White mica trace element and boron isotope evidence for distinctive infiltration events during exhumation of deeply subducted continental crust

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Abstract

Previous study of subducted continental crust within the Luliang Shan terrane in Northwest China has documented metasomatic formation of thick, hydrated phengite + garnet-rich selvages at the interface between mafic eclogite blocks and quartzofeldspathic host gneiss. Whole rock concentrations of Cs and Ba within the selvage are enriched by two orders of magnitude relative to the eclogite blocks and host gneiss. We performed in situ ion microprobe analyses of Li, Be, B, Rb, Sr, Cs and Ba and δ11B of phengite within the Luliang Shan terrane to better constrain the source(s) of the infiltrating fluid. The phengite within the selvage are enriched in Li, Cs and Ba and yield δ11B values between −30‰ and −9‰, values that are lower than mantle values. High Ba/Rb, Cs/Rb coupled with low B/Be, B/Li and highly negative δ11B values indicate that the high-pressure fluid that formed the selvage was derived from highly devolatilized rocks within the subduction channel. In contrast, muscovite, which crystallized in the adjacent host gneiss during a subsequent lower pressure phase of fluid infiltration at approximately 0.9 GPa depths, has much lower Li, Cs and Ba relative to the high-pressure phengite. These retrograde muscovite have very high concentrations of B (up to 5500 ppm) and Be (up to 50 ppm) and high (−2 to +8‰) δ11B values that are consistent with crystallization from a fluid derived from shallower and less devolatilized regions of the subduction zone. Additional host gneiss samples, regionally distributed and kilometres away from the studied area lack the B-rich signature and indicate that the late stage fluids were likely localized to the region near the studied traverse.

Introduction

Discordant views exist regarding the extent of fluid–rock interaction that occurs during the subduction of continental vs. oceanic crust. It is generally thought that subduction of continental crust is a ‘dry’ process due to the high-temperature stability of mineral assemblages typically present in basement rocks (Proyer 2003; Rumble et al. 2003; Massonne 2009). This is supported by the preservation of coesite requiring low fluid abundance and limited fluid mobility (Ernst 1999; Chopin 2003; Mosenfelder et al. 2005; Hermann et al. 2013). In contrast, abundant evidence exists suggesting that subduction of oceanic crust produces considerable fluids that can metasomatically alter the subducting materials and overlying mantle wedge. In addition, these fluids trigger arc magmatism (Spandler et al. 2003; Bebout 2007; Bebout et al. 2007; Pennistion-Dorland et al. 2012). A review by Kylander-Clark et al. (2012) described examples where subduction of small masses of continental crust occurred during oceanic subduction prior to continental collision. In such settings, fluids are primarily released from devolatilization of altered oceanic crust and weakly metamorphosed sedimentary rocks should be available to interact with subducted continental crust. Since the subducting continental crust is relatively dry, major dehydration reactions occurring within these rocks do not occur until greater depths (80–130 km; Zhao et al. 2015), especially in the case of colder subduction zones (Zheng 2012; Zhao et al. 2015).

Calculations of fluid release during oceanic subduction indicate that altered oceanic crust and overlying sediments are expected to release a large portion of their H2O at relatively shallow levels (65–90 km) with only a small fraction reaching the deeper mantle in phases such as phengite (e.g. Schmidt and Poli 1998; Hacker 2008). However, the infiltration of fluids derived from oceanic crust and sediments is expected to stabilize chlorite-amphibole-serpentine-bearing assemblages along the subducting slab interface, thus allowing the stabilization of a large volatile component to greater depths (e.g. 100–200 km), leading to the depths...
required for arc magmatism (Bebout and Barton 2002; Pawley 2003; Till et al. 2012; Spandler and Pirard 2013).

Progressive devolatilization of materials during subduction produces systematic variations in the concentrations and isotope ratios of fluid-mobile trace element as subducted rocks devolatilize (Bebout and Barton 1993, 2007, 2013; You et al. 1996; Zheng et al. 2003; Scambelluri and Tonarini 2012). White mica trace element chemistry and isotopic compositions provide a sensitive tool for assessing fluid–rock interactions in subduction zones (Bebout et al. 2007). Boron concentrations and isotopic compositions have proven particularly useful for assessing the extent to which the source rocks contributing fluid have devolatilized (Moran et al. 1992; Bebout and Barton 1993; Peacock and Hervig 1999; Marschall et al. 2007; Konrad-Schmolke and Halama 2014).

In this study, we measured the concentrations of fluid-mobile trace elements (Li, Be, B, Rb, Sr, Cs and Ba) and boron isotope compositions in white mica to constrain the source of the fluids that infiltrated the high-pressure Luliang Shan gneiss terrane of Northwest China (Figure 1(a)). The Luliang Shan is a ca. 100 km² exposure of continental crust that was subducted to 2.5 GPa depths, near the coesite stability field, during a phase of subduction that has been regarded as fundamentally oceanic in character (Menold et al. 2009; Zhang et al. 2013). Geologic mapping of the Luliang Shan gneiss have revealed that eclogite blocks hosted within the gneiss are characteristically mantled by thick phengite + garnet rich selvages (Menold et al. 2009, 2016) (Figure 1). Menold et al. (2016) concluded based on phengite-quartz thermometry that the selvages formed metasomatically in response to influx of heavy δ¹⁸O fluids at temperatures of 607 ± 65°C and compositionally resemble either a combination of the host gneiss and eclogite, or the host gneiss itself. Our samples were collected along a well-studied 23-m traverse (Menold et al. 2009, 2016) that extends from the host gneiss into the interior of an eclogite block (Figure 1(c)). Three additional gneiss samples collected throughout the UHP terrane were also examined (Figure 1(b)). These previous results combined with the results yielded from muscovites and phengites from the host gneiss and selvage lithologies in this study allow us to evaluate the source of the selvage-forming fluids within the Luliang Shan gneiss terrane.

**Previous work and geological setting**

Located on the northeastern margin of the Tibetan Plateau in Northwest China, the North Qaidam metamorphic belt consists of discontinuous exposures of orthogneiss, paragneiss, eclogite, peridotite and marble (Figure 1(a)) that record evidence of UHP metamorphism in the form of coesite inclusions and high-pressure pseudomorphs, kyanite and high-Si muscovite (Yang et al. 2002; Song et al. 2003b, 2006; Liu et al. 2006; Zhang et al. 2013). These features provide evidence that some regions within the North Qaidam metamorphic belt were subducted to upper mantle depths (e.g. at least 100 km). Studies suggest that the HP to UHP metamorphism was not coeval throughout the metamorphic belt, with ages yielded from units throughout the North Qaidam ranging from approximately 490–420 Ma for peak-grade metamorphism (Mattinson et al. 2007; Zhang et al. 2013). Moreover, peak temperature estimates vary from 600°C to 1000°C for different exposures throughout North Qaidam (Zhang et al. 2001, 2002, 2005; Song et al. 2003a; Menold et al. 2009).

The Luliang Shan consists primarily of quartzofeldspathic gneiss with small, locally abundant, deformed eclogite masses (Figure 1(b)). The protolith of the host gneiss was heterogeneous, consisting of both igneous and sedimentary precursors that were intruded by basaltic dikes (Rowley et al. 1997; Gehrels 2003; Menold et al. 2016). The Luliang Shan records the earliest timing (zircon U/Pb ages of 487 ± 1 Ma via SHRIMP-RG; Zhang et al. 2005) and the coolest temperatures for eclogite-facies metamorphism (600 ± 25°C; Menold et al. 2009) in the North Qaidam belt. Zhang et al. (2013) have interpreted that the Luliang Shan rocks were subducted during a period of fundamentally oceanic subduction that preceded continental collision in the North Qaidam region.

Previous studies defined a pressure–temperature path for the Luliang Shan that attained peak conditions of 2.5 ± 0.2 GPa and 590 ± 25°C between 486–488 Ma (Zhang et al. 2005; Menold et al. 2009). During exhumation the Luliang Shan terrane re-equilibrated under epidote-amphibolite facies conditions of 0.8–0.9 GPa and ~415–510°C (Menold et al. 2009) by 450–470 Ma based upon phengite ⁴⁰Ar/³⁹Ar cooling ages (Menold et al. 2016). These results suggest that exhumation of the Luliang Shan block to the middle crust predated attainment of UHP metamorphism in other North Qaidam gneiss exposures (Zhang et al. 2003, 2013). Previous thermobarometry and pseudo-section analysis of the Luliang Shan demonstrated that eclogite crystallization and selvage formation occurred at pressures near the quartz–coesite transition (Menold et al. 2009).

Menold et al. (2016) presented evidence that an influx of isotopically heavy δ¹⁸O fluid metasomatically hybridized the contacts between the host gneiss and mafic eclogite bodies to create thick, hydrous selvages...
at ca. 600°C. Water/rock ratios were in excess of unity for an infiltrating fluid with $\delta^{18}O = +14 \pm 1$‰. This study was focused on an 18-sample traverse that extended from the host gneiss into a thick metasomatic selvage mantling a 5-m diameter eclogite block (Figure 1(c)). A subset of the samples collected along this traverse were analysed in this study. Based upon Menold et al.’s (2009) petrography and whole rock chemical analysis, the selvage can be subdivided into two separate lithologies.

Selvage-A (CM 7/17/02–4, CM 7/17/02–6 and CM 7/17/02–7) is a phengite-garnet-rich (Figure 2a–c) rock that formed via a fluid-mediated metasomatic reaction between the host gneiss and the eclogite that enriched the selvage-A lithology in K$_2$O and H$_2$O, and incompatible elements such as Cs, Ba, U and Th. Selvage-B (CM 7/17/02–11) is more SiO$_2$-rich, contains less garnet and phengite (Figure 2d–e)), and is compositionally more similar to the host gneiss (Menold et al. 2016).

Figure 1. (a) Generalized map of North Tibet showing major tectonic units and lithologies throughout the terrane (modified from Menold et al. 2009) (b) Simplified geologic map of the Luliang Shan area with location of traverse and additional host gneiss used in this study shown. (c) Sketch of traverse with the location of samples used in this study circled and numbered. Smaller circles along traverse represent other samples collected as part of the original 18-sample traverse (images modified after Menold et al. 2009). All samples have the prefix CM/7/17/02.
Sampling and methods

We measured white mica trace element and B isotope concentrations from six representative samples selected from the Menold et al. (2009) sample traverse (Figure 1(c)) using the Stanford-USGS SHRIMP-RG ion microprobe. Samples CM 7/17/02–1 and CM 7/17/02–2 represent the quartzofeldspathic host gneiss lithology. Samples CM 7/17/02–4, CM 7/17/02–6 and CM 7/17/02–7 represent selvage-A. Sample CM 7/17/02–11 represents selvage-B and occurs within a shear zone near the selvage–eclogite contact. We selected three additional host gneiss samples (AY 6/01/00-6b, CM 6/21/02–3c and CM 6/22/02–6) to assess the homogeneity of the host gneiss throughout the Luliang Shan (Figure 1(b)).

Samples were prepared as polished, 1-inch diameter, epoxy-mounted thick sections. They were characterized using Stanford’s JEOL JXA-8230 electron microprobe to acquire back scattered electron (BSE) images of model mineralogy and textural relationships (Figure 2). These images were used to create maps that cover the entire mount to aid in analysis positioning. The major element composition of white micas were determined using wave-length dispersive (WDS) measurements to help calibrate trace element measurements undertaken with ion probe measurements. Ion probe measurements of Li, Be, B, Ti, Rb, Sr, Cs and Ba were collected for the six traverse samples (Figure 1(c)) plus three regionally distributed gneiss samples (Figure 1(b)). Trace element concentrations were calculated relative to the standards NIST-611, NIST-613 and NIST-615. Electron microprobe Si-contents were only available for a subset of the trace element data set and for this reason we used ion probe Mg plus Fe contents as a proxy for silica content. Figure 3 shows the line of regression used to calculate Si-contents that serve as the independent variable in Figures 6–8.

Si-contents were only available for a subset of the trace element data set and for this reason we used ion probe Mg plus Fe contents as a proxy for the celadonite content (Si component). Figure 3 shows the line of regression used to calculate the Si-contents that serve as the independent variable in Figures 6–8.

We completed analytical experiments to determine our ability to quantitatively measure B isotopes from the Luliang Shan samples using the Stanford-USGS SHRIMP-
RG ion probe. The first set of measurements were performed on polished fragments of NIST-611 glass that were distributed within a ±5 mm area centered within a separate standard mount. Secondary ions sputtered from the sample surface are focused into the optic axis of the mass spectrometer primarily by adjusting the quadrupole triplet lens deflector (Qt1). The need to adjust the voltage to the Qt1 deflectors prior to each analysis arises from variation in sample topography, electronic potential (e.g. charging), and other factors that influence secondary ion focus. For light isotopes such as boron, a negative consequence of varying the voltage applied to the Qt1 deflectors is that it may fractionate the isotopic ratio by up to 20 ‰. To mitigate this problem, we systematically varied the voltage applied to Helmholtz coils centered upon the source chamber to find a setting that minimized instrument mass fractionation when Qt1-y deflector settings varied depending on analysis location (Ickert et al. 2008). When the Helmholtz coils were optimally tuned with a −200 V setting, we were able to limit scatter in δ¹¹B to 2–3‰ for measurements performed across a ±5 mm region of the sample mount (Figure 4(a)). The variation in δ¹¹B performed with NIST 611 glass was −0.53 ± 1.23‰ (2σ, SD, Figure 4(b)).

We performed a second set of measurements with muscovite from a tourmaline-bearing pegmatite sample 30,207 (Stanford Mineralogical Collection from the Pala pegmatite (Stewart Mine, San Diego County, California) to investigate the influence of crystallographic orientation. Grains were mounted in epoxy parallel and perpendicular to cleavage. The total variation of δ¹¹B for both parallel and perpendicular orientations was 0.69 ± 1.82‰ and 1.30 ± 1.82‰ (2σ, SD, Figure 4(d)), respectively. Based upon these results, we conclude that no effect of crystallographic orientation could be detected within analytical error for δ¹¹B measurements performed on SHRIMP-RG (e.g. Figure 4(d)).

Finally, we quantitatively measured pit depths of in situ grains using a Zygo NewView 7200 white-light interferometer at the University of California, Santa Cruz to determine if variation in sputter rate was...
influenced by crystallographic orientation and negatively impacted $\delta^{11}B$ reproducibility in mica. The average pit depth was 3.05 ± 0.34 µm, and thus, we can conclude that the crystallographic orientation does not likely impact the ion probe pit depth or $\delta^{11}B$.

Results

Petrographic observations

Selvage-A

Phengite and garnet constitute ca. 45–55% and 7–20% of the modal mineralogy, respectively, in the selvage (Figure 2(a–c)). Phengite occur as platy, up to 2 mm grains with well-defined edges. The phengite have Si-contents of 3.25–3.45 per formula unit (p.f.u.) and Ti of 0.015–0.040 atoms p.f.u. (Figure 5, Table 1). Retrograde muscovite with much lower Si and Ti contents (3.00 to 3.15 and 0.005–0.015 atoms p.f.u., respectively; Figure 5) are associated with biotite and/or chlorite. Sample CM 7/17/02–4 is the most retrograded sample (Figure 2(a)). Garnets from this selvage sample are fractured and partially replaced by muscovite and/or chlorite and feldspar masses of fine-grained, intergrown muscovite, biotite and chlorite occur between phengite and garnet (Figure 2(a)). The less altered samples (CM 7/17/02–6 and CM 7/17/02–7) have a distinct foliation expressed by phengite (Figure 2(b–c)).

Host gneiss

Samples from host gneiss possess a dominantly quartzofeldspathic modal mineralogy, with minor amounts (<15 vol.%) muscovite, and trace amounts of garnet, tourmaline and oxides (Figure 2(d,e)). CM 7/17/02–1 has approximately 5% more quartz and feldspar than CM 7/17/02–2 and contains coarse muscovite with Si and Ti contents between 3.10–3.25 atoms p.f.u. and 0.003–0.010 atoms p.f.u., respectively (Figure 5). The muscovite occur as blocky, up to 1 mm grains that define a weak foliation (Figure 2(d)). Garnet is sparse and occurs as 5 mm poikoblastic grains. The garnet have minor fractures that are replaced by muscovite and quartz. Tourmaline is also poikoblastic with quartz inclusions. CM 7/17/02–2 is quartz-rich but contains less feldspar than...
other host gneiss samples. The muscovite occur as large, up to 7 mm grains, or as small weakly oriented flakes (Figure 2e). Garnet grains are smaller (~100 µm), anhedral and free of inclusions. No tourmaline was observed in CM 7/17/02–2 during this study but has been reported in other host gneiss samples (Menold et al. 2009).

**Selvage-B**
Sample CM 7/17/02–11 was collected from the shear zone that developed in the quartz-rich selvage-B lithology adjacent to the eclogite (Figure 1b, Figure 2f). Fine-grained (~80 µm) muscovite have low Si and Ti between 3.05–3.15 atoms p.f.u. and 0.002–0.007 atoms p.f.u., respectively (Figure 5). The muscovite also have high Na-contents and coexist with paragonite (Figure 5).

**Trace element measurements**

**Selvage-A**
The phengite from the three selvage-A samples (CM 7/17/02–4, CM 7/17/02–6 and CM 7/17/02–7) all have unexpectedly high concentrations of incompatible trace elements relative to previously published vales. Lithium concentrations range from 80 to 690 ppm (Figure 6a), Be ranges from 1 to 10 ppm (Figure 6b),

![Figure 6](image-url)

**Figure 6.** (a–h) Variations of concentrations of selected trace elements from white mica compositions in selvage samples CM 7/17/02–4, CM 7/17/02–6 and CM 7/17/02–7 as a function of Si-content. Open boxes denote concentrations from muscovite and closed boxes denote phengite.
B values range from 100 to 300 ppm (Figure 6(c)), and Cs ranging from 10 to 90 ppm (Figure 6(g)) (Table 1 and Data Repository). Retrograde muscovite in sample CM 7/17/02–4 (open symbols in Figure 6) has lower Li and Cs concentrations, compared to the associated phengite. Some muscovite analyses yielded higher Ba (up to 4000 ppm, open symbols Figure 6(h), Table 1), than the phengite (1800 ppm, closed symbols Figure 6(h)). The other trace elements display less variation between phengite and retrograde muscovite within the selvage (Figure 6(b,e,f)).

Host gneiss

Host gneiss muscovite present in CM 7/17/02–1 and CM 7/17/02–2 is highly enriched in Be, B and Rb. Be values range from 10 to 30 ppm (Figure 7(b), B concentration from 1500 to 3800 ppm (Figure 7(c)), and Rb concentration from 850 to 1500 ppm (Figure 7(e), Table 1, and Data Repository). While muscovite in the host gneiss has very similar concentrations of Li, Sr and Cs compared to retrograde muscovite in the selvage, the latter contains much higher Ba concentrations (Figure 7(h)).

Figure 7. (a–h) Variations of concentrations of trace elements from muscovite in the host gneiss (CM 7/17/02-1 and CM 7/17/02-2) and muscovite paragonite from selvage-B lithologies affected by the shear zone at the eclogite contact (CM 7/17/02-11) as a function of Si-content. Green fields represent the average range of values for phengite (bold dashed line) and retrograde muscovite (dash-dot line) from the selvage compositions (see Figure 6).
**Shear zone**

Muscovite from the quartz-rich selvage-B sample (CM 7/17/02-11) present within the shear zone along the contact with the eclogite exhibits trace compositions that are similar to those of the host gneiss muscovite (Figure 7). The magnitude of enrichment of B and Rb in selvage-B muscovite within the shear zone are only about half as high as for the host gneiss muscovite. Muscovite from both lithologies have comparable Be and Sr, whereas Ba is slightly higher in selvage-B muscovite from the shear zone (Figure 7).

**Additional gneiss samples**

Because of the high Be and B concentrations in the host gneiss from the traverse, we also examined white micas from three additional gneiss samples from locations scattered throughout the Luliang Shan terrane (Figure 1(a)) to evaluate whether these regionally distributed gneisses were also highly enriched in Be and B. We found that the regionally distributed gneiss samples did not yield the same significantly high concentrations of Be and B (Figure 8(b,c)). The concentrations of other trace element compositions from these regionally distributed gneiss samples did not yield the same significantly high concentrations of Be and B (Figure 8(b,c)). The concentrations of other trace element compositions from these regionally distributed gneiss samples did not yield the same significantly high concentrations of Be and B (Figure 8(b,c)).

**Figure 8.** (a–h) Variations of concentrations of trace elements from white mica compositions in additional host gneiss samples (AY 6/01/00-6b, CM 6/21/02-3c and CM 6/22/02-6) as a function of Si-content. Outlined fields derived from data from white micas from the selvage and host gneiss lithologies (see Figure 6 and 7).
distributed gneiss samples were within the range of values reported from those measured for the phengite and retrograde muscovite from the selvage (Figure 6).

**Boron isotopes**

Here we present an expanded B isotope data set that includes a subset of the B isotope results from the host gneiss, selvage and shear zone that were previously reported in Menold et al. (2016) as well as results from transects from individual muscovites from sample CM 7/17/02–1. All \( \delta^{11}B \) isotopic results presented in this paper and in the Menold et al. (2016) were collected in the same SHRIMP-RG analytical sessions.

As described in Menold et al. (2016), boron isotope measurements were acquired from samples CM7/17/02–1 (host gneiss), CM 7/17/02–4 (retrograded selvage), CM 7/17/02–7 (pristine selvage) and CM 7/17/02–11 (shear zone near eclogite contact). Phengite from selvage sample CM 7/17/02–4 yielded boron-contents and \( \delta^{11}B \) values that ranged from 160 to 250 ppm and \(-15.0\%\) to \(-8.8\%\), respectively. Three retrograde muscovites yielded boron contents and \( \delta^{11}B \) values ranging from 70 to 140 ppm and \(-26.4\%\) to \(-15.0\%\). Phengite from the more pristine selvage sample CM 7/17/02–7 yielded boron-contents and \( \delta^{11}B \) values ranging from 50 to 230 ppm and \(-28.7\%\) to \(-6.5\%\), respectively. Boron contents and \( \delta^{11}B \) values from the host gneiss muscovite from CM 7/17/02–1 were much higher than for the selvage phengite and ranged from 3300 to 5500 ppm and \(-2.4\%\) to \(8.4\%\), respectively. Similar boron contents and \( \delta^{11}B \) values were obtained for muscovite from the shear zone. Muscovite in CM 7/17/02–1 had boron contents and \( \delta^{11}B \) values from 500 to 2100 ppm and \(-19.2\%\) to \(-2.9\%\), respectively. An additional \( \delta^{11}B \) measurement from paragonite of \(-13.75\%\) fell within the range of values reported for the host gneiss.

Given the large range in B concentrations exhibited in the host gneiss (Figure 7), and the \( \delta^{11}B \) isotopic values previously reported by Menold et al. (2016), we used the ion probe to measure profiles of B concentrations and \( \delta^{11}B \) isotope values across six representative muscovite grains from sample CM7/17/02–1 to determine if they were isotopically zoned (see Data Repository). The cores appear to be slightly more enriched in Si (3.2 atoms p.f.u.) relative to the grain rims (3.1 Si p.f.u.). Titanium concentrations are essentially constant throughout at 0.005 ± 0.001 atoms p.f.u. The concentration of the interlayer site occupants, K and Na, are not zoned at a level that can be analytically resolved (Figure 9(d)). The B concentrations measured from grain 13 range from approximately 3000 to 4000 ppm, and appear to be slightly higher in the grain interior compared to the rim values, although the results are scattered (Figure 9(b)).
The corresponding $\delta^{11}B$ compositions range between $-7\%$ to $+4\%$ (Figure 9(b)).

Discussion

Evidence for fluid infiltration at near-UHP conditions

Most HP to UHP exposures within the North Qaidam terrane are thought to have formed as a result of continental collision between 450–430 Ma (Chen et al. 2012; Zhang et al. 2013). The Luliang Shan terrane is unique within the North Qaidam UHP belt in that it is believed to represent a continental fragment that was subducted before the onset of major continental collision (Kylander-Clark et al. 2012; Menold et al. 2016). According to Menold et al. (2009, 2016), the selvage phengite developed due to the infiltration of heavy $\delta^{18}O$ (+14%) fluids at ~2.5 GPa and 600°C, near the coesite stability field.

The range of Si- and Ti-contents of selvage-forming phengite from the Luliang Shan (Figure 5 and Figure 12) is consistent with experimentally derived phengite crystallization estimates for near peak pressure conditions (Massonne and Schreyer 1987; Auzanneau et al. 2010) and agree well with phengite – quartz $\delta^{18}O$ thermometry estimates of ~600 ± 65°C for the selvage (Menold et al. 2016). Infiltration of this heavy $\delta^{18}O$ fluid enriched the selvage bulk rock composition in fluid-mobile trace elements such as Ba and Cs concentrations that are considerably higher than those present in the host gneiss and the eclogite. Figure 10 illustrates Menold et al.’s (2009) whole rock data as well as the white mica trace element compositions from equivalent

![Figure 10](image-url) Trace element concentrations of individual micas compared to whole rock compositions illustrating mica compositions produced in the selvage cannot be derived from simple mixing of the host gneiss and shear zone alone. (a) Whole rock Ba vs. Ba/Rb for lithologies described in text (see key in plot). (b) Whole rock Cs vs. Cs/Rb. Note altered eclogite sample plots high. (c) Ion microprobe Ba vs. Ba/Rb from all samples (see key in plot). Note that open symbols denoting retrograde muscovite in the selvage plot much higher than muscovite from the host gneiss and shear zone. (d) Ion microprobe Cs vs. Cs/Rb same symbols as in previous plot. Note that high-pressure phengite from the selvage plot in a distinct field. Abbreviations: ms, muscovite; phn, phengite; pg, paragonite.
samples gathered in this study. As indicated, the concentrations of both Ba and Cs in the selvage samples are much higher than what can be explained only by local hybridization of host gneiss and eclogite and thus require fluid-mediated transfer of these elements into the selvage. The contrast in chemical composition for the host gneiss and selvage results is consistent with previous studies that suggest a significant amount of external fluid and/or the presence of biotite is required to re-equilibrate quartzofeldspathic units during HP-UHP metamorphism (Proyer 2003; Ernst 2006). Figures 10(c, d) illustrate the same compositional plots for white mica from the traverse. The results are consistent with addition of fluid-mobile trace elements into phengite during selvage formation in response to fluid infiltration near peak-pressure conditions (Menold et al. 2009, 2016).

Within the subduction channel, B/Be ratios in white mica decreases as a function of depth. This is largely associated with the preferential loss of B, relative to Be, from white mica during devolatilization reactions. Previous studies have shown that the devolatilization reactions that drive the degree of element depletion is dependent on the P-T path experienced by the rocks (Bebout and Barton 1993; Bebout et al. 1999, 2007, 2013; Marschall et al. 2009; Scambelluri and Tonarini 2012). During progressive devolatilization, $^{11}$B is preferentially fractionated into the fluid phase (Marschall et al. 2007). As a result, fluids devolatilized at shallow depths from subducting rocks will produce fluids with more enriched $^{11}$B values compared to fluids devolatilized at greater depth (Marschall et al. 2007; Konrad-Schmolke and Halama 2014). The progressive depletion of rocks in B ultimately produces $^{11}$B values lower in residual phengite and in devolatilized fluids than the $^{11}$B ratios that characterize the mid-oceanic ridge basalts and the mantle ($^{11}$B = 0‰ to −10‰; Bebout and Nakamura 2003; Marschall et al. 2007; Pabst et al. 2012; Scambelluri and Tonarini 2012). The selvage phengite shows this relationship with the majority of the $^{11}$B values within the range of −28‰ to 6‰ (see Figure 11(a); Menold et al. 2016). The selvage phengite also exhibits relatively low B/Be (15–65; see Figure 11(b)) and B/Li (< 1; see Figure 11(c)) values that are consistent with interaction with fluids devolatilized from deeply subducted materials (Bebout and Barton 1993).

Peak-pressure conditions and eclogite formation in the Luliang Shan terrane occurred at ca. 490 Ma (Zhang et al. 2005). Based upon the comparison of Ti-contents gathered from selvage phengite in this study to estimates of Ti-contents collected experimentally to produce the Ti-in-phengite thermobarometer from Auzanneau et al. (2010), we can further constrain the conditions of selvage formation. Although the Si-contents of white mica depend significantly on bulk rock composition (Massonne and Schreyer 1987), the Ti-content of phengite is much less compositionally dependent if rutile is present (Auzanneau et al. 2010). Rutile is abundant within all of the studied selvage samples and also occurs sparingly within the host gneiss (Menold et al. 2009); therefore, the measured Ti-contents of the selvage phengite (0.016–0.034 p.f.u.; Figure 3) corresponds to the peak-grade event of Menold et al.’s (2009) P-T history for the eclogite and selvage (green portion; Figure 12). As previously discussed, selvage formation is indicated to have occurred on the retrograde portion of the P-T path during initial decompression near peak temperature conditions of approximately 660°C (Menold et al. 2009). These results are consistent with the Menold et al. (2016) phengite–quartz oxygen thermometry results of ~600 ± 65°C and indicate that high-pressure fluid infiltration occurred during initial decompression of the Luliang Shan. The Ti-contents from phengite from the selvage further suggest formation at these conditions. We conclude that the source of these high $^{18}$O fluids (Menold et al. 2016) infiltrating the selvage most likely consisted of highly devolatilized rocks within the subduction channel at approximately 75 km depths.

Several authors have modelled the changes in the compositions and isotopic ratios of incompatible trace elements within fluid as subducted rocks are progressively devolatilized (Bebout and Barton 1993; Zack et al. 2001; Marschall et al. 2007). While such calculations require detailed knowledge of fluid–mineral partition coefficients, modal mineralogy, P-T paths and phase equilibria, the general outcome of progressive devolatilization is that parameters such as Cs/Rb and Ba/Rb increase while B/Be, B/Li and $^{11}$B decrease in the evolved fluid phase as devolatilization proceeds. Hence our results from the high-pressure phengites (Figures 10, 11) indicate the source region of the fluids that crystallized them in the selvage was substantially devolatilized. Field and theoretical studies indicate that in ‘cooler’ subduction zones, sufficient H$_2$O, B and Cs can be retained in subducted rocks to UHP depths (see Bebout et al. 2013) to account for the compositions that we observe in the high-pressure phengites (Figure 6). Even if subduction occurred under warmer conditions, it is further possible that fluid-mediated transfer of incompatible elements to the Luliang Shan could have occurred via devolatilization of chlorite-amphibole-serpentinite-bearing assemblages in the mantle hanging wall that have a higher temperature stability (Schmidt and Poli 1998; Bebout and Barton 2002; Pawley 2003; Till et al. 2012).
Fluid infiltration during exhumation

Both the Si- and Ti-contents of the muscovite from the host gneiss and within the shear zone are much lower than the values measured for the phengite (Figure 5). The noticeable lower measured Si- and Ti-contents suggest equilibration of the host gneiss muscovite at lower pressures than the selvage (approx. 1.0 GPa; Figure 12).

Figure 11. Boron isotopic results from Luliang Shan micas. (a) Ion microprobe $\delta^{11}$B vs. B (ppm) values in white mica from samples discussed in the text (see key in plot). Values of $\delta^{11}$B corresponding to the mid-oceanic basalts (MORB) and mantle fall within the hatched region (Marschall et al. 2007). (b) Ion microprobe B/Be vs. B values in white mica (see key above). (c) Ion microprobe B/Li vs. B concentrations in white mica (see key above). For all three plots, the low boron concentrations associated with fluids derived from highly devolatilized rocks plot in lower left-hand corner.
Fluid pathways

This extreme dichotomy in the B concentration and B isotopic compositions of selvage-forming phengite compared to the retrograde muscovite formed during exhumation both in the selvage, host gneiss and shear zone requires a much more complicated scenario in which the rocks of the Luliang Shan reacted with fluids produced from markedly different environments within a subduction channel (Figure 12). As previously presented, the trace element concentrations (Li, Cs and Ba) from the host gneiss and eclogite are lower than those of the selvage. For these reasons, we consider it highly unlikely that the anomalously high B concentrations recorded by the host gneiss muscovite were inherited from a protolith within the gneiss terrane or from the boron-poor fluid that triggered the development of the phengite-rich selvage during near-UHP conditions. It instead seems most likely that the B-rich fluids were derived from volatile-rich rocks at shallower depths within the subduction zone.

Our interpretation of distinct high-pressure and low-pressure phases of fluid infiltration requires that: (1) high pressure fluids derived from substantially devolatilized rocks in the subduction channel were able to flow through the host gneiss to trigger fluid-mediated metasomatic hybridization at the reactive gneiss/eclogite contacts; and (2) lower-pressure fluids derived from shallow crustal regions of the subduction zone transformed the gneiss but left the selvage unaffected.

Both phases of fluid infiltration require that the gneiss was permeable to fluid flow. The similar concentrations of the phengite in the selvage and those in the regionally distributed gneiss samples provide evidence that the high-pressure fluid also promoted growth of phengite within the gneiss (Figure 8). The most significant growth of phengite during the initial high-pressure phase of fluid influx occurred within the selvages that formed around eclogite and received metasomatic addition of fluid-mobile elements. Once formed, the selvage must have become impermeable to infiltrating fluid. Otherwise, it is not possible to explain how the selvage

Figure 12. Pressure–temperature–time (P-T-t) path for the Luliang Shan eclogites and associated selvages based upon thermobarometry and pseudosection analysis (data from Menold et al. 2009). Ti-in phengite isopleths based upon Auzanneau et al. (2010). The green section illustrates the constrained conditions for infiltration of high-pressure fluids related to selvage formation around eclogite based upon measured Ti-contents of phengite (see Figure 5). Similarly, the conditions for retrograde muscovite growth in the host gneiss and shear zone that we relate to lower pressure infiltration of B-rich fluids is represented by the purple section.

Yin et al. (2007) described a regionally pervasive epidote-amphibolite facies metamorphism that overprinted rocks within the Luliang Shan region as they were exhumed to crustal depths. Menold et al. (2009) estimated these epidote-amphibolite conditions to be 0.8–0.9 GPa and ~415–510°C. The host gneiss muscovite yield ⁴⁰Ar/³⁹Ar cooling ages of 450–470 Ma that are consistent with regional cooling trends within the Luliang Shan (Menold et al. 2016).

The observation that the host gneiss muscovite contain high B concentrations (Figure 7) and yield δ¹³B values higher than those of the mantle (>0‰ to −10‰; Figure 11(a)) suggests that fluids derived from a weakly devolatilized source that retained most of its boron infiltrated the gneiss (Marschall et al. 2007). This interpretation is supported by B/Be ratios that are mostly >100 (Figure 11(b)) and B/Li ratios >10 (Figure 11(c)) in the host gneiss muscovite. These compositional attributes are completely different from those of the selvage phengite and are more consistent with interaction with fluids devolatilized from shallowly subducted and weakly metamorphosed sedimentary materials (Bebout et al. 2007).

By invoking derivation of late-stage fluids from much shallower depths within the subduction zone, our model requires that the Luliang Shan gneiss terrane was likely exhumed parallel to, and in close proximity, to the subduction channel. Ernst et al. (1997) among others have invoked such a process as an effective mechanism for exhuming buoyant continental crust subducted to UHP depths. While the model predictions from Ernst et al. (1997) are consistent with higher temperature rocks of the North Qaidam UHP terrane, the isotope and trace element data presented here preclude diapiric ascent as a mechanism for exhumation of the Luliang Shan gneiss terrane.
was unaffected by the retrograde phase of fluid infiltration where only the host gneiss and discrete shear zones interacted with the B-rich fluids. Finally, results obtained from the three regionally distributed gneiss samples (Figure 8) requires that permeation of the B-rich fluids into the host gneiss of the main traverse in this study was of limited extent since the samples within the main traverse (Figure 1(c)) appear only to be affected by those fluids.

Muscovite from the shear zone also likely formed during the late-stage epidote-amphibolite facies metamorphism, yielding cooling ages similar to those of the host gneiss (Menold et al. 2016). The compositional patterns of the rocks within the terrane suggest a more channelized mode of fluid migration around the selvage. Fracturing and shearing of rocks during exhumation may have channelled external B-rich fluids into the selvage to infiltrate the shear zone near the eclogite contact (e.g. Angiboust et al. 2014). The δ11B, B/Be and B/Li values measured from the shear zone muscovite reflect intermediate compositions between the selvage phengite and the host gneiss muscovite (Figure 11). This may indicate that the late-stage fluids that attended the epidote-amphibolite facies conditions caused crystallization of the host gneiss but were only partially able to react with the shear zone muscovite.

Aside from selvage-B type lithologies from the shear zone, we have strong evidence that the late stage, B-rich fluids overprinting the host gneiss were unable to permeate the selvage. Although retrograde muscovite is present within the selvage, its B-content and δ11B composition is quite different from that of the B-rich host gneiss muscovite. Retrograde muscovite from the selvage has the highest Ba contents of any of the micas we have examined, whereas muscovite from the host gneiss and the shear zone exhibit the lowest Ba values (Figure 5(h), Figure 10(c)). Additionally, the retrograde muscovite contains consistently lower B/Be and B/Li values than the selvage phengite (Figure 11(b,c)). Furthermore, the retrograde muscovite from the selvage is still largely distinct in Cs vs. Cs/Rb from the muscovite within the host gneiss and the shear zone (Figure 10(d)). These systematic compositional patterns are consistent with a more retrograde-type muscovite growth in the selvage occurring from remnant fluids that had already crystallized appreciable phengite.

Conclusions

Petrographic, compositional and δ11B results collected from the Luliang Shan locality in the North Qaidam UHP terrane allow us to constrain the fluid events and sources during the region’s evolution. Based on the results of this study we can confidently conclude the following:

1. Metasomatic phengite+garnet rich selvage lithologies around the mafic eclogite bodies formed as a response to infiltration of fluids rich in Li, Cs and Ba. The δ11B compositions of the phengite are much more negative compared to mantle values and require a more devolatilized source region. Therefore, the source of these fluids appear to be from deeper regions of the subduction zone.

2. The host gneiss muscovite from the traverse samples is Be- and B-rich, and contains much lower concentrations of Li, Cs and Ba relative to the selvage-A phengite. The δ11B values in these samples are consistently higher than the values for selvage-A phengites, suggesting that the infiltrating fluids were derived from shallower regions in the subduction channel. We interpret that the Luliang Shan area interacted with these fluids as it was exhumed to crustal depths in the subduction channel.

3. Regionally distributed gneiss samples are compositionally dissimilar to the host gneiss samples from the traverse, most notably in the case of B-contents. This is also the case when the host gneiss is compared to selvage-A micas, which also lack this B enrichment. We interpret this as late stage influx of B-rich fluid which was localized within the Luliang Shan.

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