al. (1999), Ding et al. (2003, 2006), Williams et al. (2004), Gao et al. (2007a, b), Zhao et al. (2009), Chen et al. (2012), and Wang et al. (2014).

Fig. 3. Harker diagrams for mineralized porphyries on the eastern Pacific Rim and in southern Tibet; SiO_2 vs. Mg# diagram based on Wang et al. (2008), and data sources and symbols are as in Fig. 2.

Fig. 4. Diagrams showing variations in trace element concentrations with SiO_2 for mineralized porphyries on the eastern Pacific Rim and in southern Tibet; LC = lower crust, UC = upper crust, values for both are from Rudnick and Gao (2003), and all other data sources and symbols are as in Fig. 2.

Fig. 5. Chondrite-normalized REE (a, b, c) and primitive mantle-normalized multi-element (d, e, f) variation diagrams for porphyry Cu deposits on the eastern Pacific Rim and in southern Tibet; normalizing values are from Sun and McDonough (1989), and all other data sources are as in Fig. 2.

Fig. 6. A $^{87}Sr/^{86}Sr_{(i)}$ vs. $\varepsilon Nd_{(t)}$ diagram for porphyry Cu deposits on the eastern Pacific Rim and in southern Tibet; CPEPR data from Lang and Titley (1998); MPEPR data from Reich et al. (2003), Chiaradia et al. (2004), Stern et al. (2010), and Schutte et al. (2010); MPST data from Hou et al. (2004), Lin et al. (2004), Li et al. (2011), Wang et al. (2010), and Qin et al. (2011); data for late Cretaceous–Paleogene ultrapotassic rocks on the eastern Pacific Rim from Maughan et al. (2002); data for Miocene ultrapotassic rocks on the eastern Pacific Rim from Kay et al. (1994), and Gómez-Tuena et al. (2011); and data for Miocene ultrapotassic rocks in southern Tibet from Miller et al. (1999), Ding et al. (2003, 2006), Williams et al. (2004), Gao et al. (2007a, b), Zhao et al. (2009), Chen et al. (2012), and Wang et al. (2014). MORB and marine sediment values are from Hofmann (2003); all data symbols are as in Fig. 2.

Fig. 7. Diagrams showing variations in Sr/Y vs. Y (a, b) and $(La/Yb)_N$ vs. Yb_N (c, d) for porphyry Cu deposits on the eastern Pacific Rim and in southern Tibet; diagrams are after Martin (1986), Drummond and Defant (1990), Petford and Atherton (1996), and Castillo (2012), and all other data sources and symbols are as in Fig. 2.

Fig. 8. Diagrams showing variations in K_2O vs. Mg# (a), Rb vs. Mg# (b), Ba vs. Mg# (c), and Hf/Yb vs. Ce/Yb (d) for porphyry Cu deposits on the eastern Pacific Rim and in southern Tibet; upper and lower crust values are from Rudnick and Gao (2003), and all other data sources and symbols are as in Fig. 2.

Fig. 9. Diagrams showing variations in (a) Ba vs. Nb/Y, (b) Ba/Yb vs. Th/Yb, (c) Th/Yb vs. Sr/Yb, and (d) Th/La vs. Sm/La for porphyry Cu deposits on the eastern Pacific Rim and in southern Tibet; SALATHO is the high Sm/La and Th/La component of Tommasini et al. (2011), upper and lower crust values are from Rudnick and Gao (2003), and all other data sources and symbols are as in Fig. 2.

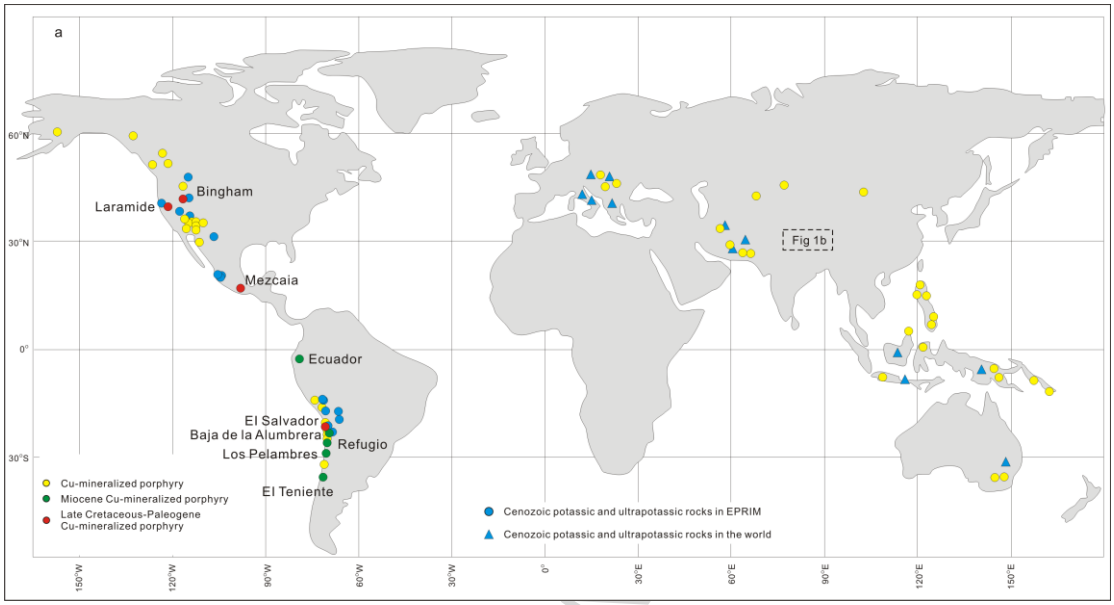
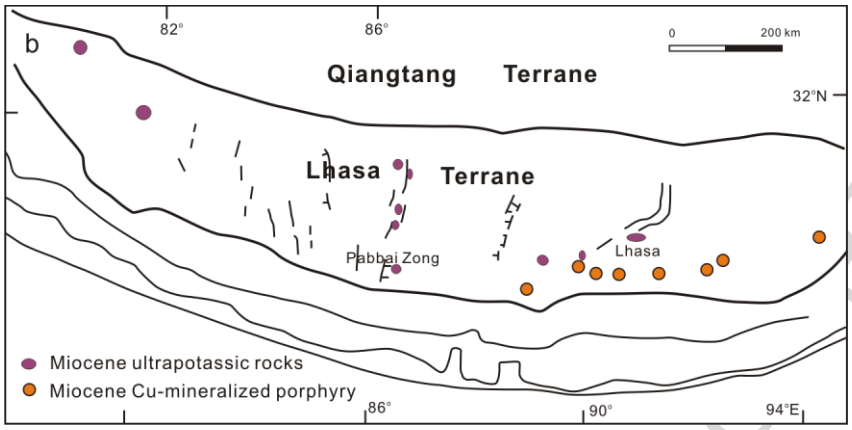


Fig. 1a



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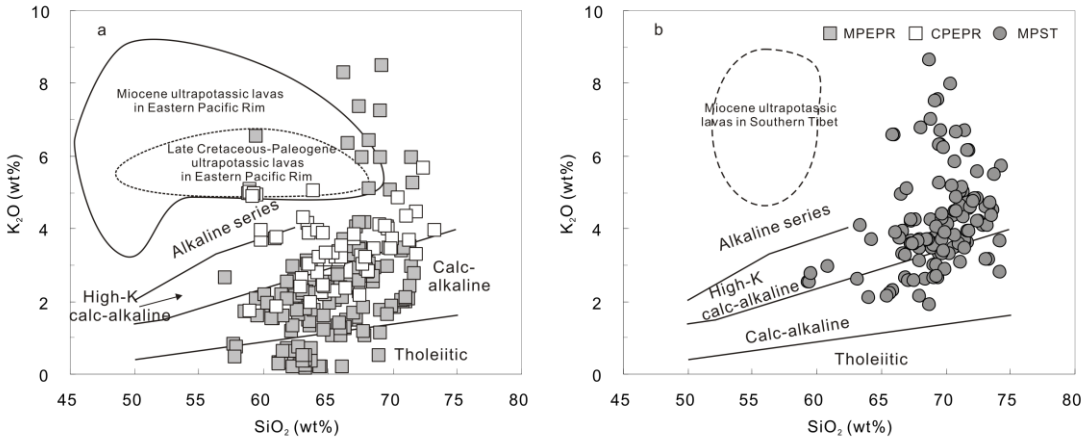

Fig. 2

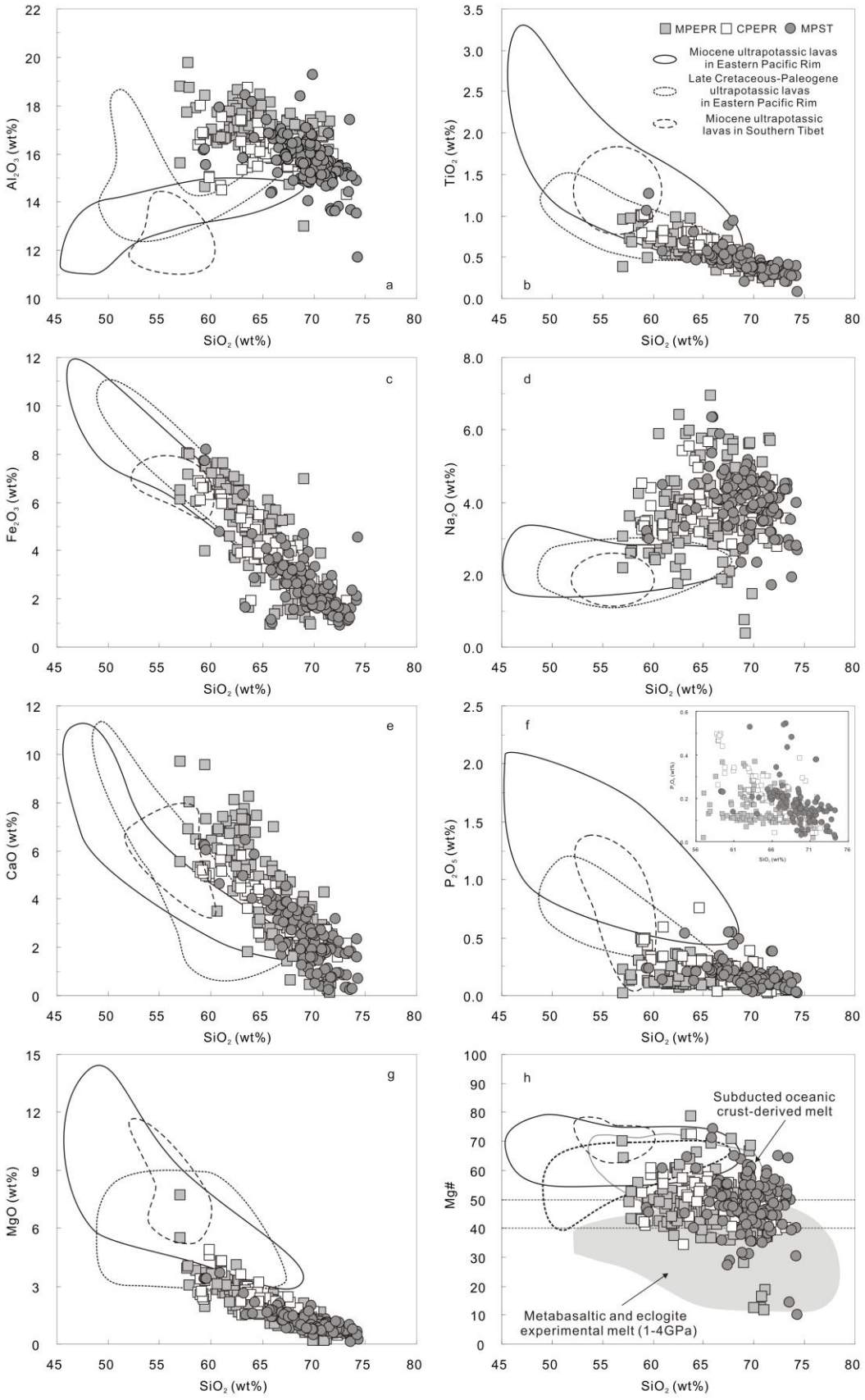

Fig. 3

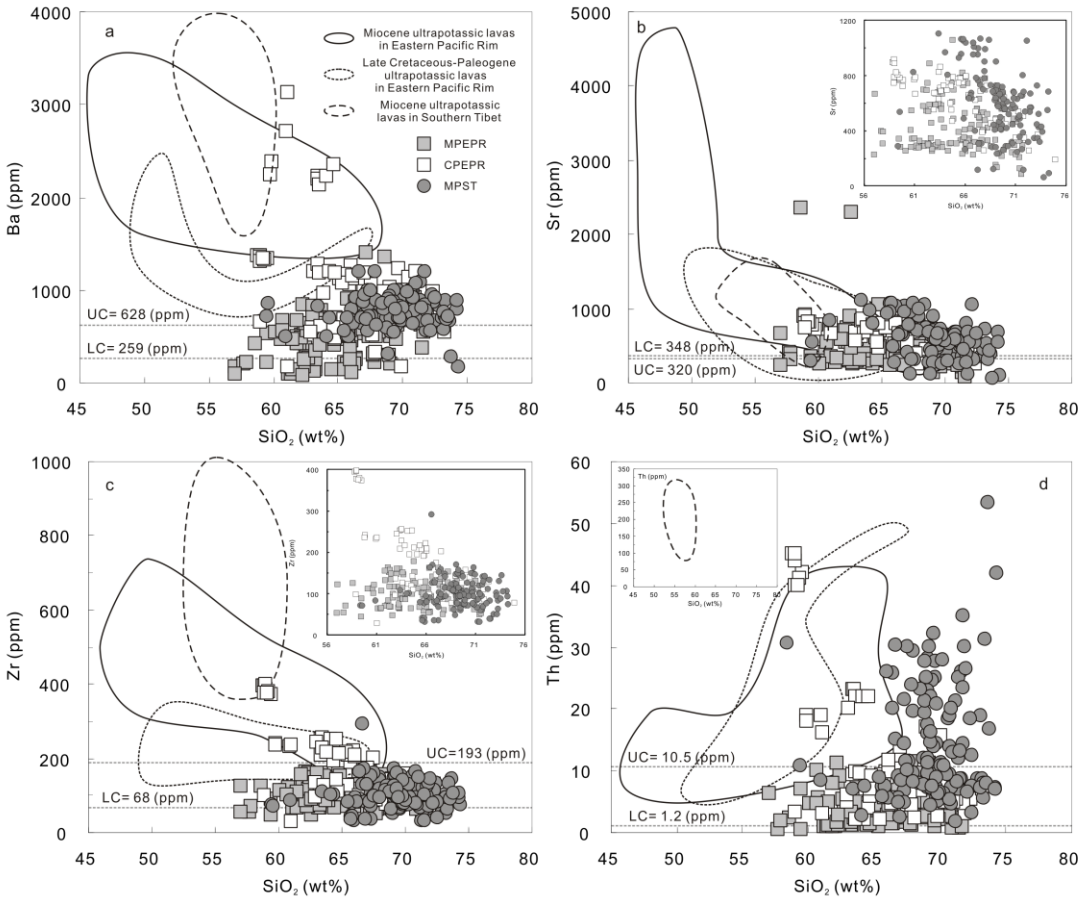

Fig. 4

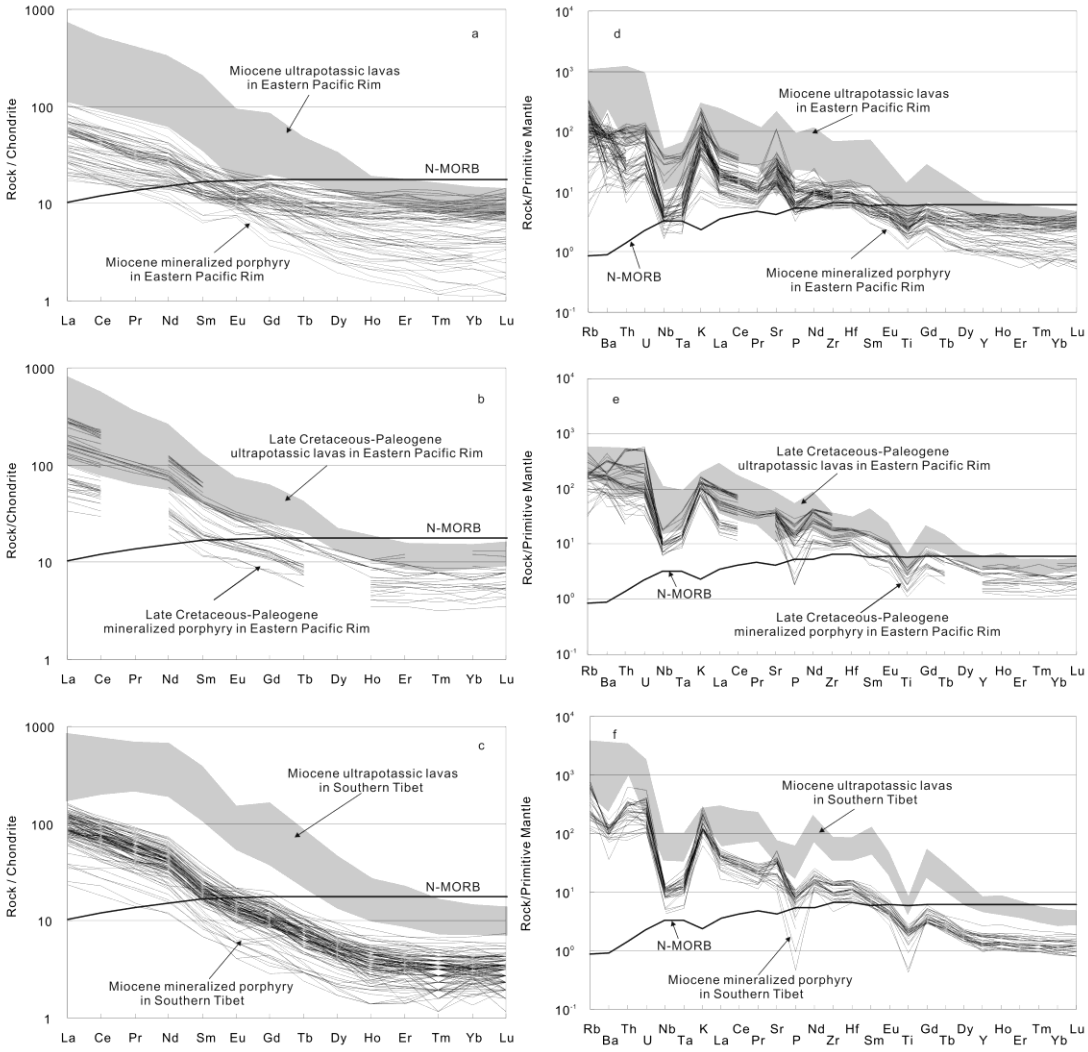

Fig. 5

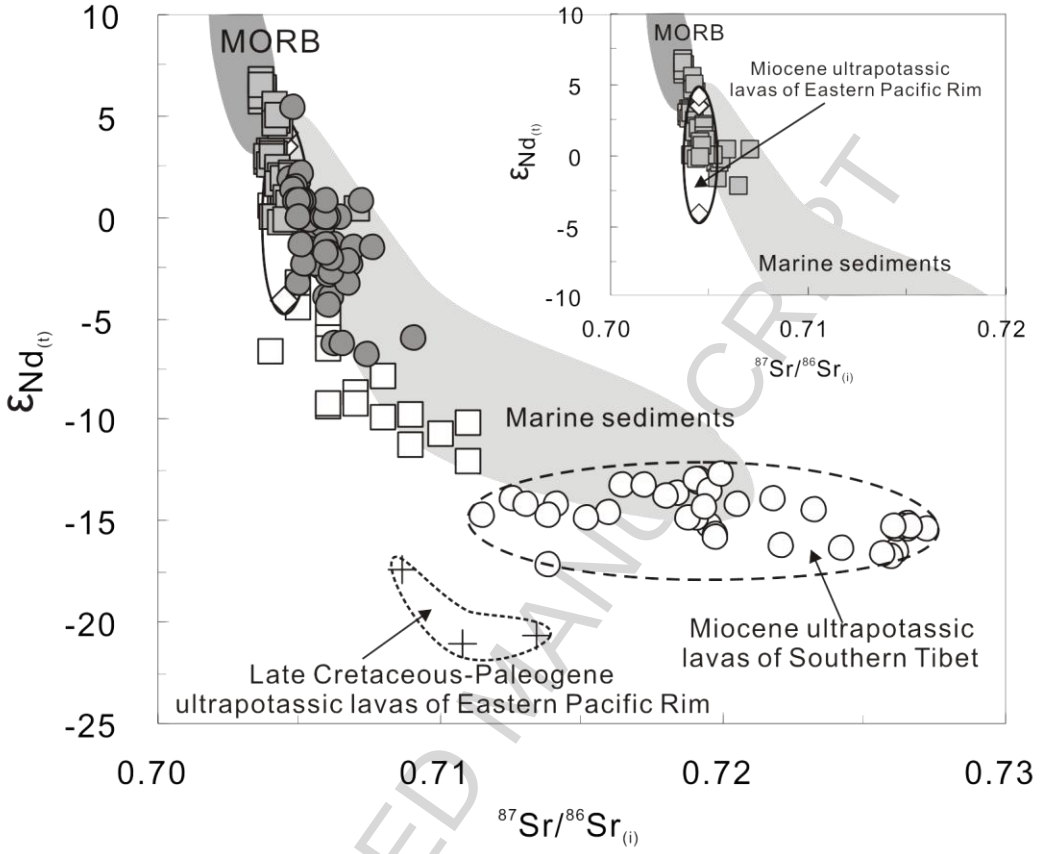

Fig. 6

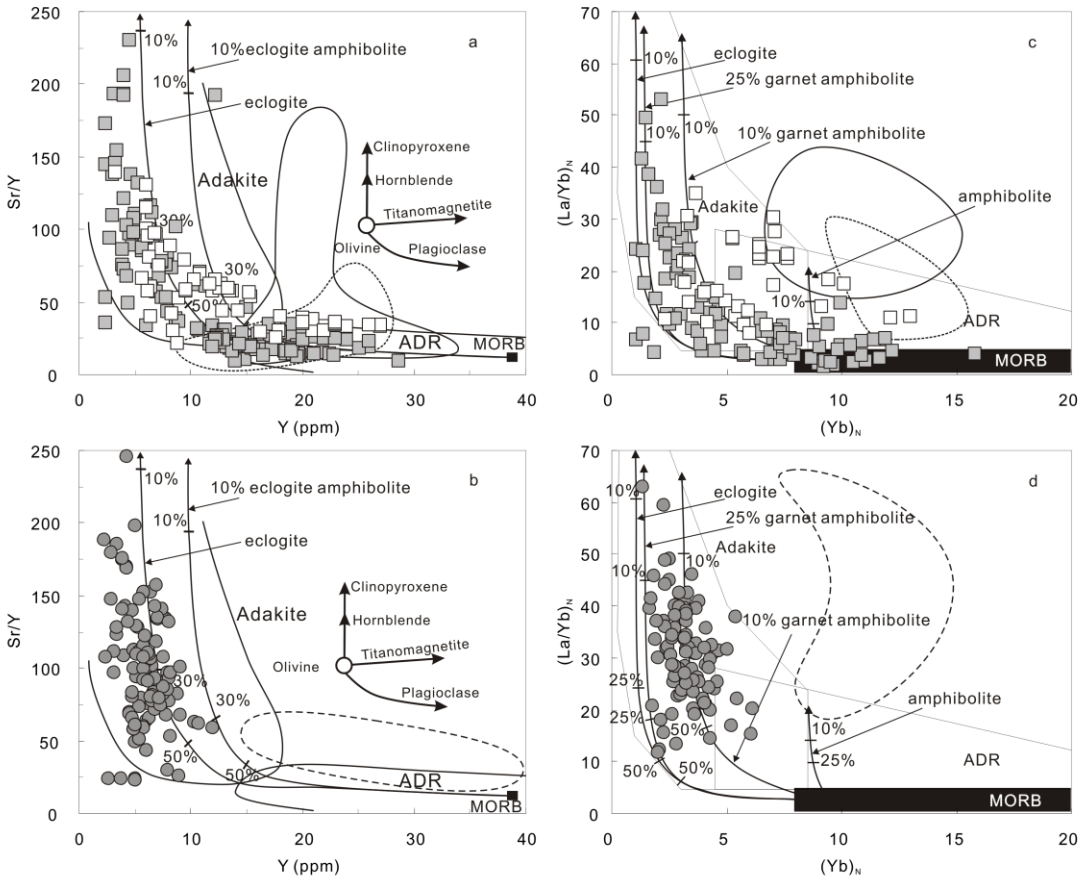

Fig. 7

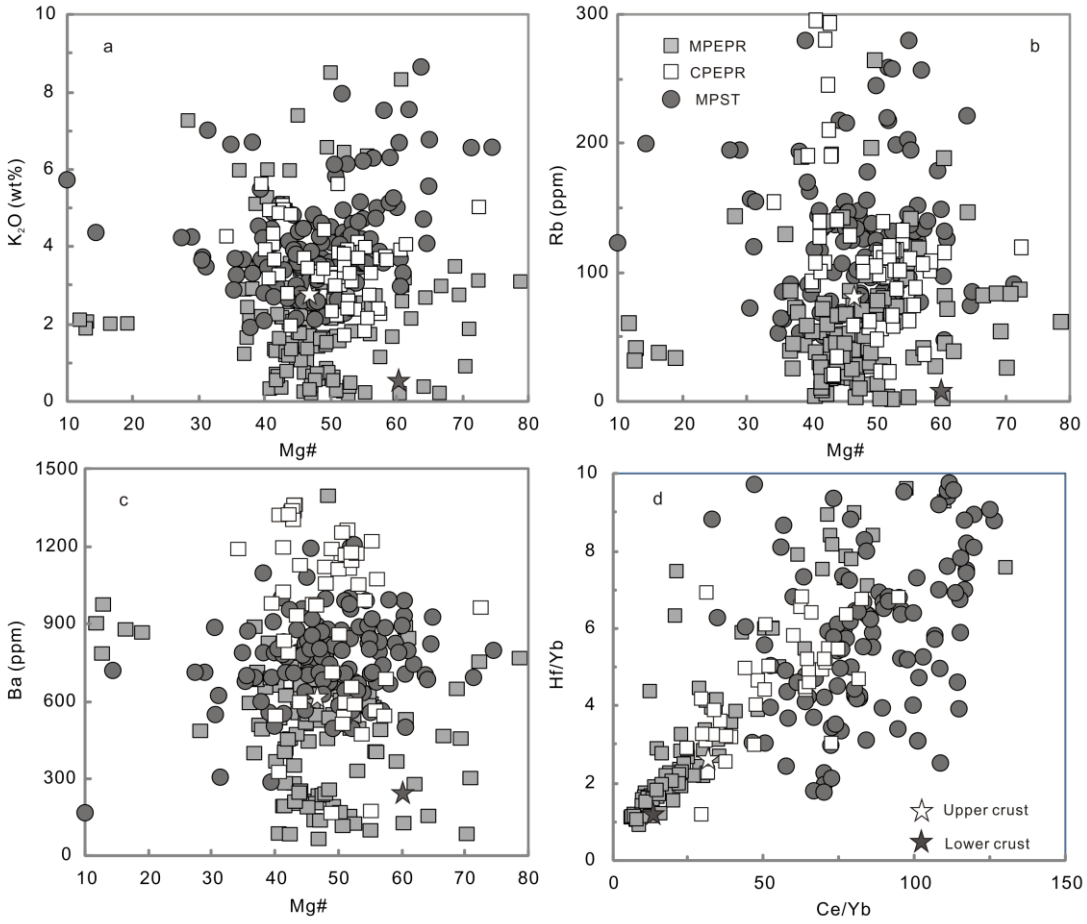

Fig. 8

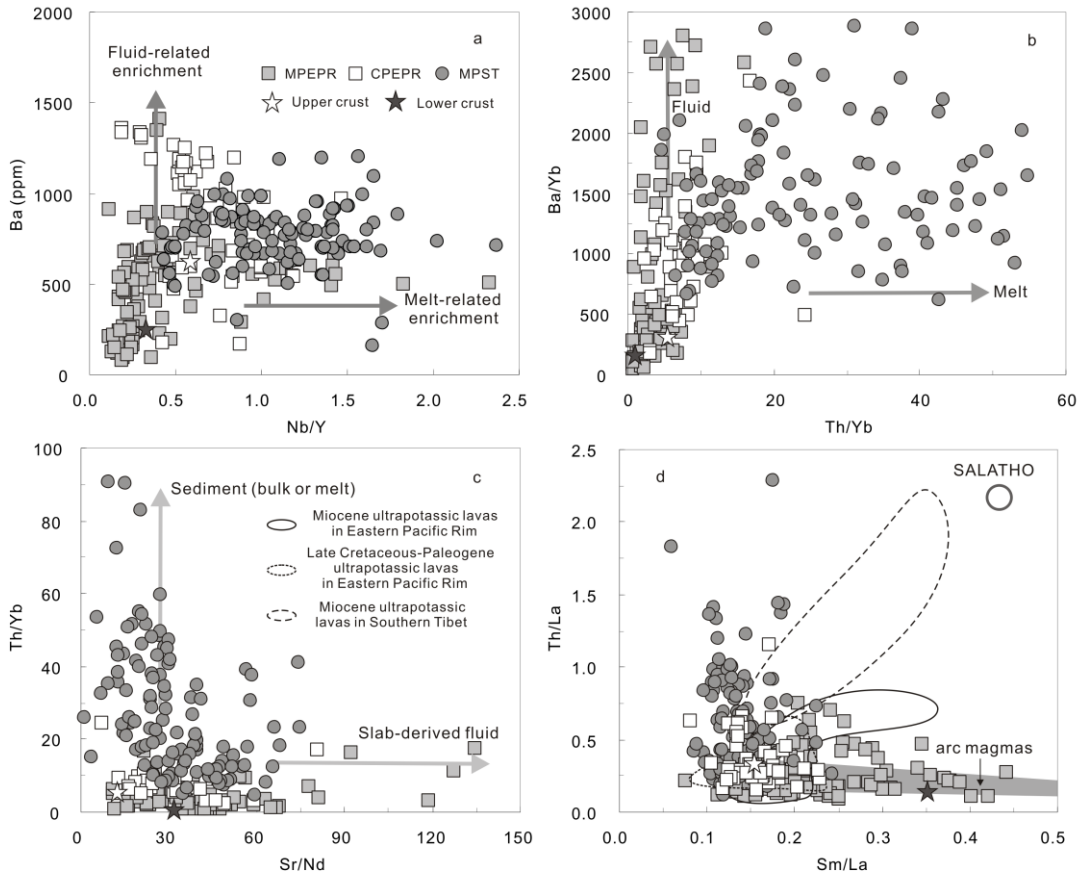

Fig. 9

Table 1. Geochemistry of subduction- and collision-related mineralized Cu porphyries.

Element	Data Range	MPEPR	CPEPR	MPST
Na_2O (wt.%)	Range	0.36~8.10	2.76~5.66	1.02~6.36
	Average	3.85 (n=142) *	3.79 (n=62)	3.95 (n=155)
K_2O (wt.%)	Range	0.17~8.47	1.73~5.64	1.64~8.65
	Average	2.25 (n=142)	3.61 (n=62)	**4.14** (n=155)
K_2O/Na_2O	Range	0.04~3.50	0.36~1.85	0.43~5.75
	Average	0.60 (n=139)	0.98 (n=61)	**1.29** (n=155)
MgO (wt.%)	Range	0.17~4.10	0.43~4.84	0.10~3.66
	Average	2.06 (n=140)	2.20 (n=62)	1.16 (n=155)
Mg#	Range	11.9~72.3	34.2~61.4	10.0~74.5
	Average	47.6 (n=141)	49.5 (n=61)	47.3 (n=155)
Sr (ppm)	Range	87.0~889	193~919	46.4~1106
	Average	418 (n=139)	657 (n=60)	576 (n=137)
Y (ppm)	Range	2.35~28.7	3.28~27.0	2.13~12.5
	Average	12.2 (n=140)	13.6 (n=60)	**6.00** (n=137)
Sr/Y	Range	9.41~206	21.8~116	18.1~261
	Average	51.5 (n=138)	55.0 (n=58)	**101** (n=135)
$(La/Sm)_N$	Range	1.46~5.76	2.82~5.44	2.66~7.56
	Average	3.25 (n=100)	**4.19** (n=53)	**4.76** (n=127)
$(Dy/Yb)_N$	Range	0.74~2.79	1.51~1.86	0.81~2.02
	Average	1.29 (n=97)	**1.68** (n=14)	**1.52** (n=127)
$(La/Yb)_N$	Range	1.67~53.1	7.95~34.7	11.7~63.0
	Average	13.0 (n=100)	18.6 (n=42)	**31.1** (n=128)
$\varepsilon Nd_{(t)}$	Range	-2.18~6.79	-12.1~-3.19	-6.83~5.70
	Average	2.97 (n=49)	-8.05 (n=18)	-1.32 (n=53)
$^{87}Sr/^{86}Sr_{(i)}$	Range	0.7037~0.7071	0.7054~0.7145	0.7034~0.7091
	Average	0.7044 (n=53)	0.7076 (n=17)	0.7058 (n=53)

*n = the number of samples = 142 (data sources are as for Fig. 2).