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1 Sediment recycling by continental subduction indicated by B-Hf-Pb-Nd isotopes from Miocene-Quaternary lavas in the northern margin of Tibet 2 3 Xiu-Zheng Zhang a, b, Qiang Wang A, b, c*, Andrew C. Kerrd, Gang-Jian Weia, b, Yue Qia, 4 Ying Liu^a, Yu-Cheng Yang^a 5 6 ^a State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, 7 Chinese Academy of Sciences, Guangzhou 510640, China 8 ^b CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China 9 ^c College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, 10 Beijing 100049, China 11 ^d School of Earth and Environmental Sciences, Cardiff University, Cardiff CF10 3AT, 12 13 UK14 15 16 **Corresponding Author:** * Qiang Wang, State Key Laboratory of Isotope Geochemistry (SKLaBIG), Guangzhou 17 Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS), Wushan Street, 18 19 Guangzhou, 510640, Tel: +8615724063366, Fax: 86-20-85290130; E-mail:

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Abstract

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Although it has been argued that sediment recycling plays an important role in the differentiation of the continental crust, boron (B) isotopic data does not support a direct input of subducted sediments into arc magmas. This raises questions about the viability of sediment recycling as a process in the differentiation of continental crust. Here, we report B isotopic data from Miocene-Quaternary lavas derived from different sources in the northern margin of Tibet. These lavas have high B contents and negative $\delta^{11}B$ values close to those of continental sediments. Strongly peraluminous rhyolites have the highest B (93 to 1559 ppm) contents with negative $\delta^{11}B$ (-9.7 to -17.9) values. Adakitic dacites and trachyandesites exhibit the lowest B (18 to 29 ppm) contents with markedly negative δ^{11} B (-12.0 to -35.7) values whereas olivine leucitites have B (37.2 to 59.3 ppm) contents with negative δ^{11} B (-8.3 to -15.6) values. These lavas also have enriched Hf-Pb-Nd isotopic compositions similar to those of sediments. This data, combined with numerical modelling and geophysical and tectonic data for Cenozoic continental subduction in the northern margin of Tibet, indicates that: (1) the strongly peraluminous rhyolites were generated by partial melting of mica-bearing continental sedimentary rocks subducted to the depth of mid-to-lower crust; (2) adakitic lavas were derived by partial melting of sediment-bearing thickened lower crust underwent dehydration and eclogites-facies metamorphism; and (3) olivine leucitites were generated by partial melting of enriched mantle metasomatized by sediment-bearing eclogite-facies crust-derived melts. Thus, at continental convergent margins, continental subduction is an important mechanism for sediment recycling and the evolution of continental crust.

45	Keywo	ords:
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- 46 Boron isotopes; Continental subduction; Sediment recycling; Miocene-Quaternary;
- 47 Tibetan Plateau

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Highlights:

- 50 > B-Hf-Pb-Nd isotopes reveal that subducted continental sediments entered the mid-to-
- 51 lower crust and mantle of northern Tibet.
- 52 > Subducted sediments in mid-to-lower crust and mantle were recycled to the continental
- crust via magmatism.
- 54 > Continental subduction is an important mechanism for sediment recycling and the
- evolution of continental crust.

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1. Introduction

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The continental crust has an andesitic bulk composition, this is however inconsistent, with 58 59 the predominantly basaltic magmas that contribute to the present-day continental crust (Rudnick, 1995; Hawkesworth and Kemp, 2006). To solve this discrepancy, a range of 60 models for the differentiation of the continental crust have been proposed, including the 61 62 removal of Mg through chemical weathering (Lee et al., 2008; Shen et al., 2009; Liu and Rudnick, 2011), direct addition of intermediate-acid magmas to the crust through melting 63 of subducted oceanic slab (Defant and Drummond, 1990; Gazel et al., 2015) or basaltic 64 lower crust (Atherton and Petford, 1993), removal of mafic/ultramafic lower crust through 65 foundering/delamination (Arndt and Goldstein, 1989; Kay and Kay, 1993; Rudnick, 66 1995; Jull and Kelemen, 2001), the reworking of sedimentary materials by mantle-like 67 magmas (Kemp et al., 2007), or subduction of continental or oceanic crust followed by 68 "relamination" of buoyant and felsic crust (Hacker et al., 2011). 69 70 It is clear, however, that the recycling of crustal materials plays an important role in the 71 differentiation of continental crust. Moreover, some crustal materials may also be recycled 72 73 into mantle, thereby contributing to mantle heterogeneity (Plank and Langmuir, 1993; Liu and Rudnick, 2011). For example, in island arc zones, sediments from subducted oceanic 74 75 slabs have been suggested to recycle to the continental crust through arc magmatism (Plank 76 and Langmuir, 1993; Hawkesworth et al., 1997; Behn et al., 2011; Marschall and Schumacher, 2012) or relamination (Hacker et al., 2011), or directly enter the overlying 77 78 mantle wedge by the buoyant diapir rise due to their low density (Behn et al., 2011; 79 Marschall and Schumacher, 2012).

Boron is an excellent tracer of crustal recycling at convergent margins, given its high concentration in subducted sediments and altered oceanic crust (AOC) relative to mantle or mantle-derived fresh rocks. Furthermore, it is highly mobile during partial melting and dehydration, and its isotopes are strongly fractionated during their transfer in seawater or crust (Morris et al., 1990; Palmer, 1991; Moran et al., 1992; Edwards et al., 1993; Ishikawa and Nakamura, 1994; Chaussidon and Marty, 1995; Leeman and Sisson, 1996). In addition, several studies have demonstrated substantial differences in the δ^{11} B values of subducted continental sediments, marine sediments, and AOC (Ishikawa and Nakamura, 1994; Chaussidon and Marty, 1995; Leeman and Sisson, 1996; Rose et al., 2001; Clift et al., 2003; Yamaok et al., 2012), highlighting the unparalleled advantage of B isotopes in tracing recycling processes in subduction zones (Palmer, 2017; De Hoog and Savov, 2018; Wang et al., 2020).

Nd-Hf-Pb isotopic systematics reveal that sediments from subducted oceanic slabs are recycled to the continental crust by arc magmatism (Plank and Langmuir, 1993; Hawkesworth et al., 1997; Shimoda et al., 1998; Chauvel et al., 2008; Behn et al., 2011; Marschall and Schumacher, 2012). However, paradoxically, B isotopic data suggests that arc magmatic rocks are derived from mantle wedge metasomatized by fluids released from subducted basaltic oceanic crust and overlying sediments, rather than directly from subducted sediments themselves (Morris et al., 1990; Edwards et al., 1993; Ishikawa and Nakamura, 1994; Leeman and Sisson, 1996; Smith et al., 1997; Clift et al., 2003). In other words, many arc lavas contain material derived from subducted oceanic crust and

sediments, but it remains unresolved whether this distinctive geochemical signature is transferred from the subducting slab by aqueous fluids, oceanic crust or sediment-derived silicate melts, or both (Peacock and Hervig, 1999). It therefore remains unclear whether subducted sediments can reenter the continental crust via arc magmatism. This raises questions about the possibility of sediment recycling in the differentiation of continental crust.

Unlike island arcs, the Cenozoic Himalayan-Tibetan Orogen resulted from the convergence (collision or continental subduction) processes between the Indian and Eurasian continents (Yin and Harrison, 2000; Chung et al., 2005). Apart of this process the Indian and Eurasian continents are subducting northward and southward beneath the Tibetan lithosphere, respectively (Kind et al., 2002; McKenzie and Priestley, 2008; Nábelek et al., 2009; Zhao et al., 2010, 2011; Ma et al., 2021; Hao et al., 2022). As a result Cenozoic magmatic rocks widely occur in Himalayan-Tibetan Orogen, and were derived by partial melting of midto-lower crustal sedimentary rocks (e.g., Himalayan leucogranites and northern Tibet tourmaline-bearing mica rhyolites) (e.g., Patiño Douce and Harris, 1998; Knesel and Davidson, 2002; Guo and Wilson, 2012; Wang et al., 2012), thickened lower crust (e.g., adakitic rocks in northern, central and southern Tibet) (e.g., Chung et al., 2003, 2005; Wang et al., 2005, 2008) and mantle (e.g., potassic and ultra-potassic rocks) (Turner et al., 1993; Chung et al., 1998, 2005; Ding et al., 2003).

Of particular interest are Miocene-Quaternary (18.0–1.5 Ma) lavas in the Hohxil area, northern margin of Tibet. The three end-member sources discussed above, contributed to

petrogenesis of these lavas (Wang et al., 2005, 2012). This therefore provides an excellent opportunity to assess whether sediment recycling took place in the convergent margin. In this study, we present detailed B as well as Nd-Hf-Pb isotopic data for the Hohxil lavas, which suggests that subducted continental sediments entered the mid-to-lower crust and mantle and were subsequently recycled to the continental crust via magmatism. These findings confirm that the recycling of subducted sediments plays an important role in the differentiation of the continental crust (Plank and Langmuir, 1993; Hawkesworth et al., 1997; Chauvel et al., 2008; Behn et al., 2011; Liu and Rudnick, 2011; Marschall and Schumacher, 2012).

2. Geological background

The Himalayan-Tibetan Orogen mainly comprises the Qaidam-Kunlun, Songpan-Ganzi, Qiangtang, Lhasa and Himalayan blocks (Yin and Harrison, 2000; Chung et al., 2005) (Fig. 1a). The Songpan-Ganzi Block is bounded by the Jinshajiang suture to the south, and the Anyimaqen-Kunlun-Muztagh suture to the north (Yin and Harrison, 2000). The exposed Songpan-Ganzi Block consists mainly of Triassic and younger strata with some Mesozoic granites exposed in the central-eastern region (Yin and Harrison, 2000) and some Miocene-Quaternary volcanic rocks in the central-western region (Chung et al., 2005). The magmatic rocks investigated in this study are exposed as volcanic domes or lava sheets in six distinct areas within the Hohxil district, situated in the central Songpan-Ganzi Block. Specifically, these rocks comprise the southern Malanshan and Bukadaban biotite rhyolites, the Hudongliang tourmaline-bearing mica rhyolites, the western Wuxuefeng trachyandesites, the Hongshuihe dacites, and the southern Hohxil Lake olivine leucitites

149 (Fig. 1b). Notably, all of these volcanic rocks unconformably overlie Lower Triassic,

Lower Cretaceous, or Tertiary strata (Wang et al., 2005; Qi et al., 2020).

The tourmaline-bearing mica and biotite rhyolites, which have a strong peraluminous composition, were generated between 9.0–1.5 Ma (Wang et al., 2012). The southern Malanshan biotite rhyolitic porphyries are characterized by phenocrysts of potassium feldspar, plagioclase, biotite, and quartz, whereas the Hudongliang tourmaline-bearing two-mica rhyolites contain phenocrysts of potassium feldspar, albite, biotite, quartz, muscovite, and tourmaline (Figs. 2a, b). The Bukadaban biotite rhyolites also have phenocrysts of potassium feldspar, plagioclase, biotite, and quartz (Fig. 2c). The groundmass of these rocks has a microlitic mineral composition that is similar to the phenocrysts and may contain cryptocrystalline-glassy materials. It has been suggested that these peraluminous felsic rocks were derived from mid-to-lower crustal sedimentary rocks (Wang et al., 2012).

The dacites and trachyandesites, which were generated between 18–15 Ma, have an adakitic composition resulting from partial melting of thickened eclogitic lower crust (Wang et al., 2005). The trachyandesites in western Wuxuefeng are characterized by porphyritic or glomeroporphyritic textures, with abundant phenocrysts surrounded by a fine-grained trachytic groundmass. The major phenocryst phases include potassium feldspar, plagioclase, clinopyroxene, and amphibole, while the groundmass is composed of a combination of potassium feldspar, clinopyroxene, plagioclase, biotite, and Fe-Ti oxides (Fig. 2d). Similarly, the Hongshuihe dacites consist of phenocrysts of potassium

feldspar, plagioclase, amphibole, and quartz, embedded in a cryptocrystalline-glassy groundmass (Fig. 2e).

The olivine leucities from southern Hohxil Lake were generated at ca. 16 Ma and originated from enriched mantle metasomatized by subducted sediments during southward subduction of the Asian continent (Wang et al., 2005; Qi et al., 2020). These rocks exhibit a characteristic porphyritic texture, with prominent phenocrysts of olivine, leucite, and clinopyroxene, and a microlitic to cryptocrystalline groundmass. The olivine and leucite phenocrysts are euhedral in shape and range in size from 0.2 to 1.5 mm (Fig. 2f). The groundmass of these rocks is composed of clinopyroxene, leucite, nepheline, titanomagnetite, sodalite, and apatite.

3. Results

We analyzed 18 whole-rock B isotopes, 16 whole-rock Hf isotopes, and 13 whole-rock Pb isotopes from Miocene-Quaternary lavas in the Hohxil area, and combined this data with previously published Nd-Pb isotopic data (Wang et al., 2005, 2012; Qi et al., 2020) to create a complete B-Hf-Nd-Pb isotope dataset. The analytical methods and all the isotopic data are listed in Supplementary data Text S1 and Tables S1–S2.

All Miocene–Quaternary lavas in the Hohxil area have high B contents and negative $\delta^{11}B$ values close to those of continental sediments (Fig. 3). Peraluminous rhyolites have the highest B (93–1559 ppm) contents with negative $\delta^{11}B$ (–9.7 to –17.9) values. The adaktic lavas exhibit the lowest B (18–29 ppm) contents with clearly negative $\delta^{11}B$ (–12.0 to –35.7)

values, and the potassic olivine leucitites have B contents (37.2 to 59.3 ppm) and $\delta^{11}B$ (-8.3 to -15.6) values broadly intermediate between the other two groups (Table S1). All of the rocks also exhibit enriched Pb-Nd-Hf isotopic compositions comparable to the sediments (Fig. 4). They have similar $^{206}Pb/^{204}Pb$ (18.56–18.75), $^{207}Pb/^{204}Pb$ (15.49–15.72) and $^{208}Pb/^{204}Pb$ (38.31–39.01) ratios (Table S2). Strongly peraluminous rhyolites have the lowest $\varepsilon_{Nd}(t)$ (-5.83 to -7.41) and $\varepsilon_{Hf}(t)$ (-0.61 to -5.14) values, adaktic lavas exhibit consistent $\varepsilon_{Nd}(t)$ (-1.80 to -4.30) and $\varepsilon_{Hf}(t)$ (-0.36 to 0.16), and potassic olivine leucitites have similar $\varepsilon_{Nd}(t)$ (-3.07 to -3.89) and $\varepsilon_{Hf}(t)$ (0.23 to 1.08) values (Table S2).

4. Discussion

4.1 The relationships between B and Th, Nd, Pb and Hf

As mentioned above, a "paradox" exists between Nd-Hf-Pb and B isotopic compositions for arc magmatic rocks. We suggest that this "paradox" is caused by the geochemical differences between Nd-Hf-Pb and B. Boron is highly soluble in aqueous fluids at low temperatures, while the light rare elements (LREEs: La, Ce and Nd) and high field-strength elements (HFSEs: Nb, Ta, Zr, Th and Hf) are relatively immobile in aqueous fluids (Leemn and Sisson, 1996; Hawkesworth et al., 1997). The situation with Pb is a bit more complex because Pb²⁺ can be soluble in aqueous fluids, but Pb⁴⁺ behaves in a similar manner to HFSEs and is immobile in aqueous fluids. During subduction, some B may be lost from subducting slab and enter subduction-related fluids prior to the melting of the subducting AOC and sediments at high temperatures (Leeman and Sisson, 1996; Rose et al., 2001; Clift et al., 2003), but Nd, Hf and Pb remain in the subducting slab and do not enter the subduction-related fluids until temperatures exceed the solidus and initiate partial melting

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In addition, at high magmatic temperatures, B isotopes do not fractionate significantly and are likely to reflect source compositions (Palmer et al., 1992; Chaussidon and Marty, 1995). However, in subduction zones, the source compositions of arc magmatic rocks are complex, and include fluids or melts from the subducting AOC, sediments, and mantle wedge peridotites. Moreover, subduction-related fluid-triggered melting of mantle wedge peridotites or the interaction between subduction-related melts and mantle wedge peridotites results in substantial amounts of mantle wedge peridotite material contributing to the source of arc magmatic rocks. Boron and its isotopes in arc magmatic rocks are considered to resemble those of major fluid reservoirs, such as AOC or slab sediments (Morris et al., 1990; Edwards et al., 1993; Ishikawa and Nakamura, 1994; Leeman and Sisson, 1996; Smith et al., 1997; Clift et al., 2003). In contrast, Nd-Pb or Hf isotopes in arc rocks are likely to broadly reflect mantle wedge compositions (e.g., Edwards et al., 1993) or melt compositions from subducting sediments or oceanic crust if the subducting slab has melted (Kay et al., 1978; Plank and Langmuir, 1993; Hawkesworth et al., 1997; Shimoda et al., 1998; Chauvel et al., 2008; Behn et al., 2011).

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Unlike magmatic arc rocks the magmatic rocks from continental collisional zones (e.g., the Himalayan-Tibetan Orogen) may contain some rocks directly derived by partial melting of crustal sedimentary rocks (e.g., tourmaline-bearing leucogranites or strongly peraluminous rhyolites), which can provide important information on the relationship between B and other elements (Th, Nd, Pb and Hf) during partial melting of continental sediments (Figs.

5 and 6). In the Hohxil area, Miocene-Quaternary (9.0–1.5 Ma) strongly peraluminous rhyolites were generated by partial melting of mid-crustal sedimentary rocks (Wang et al., 2012). The geochemical similarities (i.e., their incompatibility) of B, Pb and Th result in their enrichment in sediments, and allow Pb and Th to readily enter melts, while B enters melts or fluids during sediment melting (Kay et al., 1978; White et al., 1986; Morris et al., 1990; Plank and Langmuir, 1993; Leeman and Sisson, 1996; Hawkesworth et al., 1997). However, unlike B, Th is only mobilized in the sediment component (Hawkesworth et al., 1997). Thus, for the Hohxil strongly peraluminous rhyolites, the negative correlation between Th and B contents (Fig. 5a) indicates geochemical differences during sediment melting.

High B/Nb and Th/Nb ratios are likely to indicate predominantly sediment-derived aqueous fluid (Ishikawa and Nakamura, 1994) and sediment-derived melt components (Hawkesworth et al., 1997), respectively. Thus, the Th/Nb vs B/Nb diagram can help reveal the trends of sediment melting and aqueous fluid for the Hohxil strongly peraluminous rhyolites (Fig. 4b), which suggests that both sediment-derived fluids and melts played a critical role in their petrogenesis. The negative correlations between B and Nd, Pb and Hf (Fig. 5c, e and g), and the two composition trends in Nd/Nb, Pb/Nd and Hf/Nb vs B/Nb space (Fig. 5d, f and h) suggest that Nd, Pb and Hf have geochemical characteristics similar to Th during sediment melting, thus providing further evidence of the contributions of both sediment-derived fluids and melts in the formation of the Hohxil strongly peraluminous rhyolites.

Based on detailed studies of elemental and Sr-Nd-Pb-Hf geochemistry, as well as experimental petrology data (Fig. 4a-c), the Hohxil strongly peraluminous rhyolites are considered to have been generated by dehydration melting of muscovite- and biotite-bearing sedimentary rocks (Wang et al., 2012). As B is primarily hosted by micas and clay minerals in silicic rocks (Leeman and Sisson, 1996), it can easily enter sediment-derived fluids and melts due to its incompatibility during dehydration melting. The Hohxil strongly peraluminous rhyolites exhibit negative $\delta^{11}B$ (-9.7 to -17.9) values, similar to continental sediments, and B (93–1559 ppm), B/Zr (1–27) and B/Ce (1–70) values close to, or slightly higher than, those of continental or marine sediments (Figs. 3 and 6). This confirms that B behaves as an incompatible trace element, preferentially residing in fluids and melts during sediment melting (Leeman and Sisson, 1996).

Furthermore, the rhyolites in this study have high B contents similar to those of leucogranites from the Himalayas, the Tuscan (Italy) magmatic province, strongly peraluminous rhyolites from the Spor Mountain and Honeycomb Hills (Utah, USA), Taylor Greek (SW New Mexico) and Macusani (Peruvian Andes). All of these rocks formed in areas characterized by significant crustal thickening (Leeman and Sisson, 1996). This indicates that significant B enrichment in their sedimentary source regions (Leeman and Sisson, 1996). For the Hohxil strongly peraluminous rhyolites and the Himalaya leucogranites in the northern and southern margins of Tibet, respectively, the most likely source rocks are sedimentary rocks that entered the mid-to-lower crust during crustal thickening by the subduction or underthrusting of continental crust (e.g., Searle et al., 1997; Guo and Wilson, 2012; Wang et al., 2012). Furthermore, in the northern margin of Tibet,

the B-Pb isotope systematics of the Hohxil strongly peraluminous rhyolites (Figs. 3 and 4d) suggest that such sedimentary rocks are likely to be of continental affinity.

4.2 Subducted continental sediments entered the eclogites-facies lower crust

The discovery of the relationship between B and Th, Nd, Pb and Hf during sediment melting may help to further constrain the petrogenesis of the Hohxil Miocene adakitic lavas. Based on element and Sr-Nd isotopic data, these adakitic rocks were considered to have been generated by partial melting of eclogitic lower crust thickened by continental subducting (Wang et al., 2005). However, the new data for whole rock Pb-Hf, as well as Nd isotopes, further indicate that the adakitic rocks clearly contain a sediment component (Fig. 4a-c). They have more negative $\delta^{11}B$ (-12.0 to -35.7) values, and lower B (18–29 ppm) contents than those of the Hohxil strongly peraluminous rhyolites. Added to this, their B contents are close to, or slightly lower than, those of continental or marine sediments (Figs. 3 and 6), but similar to the average value (20 ppm) of continental upper crust and are clearly higher than the average values (1.0, ~ 0.1 and < 0.05 ppm) of continental lower crust, primitive mantle and depleted mantle, respectively (Fig. 6b) (Chaussidon and Marty, 1995; Leeman and Sisson, 1996).

B-Pb isotope systematics (Figs. 3 and 4d) suggest the source of these adakitic rocks should contain continental-affinity rocks. However, they also exhibit Nb/Ta (15–21) and B/Ce (0.08–0.13) ratios similar to those of mantle (Fig. 6) (Leeman and Sisson, 1996; Rudnick et al., 2000; Wang et al., 2005), but different from those (3–10 and 1.0–70) of the Hohxil strongly peralumious rhyolites (Fig. 6) (Wang et al., 2012). This indicates that their source

region also contained a mafic component from mantle, in addition to a continental sediment component. They have the lowest B contents (Figs. 3 and 5) among Miocene-Quaternary crust and mantle-derived magmatic rocks in the Hohxil area, suggesting that they could not be generated by mixing between crust- and mantle-derived magmas. Therefore, the mafic endmember component of the source region of adaktic rocks is likely to be mafic rocks in the lower crust rather than mafic magmas entering the lower crust. These adaktic rocks are likely to be derived by partial melting of this mixed source with meta-mafic and sedimentary rocks under eclogite-facies conditions (Wang et al., 2005). The metasedimentary rocks possibly entered the lower crust through continental subduction, as suggested by previous investigations in petrology, geochemistry, numerical modelling, and geophysics (e.g., Willett and Beaumont, 1994; Hacker et al., 2000, 2012; Yin and Harrision, 2000; Tapponnier et al., 2001; Kind et al., 2002; Kapp et al., 2003; McKenzie and Priestley, 2008; Zhao et al., 2010, 2011; Huangfu et al., 2018; Ma et al., 2021; Hao et al., 2022).

Prograde metamorphism and accompanying dehydration of subducting continental crust at lower crust to mantle depths may cause B isotopic fractionation similar to that of a subducting oceanic slab. This is because dehydration of a subducting oceanic slab extracts B into the fluid and leaves residues that are depleted in B (Rose et al., 2001). Some studies have shown that $\delta^{11}B$ of dehydration residues (prograde metamorphic rocks) become progressively lighter with increasing degrees of dehydration (Moran et al., 1992; Bebout et al., 1993; Peacock and Hervig, 1999; Nakano and Nakamura, 2001; Rose et al., 2001). Therefore, the dehydration process results in increasingly lower B concentrations and increasingly light B isotopic compositions in both residual rock and instantaneous fluid

(Rose et al., 2001). Eclogitic lower crust-derived adakitic rocks have the lowest B contents and some samples also have the lowest $\delta^{11}B$ values (Figs. 3, 5 and 6) among Miocene-Quaternary crust and mantle-derived magmatic rocks in the Hohxil area. This indicates that their sources may have undergone B isotopic fractionation during dehydration and eclogites-facies metamorphism. Consequently, their sources (subducted sediment-bearing continental crust) should have lower B contents and $\delta^{11}B$ values than those of source rocks for the Hohxil strongly peraluminous rhyolites.

4.3 Mantle metasomatized by subducted continental sediments

Mantle-derived olivine leucitites were likely generated by partial melting of mantle that was metasomatized by subducted sediment-bearing eclogitic continental crust-derived melts or fluids. Generally, mantle has low B contents (≤ 0.1 –0.05 ppm), which lead to mantle-derived magmas with low B contents (≤ 1 ppm) (Chaussidon and Marty, 1995). However, the leucitites in this study exhibit relatively high B (37 to 59 ppm) contents with negative δ^{11} B (-8.3 to -15.6) values, similar to those of continental or marine sediments, or the continental upper crust (Figs. 3 and 6). This suggests that these leucitites may be derived from mantle that was enriched by subducted sediments. They have Nd-Hf-B isotope compositions broadly similar to eclogitic lower crust-derived adaktic rocks (Figs. 3 and 4). Additionally, both leucitites and adaktic rocks exhibit many similar trace element geochemical characteristics (Figs. 5 and 6), indicating a sediment melt composition trend (Figs. 5 and 6). Therefore, we suggest that the leucitites were likely generated by partial melting of mantle that was metasomatized by subducted sediment-bearing eclogitic lower crust-derived melts and/or fluids. Nevertheless, the leucitites exhibit clearly higher B

contents than those of the adakitic rocks (Fig. 3). It is worth noting that subducting continental crust-derived melts and/or fluids could metasomatize portions of the upper mantle and induce melting to produce B-rich and high $\delta^{11}B$ magmas.

5. Conclusions

- Evidence based on B-Hf-Pb-Nd isotopes of Miocene-Quaternary lavas in the northern margin of Tibet indicates that subducted continental sediments entered the mid-to-lower crust and mantle, and then were recycled to the continental crust via magmatism.
- 2) The strongly peraluminous rhyolites with the highest B contents were generated by partial melting of mica-bearing continental sedimentary rocks at mid-to-lower crustal depths.
- 3) The adaktic lavas with the lowest B contents were derived by partial melting of sediment-bearing thickened lower crust at eclogites-facies conditions.
- 4) The olivine leucitites with intermediate B contents were generated by partial melting of mantle metasomatized by sediment-bearing eclogitic continental crust-derived melts.
- 5) Our new results indicate that the recycling of subducted sediments plays an important role in the differentiation of the continental crust at continental convergent margins.

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Figure captions

- Figure 1. (a) Geological sketch map of Tibet showing major blocks and temporal-spatial
- 570 distribution of Cenozoic volcanic rocks (modified from Chung et al., 2005). Cenozoic
- volcanic rocks data are from Chung et al. (2003), Ding et al. (2003), and Wang et al. (2005).
- Main suture zones between major blocks: AKMS—Anymaqen–Kunlun–Muztagh Suture;
- 573 JS—Jinsha Suture; BS—Bangong–Nujiang Suture; IS—Indus–Yarlung Zangbo Suture.
- Major faults: STDS—southern Tibet detachment system; MBT—Main Boundary thrust.
- 575 (b) Simplified geologic map showing outcrops of magmatic rocks in Hohxil area, Songpan-
- 576 Ganzi block, northern Tibet

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- Figure 2 Photomicrographs of the Miocene–Quaternary lavas. (a) The southern Malanshan
- 579 biotite rhyolitic porphyries (sample 2303, crossed polarized light); (b) the Hudongliang
- tourmaline-bearing two-mica rhyolite (sample 1P2JD7-1, plane-polarized light); (c) the
- Bukadaban biotite rhyolite (sample 2303, crossed polarized light); (d) the western
- Wuxuefeng trachyandesites (sample 3302, plane-polarized light); (e) the Hongshuihe
- dacites (sample 3304-3b, crossed polarized light); (f) the Hoh Xil olivine leucitites (sample
- 6304b, crossed polarized light). Ab = albite, Bt = biotite, Kf = potassium feldspar, Mus =
- muscovite, Pl = plagioclase, Qtz' = quartz, Tm = tourmaline, Ol = olivine, Amp =

amphibole, Cpx = clinopyroxene, Lec = leucite, Xe = nepheline; Ap = apatite; Tmt = titanomagnetite.

Figure 3 δ^{11} B—boron contents (B) diagram (modified from Rose et al., 2001). MORB—mid-ocean ridge basalts; OIB—ocean island basalts; AOC—altered oceanic crust; DMM—depleted MORB mantle. Striped fields for B reservoirs (MORB, OIB, AOC and DMM), as well as melt inclusions hosted by high-Mg olivines in basaltic andesite from Mt. Shasta and their potential source rock are from Rose et al. (2001) and references therein. The fields for continental sediments, marine sediments and arc lavas are after Leeman & Sisson (1996). The B-Pb data for Setouchi high-Mg andesites in Japan are from Ishikawa & Nakamura (1994).

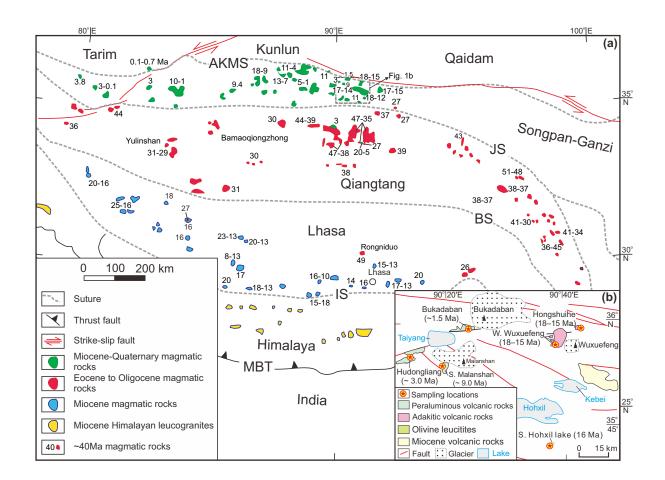
Figure 4 (a) 206 Pb/ 204 Pb- 207 Pb/ 204 Pb diagram. (b) 206 Pb/ 204 Pb- 208 Pb/ 204 Pb diagram. (c) $\varepsilon_{Nd}(t)$ - $\varepsilon_{Hf}(t)$ diagram. (d) δ^{11} B- 207 Pb/ 204 Pb diagram. NHRL: Northern Hemisphere Reference Line. EM1 and EM2: enriched mantle end-members (Zindler & Hart, 1986). The field for marine sediments is constructed using the data of Plank & Langmuir (1998). The fields for MORB, OIB and sediments (Fe-Mn crusts and nodules, subducted oceanic sediment, clays and biogenic muds, sands and Himalayan sediments) are after Richards et al. (2005), Chauvel et al. (2008) and references therein. The B-Nd-Pb-Hf data for Setouchi high-Mg andesites in Japan and AOC are from Ishikawa & Nakamura (1994) and Shimoda et al. (1998).

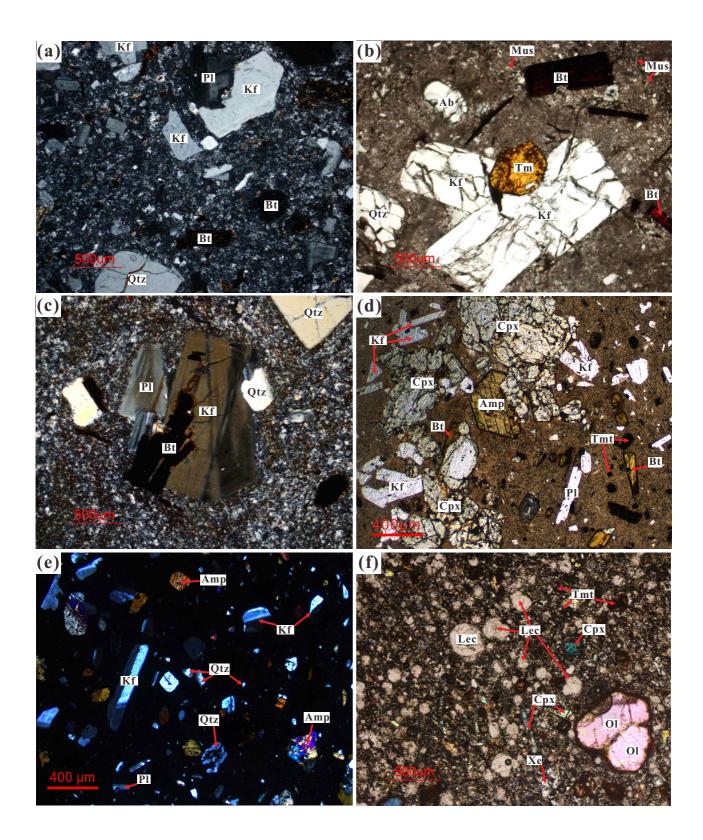
Figure 5 (a, c, e, g) B vs. Th, Nd, Pb, and Hf contents, respectively. (b, d, f, h) B/Nb vs.

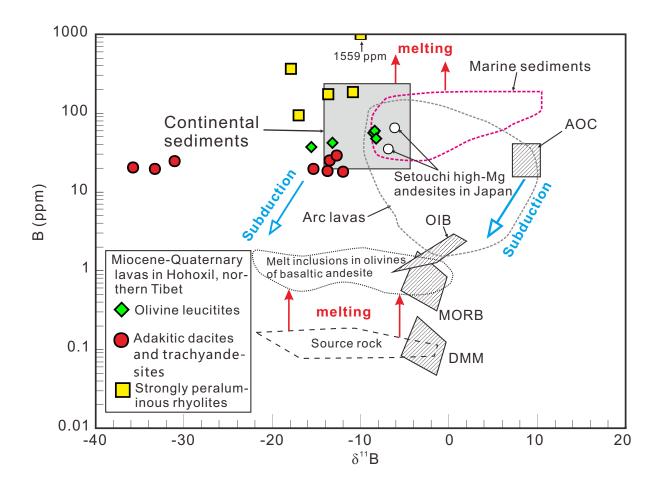
Th/Nb, Nd/Nb, Pb/Nb, and Hf/Nb, respectively.

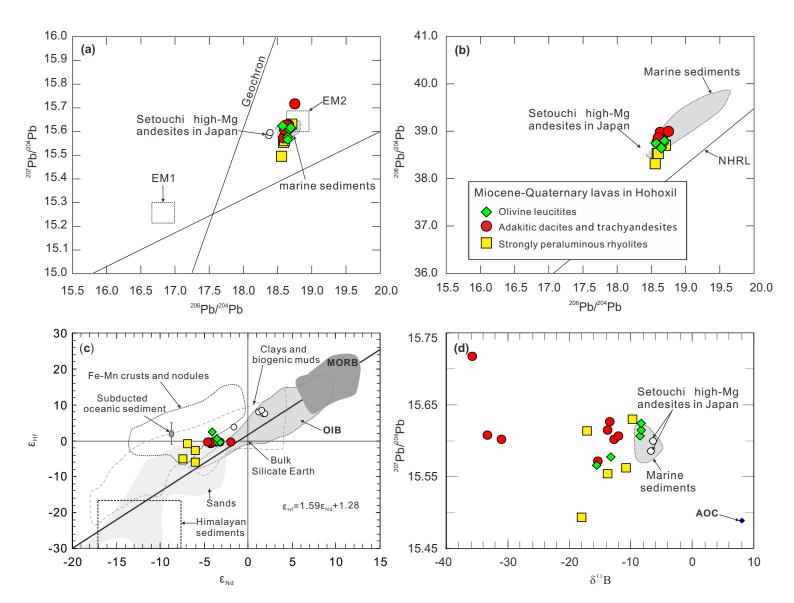
Figure 6 (a) B vs. B/Zr diagram. (b) B vs. B/Ce diagram. The data (averages) for pelagic clay (PC), upper crust (UC), and estimated primitive upper mantle (PUM) are from Taylor

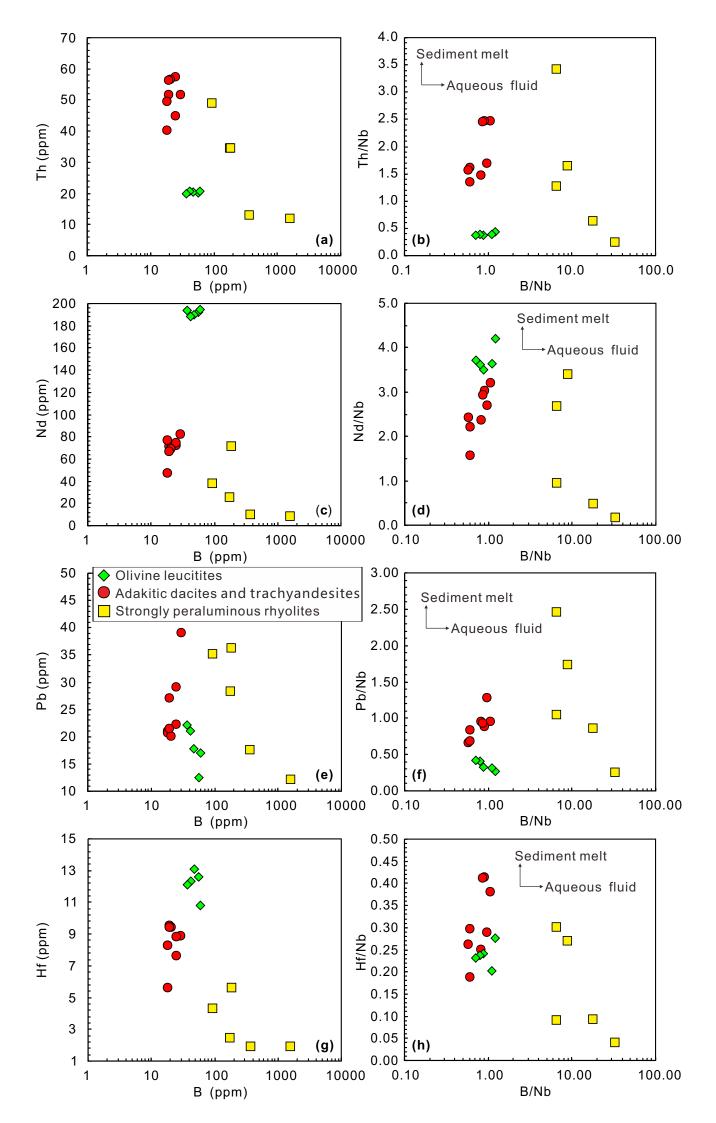
& Mclennan (1985). The fields for typical granulites, B-enriched granulites, sediments, peridotites, island arc lavas, and mantle B/Ce ratios are after Leeman & Sisson (1996) and references therein.

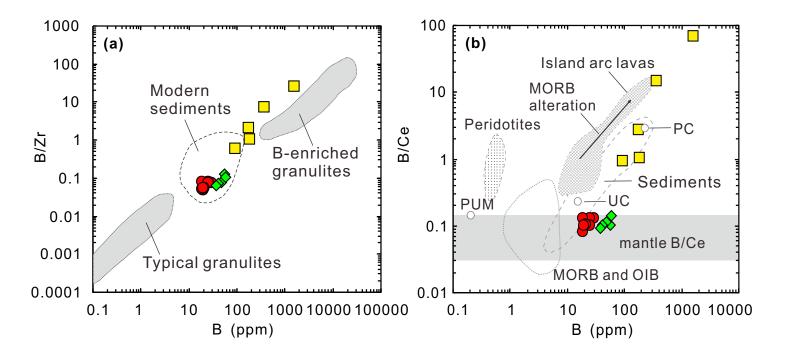












Supplementary data for

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2	Se	diment recycling by continental subduction indicated by B-Hf-Pb-Nd isotopes
3		from Miocene-Quaternary lavas in the northern margin of Tibet
4	y	Xiu-Zheng Zhang a, b, Qiang Wanga, b, c*, Andrew C. Kerrd, Gang-Jian Weia, b, Yue
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13	Cor	responding Author: * Qiang Wang, E-mail: wqiang@gig.ac.cn
14		
15	Inc	cludes the following Materials
16	>	Text S1 Methods
17	\triangleright	Table S1 Boron (B) concentrations and isotopes for the Miocene–Quaternary
18		lavas in the Hohxil area, northern Tibet
19	>	Table S2 Hf-Pb-Nd isotopes for the Miocene–Quaternary lavas in the Hohxil area,
20		northern Tibet
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Text S1. Methods

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1. Whole-rock Pb-Hf isotopic compositions

24 Whole-rock Pb-Hf isotope analyses were performed at the State Key Laboratory of Isotope 25 Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (SKLaBIG, 26 GIGCAS), Guangzhou, China. The powder samples were weighed into the Teflon beaker, spiked 27 and dissolved in concentrated HF and 1:1 HNO3 at 180 °C for 7 days. Lead was separated and 28 purified by conventional cation exchange technique (AG1× 8, 200-400 resin) with diluted HBr as 29 an eluant. Total procedural blanks were less than 50 pg Pb. The measured lead isotopic ratios were normalized to ²⁰⁵Tl/²⁰³Tl = 2.38714. Repeated analyses of SRM981 yielded average values of 30 $^{206}\text{Pb}/^{204}\text{Pb} = 16.9298 \pm 4 \text{ (1SD)}, \ ^{207}\text{Pb}/^{204}\text{Pb} = 15.4821 \pm 5 \text{ (1SD)} \text{ and } \ ^{208}\text{Pb}/^{204}\text{Pb} = 36.6718 \pm 11 \text{ (1SD)}$ (1SD). The analyses of BHVO-2 standard yielded ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios of 32 33 18.6287 ± 40 , 15.5335 ± 25 , and 38.2412 ± 55 , respectively (1SD, n = 6), which were within errors 34 of published values (e.g., Weis et al., 2006). About 100 mg of sample powder was mixed with 200 35 mg of Li₂B₄O₇, placed in a platinum crucible, and melted in a Rigaku high-frequency fusion 36 apparatus at 1200 °C. The melt was cooled rapidly to form glasses that were dissolved in 2 M HCl. 37 Hf was separated from the matrix and interfering elements by HCl-single-column Ln-Spec 38 extraction chromatography. The Hf isotopic compositions of the selected samples were determined 39 using a Micromass Isoprobe multicollector-inductively coupled plasma-mass spectrometry (MC-40 ICP-MS) system. The detailed analytical procedures are described in Li et al. (2006). The measured 176 Hf/ 177 Hf ratios were normalized to 176 Hf/ 177 Hf = 0.7325, and the measured 176 Hf/ 177 Hf ratio of the 41 42 BHVO-2 standard, determined during analysis of the unknowns, was 0.283079 ± 0.000004 (2 σ ; n 43 = 2).

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2. Boron isotopic compositions

B abundance and B isotopic analyses were conducted in the SKLaBIG GIG-CAS. About 150 mg of rock powder was precisely weighed into a pre-cleaned 7 mL PFA-Teflon beaker, along with 100 µL 1% mannitol, 100 μL H₂O₂ and 3 mL 24 M HF. The beaker was tightly capped and placed on a hot plate at a temperature of 60°C for 30 days for boron extraction. Both the solution and residue were then transferred into a pre-cleaned polypropylene (PP) tube, and centrifuged. The supernatant was collected, and boron was concentrated in this solution, at a recovery of > 99% (Wei et al., 2013).

The collected supernatant was then diluted with B-free Milli-Q deionized water to an HF molarity of 3 M for ion-exchange purification. The samples were loaded onto 20 ml columns with Bio-Rad AG MP-1 strong anion exchange resin for chromatographic purification, following procedures in Wei et al (2013).

Boron concentration was determined using a Varian Vista Pro inductively coupled plasma atomic emission spectrometer (ICP-AES) equipped with an HF-resistant Teflon spray chamber and an Al₂O₃ injector. Boron was measured using the 249.678 nm spectral line. Internal precision for our boron concentration determinations were generally better than 5% (RSD). Basalt standards JB-2 and JB-3 were measured multiple times as unknowns with our samples, yielding B concentrations $29.98 \pm 0.98 \ \mu g/g \ (1SD, n=6)$ and $19.39 \pm 0.52 \ \mu g/g \ (1SD, n=6)$, respectively. Our results for B5 are consistent with the long-time monitoring value of $10.18 \ \mu g/g \ B$ in our laboratory. $\delta^{11}B$ measurements were performed using a Finnegan Neptune MC-ICPMS in sample standard-bracketing (SSB) mode. Details of the analytical procedures of $\delta^{11}B$ are described by Wei et al. (2013). The internal precision for $\delta^{11}B$ was better than $\pm 0.05\%$ (2s standard error), and the external precision for $\delta^{11}B$ was better than $\pm 0.30\%$ (2s standard error) estimated by the long-term results of SRM 951 (Wei et al., 2013). Several basalt standards such as JB-2 and JB-3 were repeatedly analyzed along with the samples, yielding the $7.03 \pm 0.12 \%$ (1SD, n=6) and $5.94 \pm 0.40 \%$ (1SD, n=6).

Table S1 Boron (B) concentrations and isotopes for the Miocene–Quaternary lavas in the Hohxil area, northern Tibet

Sample ID	B (ppm)	δ^{11} B (per mil)	B (ppm)	1SE	Location
		Olivine leucitites (16 Ma)			
6304-1	41.7	-13.2	41.7	0.03	35°24'29"N; 91°15'48"E
6304B	55.9	-8.6	55.9	0.03	35°24'29"N; 91°15'48"E
6304C	47.3	-8.3	47.3	0.03	35°24'29"N; 91°15'48"E
6304E	59.3	-8.4	59.3	0.03	35°24'29"N; 91°15'55"E
6305	37.2	-15.6	37.2	0.04	35°24'02"N; 91°16'18"E
	Strong	gly peraluminous rhyolites (9.0–1.	5 Ma)		
2509	175	-13.7	175	0.03	35°58'09"N; 90°48'06"E
2511-1	184	-10.9	184	0.04	35°57'57"N; 90°47'15"E
1P2JD7-1	1559	-9.7	1559	0.04	35°47'26"N; 90°25'39"E
2011	364	-17.9	364	0.04	35°50'54"N; 90°29'4"E
2303	92.7	-17.0	92.7	0.04	35°45'12"N; 90°39'47"E
	Adakiti	c dacites and trachyandesites (18-	-15 Ma)		
3P1 1-1	24.8	-13.5	24.8	0.03	
3P1 2-1	18.3	-13.7	18.3	0.03	
3302	19.4	-15.4	19.4	0.03	
3304-1	24.5	-31.1	24.5	0.03	25 05 (N. 01 2000F
3302-1	29.2	-12.7	29.2	0.03	35.876°N; 91.299°E
3303	18.1	-12.0	18.1	0.03	
3304-3A	20.5	-35.7	20.5	0.04	
3304-3B	19.5	-33.3	19.5	0.04	

Note: 1SE for the internal error of $\delta^{11}B$.

Table S2 Hf-Pb-Nd isotopes for the Miocene-Quaternary lavas in the Hohxil area, northern Tibet

	Olivine leucitites (16 Ma)					Adakitic dacites and trachyandesites (18–15 Ma)							
Sample ID	6304-1	6304B	6304C	6304E	6305	3P1-1	3P2-1	3302	3304-1	3302-1	3303	3304-3A	3304-3B
T (Ma)	16	16		16	16	18	18	18	18	18	18	18	18
Lu	0.37	0.373		0.384	0.372	0.19	0.15	0.17	0.13	0.21	0.18	0.13	0.13
Hf	12.1	12.6		12.3	13	7.64	5.64	9.56	8.83	8.87	8.31	9.46	9.45
176 Lu/ 177 Hf	0.004332	0.004194		0.004423	0.004054	0.003523	0.003768	0.002519	0.002086	0.003354	0.003068	0.001947	0.001949
176 Hf/ 177 Hf	0.282770	0.282772		0.282783	0.282793	0.282752	0.282752	0.282752	0.282763	0.282752	0.282760	0.282766	0.282764
2SE	0.000026	0.000021		0.000015	0.000013	0.000009	0.000005	0.000003	0.000005	0.000003	0.000007	0.000005	0.000008
$\epsilon_{\mathrm{Hf}}(0)$	-0.08	0.01		0.39	0.76	-0.71	-0.71	-0.70	-0.32	-0.70	-0.44	-0.21	-0.27
$\varepsilon_{\mathrm{Hf}}(t)$	0.23	0.33		0.70	1.08	-0.36	-0.36	-0.33	0.05	-0.34	-0.08	0.16	0.10
TDM(Ma)	750	743		731	707	760	765	738	714	755	738	706	709
	This study				This study								
²⁰⁶ Pb/ ²⁰⁴ Pb	18.638	18.681	18.689	18.568	18.639	18.656	18.627	18.579	18.609	18.611	18.625	18.751	18.605
207 Pb/ 204 Pb	15.577	15.607	15.615	15.624	15.565	15.626	15.615	15.571	15.602	15.602	15.606	15.717	15.608
208 Pb/ 204 Pb	38.672	38.734	38.809	38.749	38.644	38.864	38.845	38.757	38.808	38.812	38.885	39.005	38.867
	This study					This study							
Sm	27.95	28.41	28.25	27.82	28.89	9.038	6.085	9.018	8.977	10.11	9.589	8.476	8.059
Nd	188.6	191.9	189.7	194.9	194.1	72.13	47.23	71.49	74.68	82.76	77.11	69.42	67.15
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.090100	0.090100	0.090600	0.086829	0.090500	0.076200	0.078400	0.076700	0.073100	0.074300	0.075600	0.074300	0.073000
$^{143}Nd/^{144}Nd$	0.512469	0.512454	0.512427	0.512459	0.512453	0.512443	0.512444	0.512418	0.512531	0.512413	0.512431	0.512470	0.512403
2SE	0.000010	0.000008	0.000008	0.000012	0.000009	0.000010	0.000010	0.000016	0.000011	0.000024	0.000010	0.000010	0.000014
$\varepsilon_{\mathrm{Nd}}\left(0\right)$	-3.30	-3.59	-4.12	-3.48	-3.61	-3.80	-3.78	-4.29	-2.09	-4.39	-4.04	-3.28	-4.58
$\varepsilon_{\mathrm{Nd}}\left(t\right)$	-3.07	-3.37	-3.89	-3.25	-3.39	-3.53	-3.51	-4.02	-1.80	-4.11	-3.76	-3.00	-4.30
TDM(Ma)	840	859	895	830	863	784	796	815	672	806	794	744	810
	Qi et al., 2020								Wang et	al., 2005			

	Strongly peraluminous rhyolites (9.0–1.5 Ma)								
Sample ID	2509	2511-1	1P2JD7-1	2011	2303				
T(Ma)		2	3	9	9				
Lu		0.089	0.046	0.058	0.087				
Hf		5.64	1.93	1.92	4.32				
176 Lu/ 177 Hf		0.002235	0.003376	0.004279	0.002853				
$^{176}{ m Hf}/^{177}{ m Hf}$		0.282672	0.282625	0.282690	0.282750				
2SE		0.000006	0.000002	0.000002 0.000019					
$\epsilon_{\mathrm{Hf}}(0)$		-3.52	-5.20	-2.89	-0.79				
$\varepsilon_{\mathrm{Hf}}(t)$		-3.49	-5.14	-2.72	-0.61				
TDM(Ma)		849	947	872	749				
			This study						
²⁰⁶ Pb/ ²⁰⁴ Pb	18.587	18.603	18.701	18.562	18.636				
$^{207}{\rm Pb}/^{204}{\rm Pb}$	15.554	15.562	15.63	15.493	15.613				
$^{208}{\rm Pb}/^{204}{\rm Pb}$	38.533	38.522	38.699	38.309	38.742				
		W	ang et al., 20	12					
Sm	4.65	11.6	1.66	2.08	6.32				
Nd	25.4	71.2	8.32	9.87	38.3				
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.111116	0.099135	0.121685	0.128318	0.100336				
143 Nd/ 144 Nd	0.512329	0.512338	0.512256	0.512330	0.512279				
2SE	0.000007	0.000011	0.000012	0.000012	0.000007				
$\varepsilon_{Nd}\left(0\right)$	-6.03	-5.85	-7.44	-6.01	-7.00				
$\varepsilon_{\mathrm{Nd}}\left(t\right)$	-6.02	-5.83	-7.41	-5.93	-6.88				
TDM(Ma)	1219	1080	1478	1462	1170				
		Wang et al., 2012							

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