

REVIEW ARTICLE

Geochemical behaviours of chemical elements during subduction-zone metamorphism and geodynamic significance

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ABSTRACT

Seafloor subduction and subduction-zone metamorphism (SZM) are understood to be the very cause of both subduction-zone magmatism and mantle compositional heterogeneity. In this article, we compile geochemical data for blueschist and eclogite facies rocks from global palaeo-subduction-zones in the literature, including those from the Chinese Western Tianshan ultrahigh pressure (UHP) metamorphic belt. We synthesize our up-to-date understanding on how chemical elements behave and their controls during subduction-zone metamorphism. Although the compositional heterogeneity of metamorphic minerals from subducted rocks has been recently reported, we emphasize that the mineral compositional heterogeneity is controlled by elemental availability during mineral growth, which is affected by the protolith composition, the inherited composition of precursor minerals, and the competition with neighbouring growing minerals. In addition, given the likely effects of varying protolith compositions and metamorphic conditions on elemental behaviours, we classify meta-mafic rocks from global palaeo-subduction-zones with varying metamorphic conditions into groups in terms of their protolith compositions (i.e. ocean island basalt (OIB)-like, enriched mid-ocean ridge basalt (MORB)-like, normal [N]-MORB-like), and discuss geochemical behaviours of chemical elements within these co-genetic groups rather than simply accepting the conclusions in the literature. We also discuss the geochemical consequences of SZM with implications for chemical geodynamics, and propose with emphasis that: (1) the traditionally accepted 'fluid flux induced-melting' model for arc magmatism requires revision; and (2) the residual subducted ocean crust cannot be the major source material for OIB, although it can contribute to the deep mantle compositional heterogeneity. We also highlight some important questions and problems that need further investigations, e.g. complex subduction-zone geochemical processes, different contributions of seafloor subduction and resultant subduction of continental materials, and the representativeness of studied HP–UHP metamorphic rocks.

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1. The geological significance of seafloor subduction-zone metamorphism (SZM)

Subduction zones are the most effective sites on the Earth for mass exchanges between the Earth's exterior and the deep mantle. The main process in subduction zones, conceptualized as the 'subduction factory' (e.g. Tatsumi and Kogiso 2003), is dehydration metamorphism. Subduction-zone metamorphism (SZM) is in fact the very cause of subduction-zone magmatism, and is also the primary contributor to mantle compositional heterogeneity in the context of plate tectonics. Hence, a correct understanding of SZM is crucial for improved models of chemical geodynamics.

Island arc basalts (IAB) are characterized by abundant volatiles (~6–8 wt.% H₂O in parental melts prior to

significant degassing; Wallace 2005), and by elevated abundances of large ion lithophile elements (LILEs) relative to high field strength elements (HFSEs) (Figure 1a; e.g. Perfit *et al.* 1980). All these are termed 'arc signatures' (McCulloch and Gamble 1991; Elliott 2003), which are distinctively different from mid-ocean ridge basalts (MORB) of the ocean crust with depletion in the progressively more incompatible elements (Figure 1a). The MORB generation is understood to have resulted from decompression melting of the upwelling mantle in response to plate separation (McKenzie and Bickle 1988; Niu and Batiza 1991; Langmuir *et al.* 1993; Niu 1997), whereas IAB are interpreted to result from slab dehydration-induced mantle wedge peridotite melting (e.g. Tatsumi 1986; McCulloch and Gamble 1991). During the slab dehydration, the released fluids are

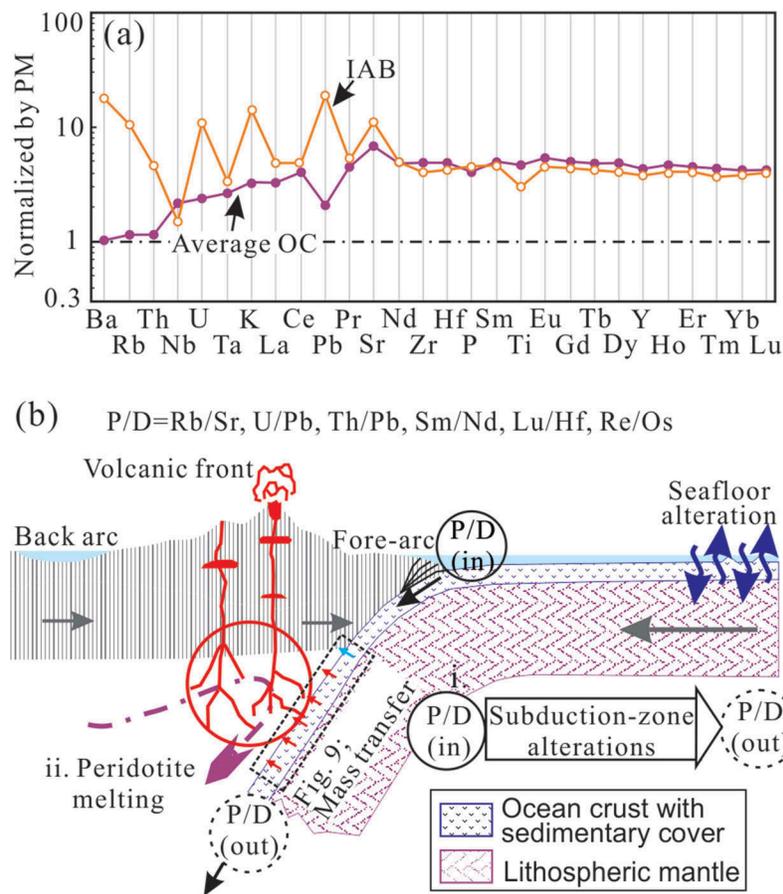


Figure 1. (a) Primitive mantle (PM) normalized trace element diagram for Island arc basalts (IAB), compared with the average composition of ocean crust (OC). The average OC, 'bulk ocean crust', is composed of 40% N-MORB + 60% average gabbro. Data for IAB and OC are from Niu and O'Hara (2003), while for PM are from Sun and McDonough (1989). (b) Schematic diagram showing the fractionation of the radioactive parent from the radiogenic daughter by subduction-zone alterations (i), which is also widely accepted to trigger the mantle wedge melting for subduction-zone magmatism (ii) (after Xiao *et al.* 2012). Conceptually, it is the radioactive parent over radiogenic daughter element ratio (P/D) of the residual subducted material that determines the mantle compositional heterogeneity, recognized in oceanic basalts (Niu 2009). The subducting slab as the inputting materials into subduction zones is mainly made up of sediments, altered/unaltered ocean crust, and lithospheric mantle, the top of which has been pervasively serpentinized.

thought to selectively carry water-soluble (or mobile) elements (such as Ba, Rb, Cs, K, Sr, Pb, U, B, As, and Sb) into the overlying mantle wedge, which further contribute to the arc signatures (McCulloch and Gamble 1991; Keppler 1996; Kogiso *et al.* 1997; Audéat and Keppler 2005; Tropper and Manning 2005). As the slab dehydration is essentially a metamorphic process, it follows that subduction-zone magmatism is a straightforward consequence of SZM.

Furthermore, it is logical to say that mantle compositional heterogeneity is a consequence of plate tectonics through introducing surface-processed and subduction-zone modified materials into the deep mantle (Niu *et al.* 2002; Niu and O'Hara 2003). This is because under solid state in the deep mantle the extremely slow elemental diffusion (Hofmann and Hart 1978; Van Orman *et al.*

2002, 2006; Holzapfel *et al.* 2005) cannot explain the observed large trace element and isotopic variability in the mantle source regions of oceanic basalts, including MORB and oceanic island basalts (OIB). The mantle compositional heterogeneity has been conceptualized in terms of radiogenic isotopes as mantle end-members, e.g. depleted MORB mantle (DMM), enriched mantle I (EMI), enriched mantle II (EMII), high μ (HIMU; $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$), 'Focus Zone' (FOZO) or the 'common' component (termed 'C') (White 1985; Zindler and Hart 1986; Hart *et al.* 1992; Hanan and Graham 1996; Hofmann 1997). These isotopic ratio differences reflect different ratios of radioactive parent (P) over radiogenic daughter (D) elements (P/D; e.g. Rb/Sr, Sm/Nd, U/Pb, and Th/Pb) in their ultimate mantle sources (Zindler and Hart 1986) as explicated by Niu and O'Hara (2003).

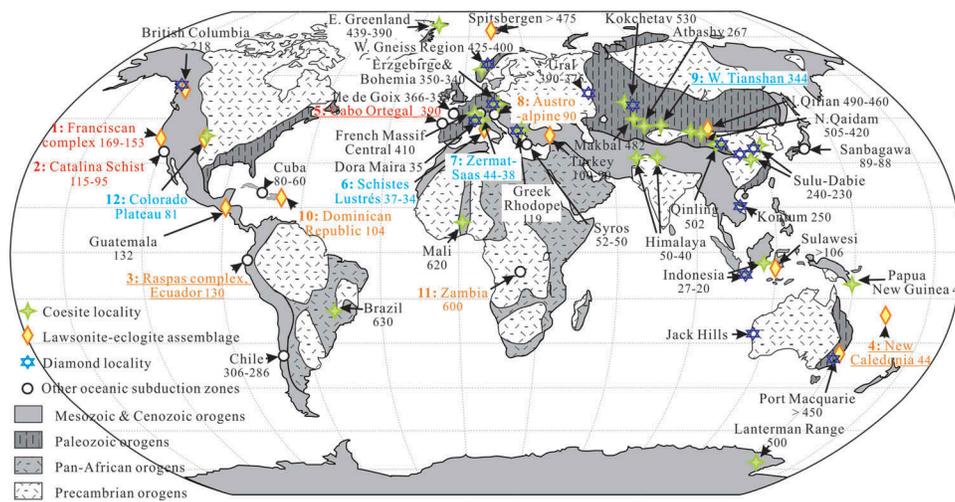


Figure 2. Worldwide distribution of HP–UHP metamorphic rocks with their subduction age (Ma) (modified after Liou *et al.* 2004; Tsujimori *et al.* 2006; Dobrzhinetskaya and Faryad 2011; the age of the HP metamorphic event for the Ile de Groix is from Bosse *et al.* 2005; El Korh *et al.* 2012).

By accepting the assumption that the primitive mantle of the Earth (after core separation in the Earth's early history) is compositionally uniform, then the present-day mantle isotopic heterogeneity is a straightforward consequence of plate tectonics accomplished through seafloor (including sediments, ocean crust, and lithospheric mantle) subduction and subduction-zone processes (Niu 2009; Figure 1b).

In the past 30 years, thanks to the discoveries of coesite and diamond inclusions in eclogites and eclogitic facies rocks hosted in the granitic gneisses (Chopin 1984; Smith 1984; Sobolev and Shatsky 1990), we have learnt that oceanic and continental crustal materials subducted to depths of >80 km can even return to the surface by a process generally termed as geological exhumation. Together with experimental petrology, studies on these subduction-zone metamorphosed rocks have challenged our traditional views on SZM and its relationship with the petrogenesis of IAB, which have also been summarized in several recent reviews (e.g. Schmidt and Poli 2003; Bebout 2007, 2013; Zheng *et al.* 2011; Klemd 2013; Spandler and Pirard 2013). This current review differs from the reviews mentioned above and emphasizes the geochemical consequences of SZM, i.e. the mass transfer from the subducting ocean crust with sediments to the source of arc magmas and the contribution to deep mantle compositional heterogeneity, through our current understanding of elemental behaviours during SZM (Xiao *et al.* 2012, 2013, 2014). Together with our recent studies on metamorphic rocks from the ultrahigh pressure (UHP) metamorphic belt of the Chinese Western Tianshan (Xiao *et al.* 2012, 2014), we first systematically discuss the controls on

compositional heterogeneity of metamorphic minerals from the subducting seafloor rocks. We then discuss the elemental behaviours during SZM of ocean crust and sedimentary lithologies using our compiled global data as a function of metamorphic facies/conditions and protolith types (Figures 2 and 3a and Supplementary Table 1; see <http://dx.doi.org/http://dx.doi.org/10.1080/00206814.2016.1147987> for supplementary tables). It is unlikely that one review can cover every detail in the literature, but we aim to objectively choose the most representative rock samples for discussion.

2. Heterogeneous trace element compositions of metamorphic minerals from the subducting seafloor

In addition to amphibole, hydrous minerals stable under HP and UHP conditions, such as phengite, lawsonite, zoisite, and allanite (Figure 3b) have been recognized in eclogite-facies rocks (Sorensen 1991; Thompson 1992; Liu *et al.* 1996; Sorensen *et al.* 1997; Hermann 2002). The stability of these minerals has been experimentally verified (Supplementary Table 2; Pawley and Holloway 1993; Pawley 1994; Schmidt and Poli 1994, 1998, 2003; Poli and Schmidt 1995, 1998, 2002; Schmidt 1995; Domanik and Holloway 1996, 2000). All these studies indicated that the breakdown of amphibole may not necessarily release all the fluids from the subducting slab as previously thought (e.g. Tatsumi 1986), i.e. the apparently 'dry eclogite' can carry ~1–2 vol.% fluids by lawsonite and phengite to up to 150 km depth (Poli and Schmidt 1995; Kerrick and Connolly 2001; Mibe *et al.* 2003), and even much more by serpentine (~13 wt.%

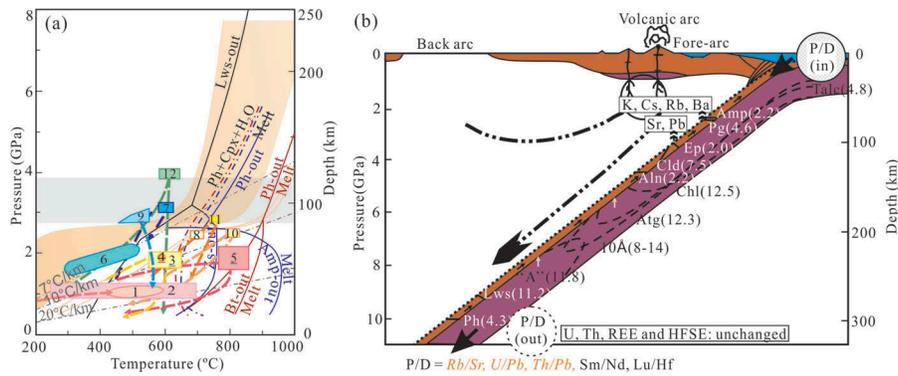


Figure 3. (a) Compiled peak metamorphic conditions and P–T paths of exhumed HP–UHP metamorphic rocks from global oceanic subduction zones compared with simulated geothermal conditions of the slab top (D80 model of Syracuse *et al.* 2010; modified after Spandler and Pirard 2013). The numbers represent relevant subduction zones listed in Supplementary Table 1 and Figure 2. (b) Schematic diagram showing stability of various hydrous metamorphic minerals from subducting rocks (modified after Schmidt and Poli 2003). The water contents of these minerals have also been given in brackets.

H₂O) to depths up to ~250 km in cold subduction zones (Syracuse *et al.* 2010; see also Rüpke *et al.* 2002, 2004; Hacker 2008; Konrad-Schmolke and Halama 2014). Furthermore, some HP–UHP metamorphic minerals have been found to contain significant amounts of trace elements, including some highly ‘mobile’ elements, e.g. LILEs (Tribuzio *et al.* 1996; Nagasaki and Enami 1998; Tamura *et al.* 2007; El Korh *et al.* 2009; Xiao *et al.* 2013, 2014).

2.1. Trace element budgets and mineral heterogeneous trace element compositions: revisited

We have compiled compositional data of metamorphic minerals from global subduction-zone metamorphosed rocks (see Figure 4). Different metamorphic minerals show their distinctive trace elemental characteristics in support of earlier studies (e.g. Tribuzio *et al.* 1996; Zack *et al.* 2001; Spandler *et al.* 2003; King *et al.* 2004; van der Straaten *et al.* 2008; El Korh *et al.* 2009; Schmidt *et al.* 2009; Beinlich *et al.* 2010; Xiao *et al.* 2013, 2014), but the abundances of some elements can vary significantly. Figure 5 is an effective summary of trace element budgets in the subducting ocean crust undergoing progressive metamorphism.

Lawsonite and epidote group minerals (including epidote, [clinzo]oisite, and allanite) plus apatite are, to varying extents, the primary hosts for rare earth elements (REE)–Sr–Pb–Th–U (e.g. Sorensen 1991; Tribuzio *et al.* 1996; Nagasaki and Enami 1998; Brunsmann *et al.* 2001; Hermann 2002; Spandler *et al.* 2003; van der Straaten *et al.* 2008; El Korh *et al.* 2009; Beinlich *et al.* 2010; Xiao *et al.* 2013, 2014). The REE content of epidote group minerals,

especially the content of light (L)-REEs, is highly variable ranging from a highly enriched pattern to a depleted one (Figure 4c). Pumpellyite and garnet are important hosts for middle-heavy REEs (M-HREEs). Garnet normally shows a pattern with high (HREE/MREE)_{chondrite} ratios (>1), but garnet crystals with the (MREE > HREE)_{chondrite} pattern are also common in metamorphic rocks (Tribuzio *et al.* 1996; Spandler *et al.* 2003; King *et al.* 2004; Konrad-Schmolke *et al.* 2008; El Korh *et al.* 2009; Beinlich *et al.* 2010; Xiao *et al.* 2013, 2014). REE contents of garnet are highly heterogeneous, even within one single crystal, e.g. a commonly observed rim-ward decrease of HREEs (Figure 6h and i; Xiao *et al.* 2013, 2014). White micas (phengite and paragonite) are the major host for Ba, Cs and Rb (Domanik *et al.* 1993; Sorensen *et al.* 1997; Becker *et al.* 2000; Melzer and Wunder 2000; Zack *et al.* 2001; Spandler *et al.* 2003; Bebout *et al.* 2007, 2013; El Korh *et al.* 2009; Beinlich *et al.* 2010; Xiao *et al.* 2013, 2014). Ti-bearing minerals (rutile and titanite) and zircon conserve essentially all the HFSEs in the bulk rock (Stalder *et al.* 1998; Hermann 2002; El Korh *et al.* 2009); titanite could also host variably high REEs (Tribuzio *et al.* 1996; van der Straaten *et al.* 2008; El Korh *et al.* 2009; Beinlich *et al.* 2010; Xiao *et al.* 2013, 2014); zircon can also host some HREEs (Hermann 2002; Rubatto and Hermann 2003; Miller *et al.* 2007). Carbonate and albite contain some Sr (Figure 4k and l; van der Straaten *et al.* 2008; Beinlich *et al.* 2010). Glaucophane and omphacite host most Li, B, and Be in the bulk rock but no other incompatible elements (Figure 4m and n; El Korh *et al.* 2009; Xiao *et al.* 2014), although these two minerals could volumetrically dominate the rocks. Other metamorphic minerals like chlorite and chloritoid (Figure 4o) contribute little to bulk-rock trace element budgets (e.g. El Korh *et al.* 2009; Xiao *et al.* 2013).

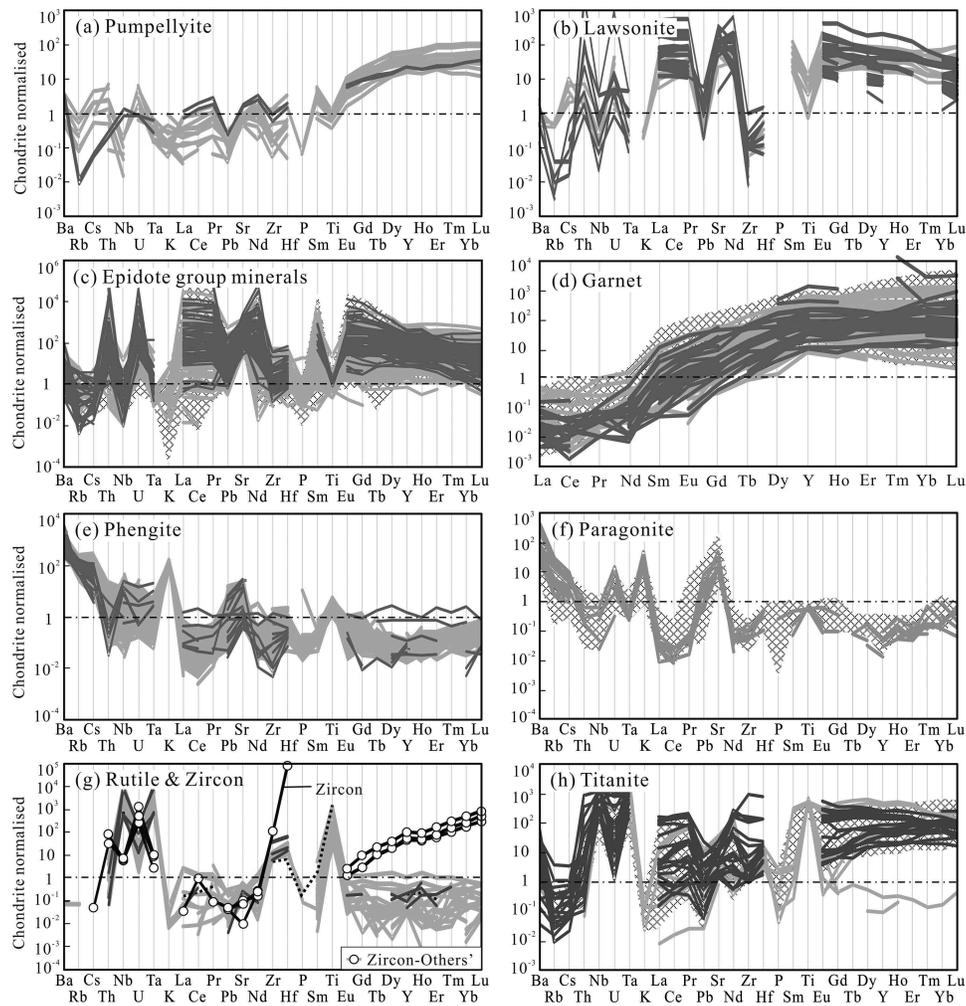


Figure 4. (a–p) Chondrite (Sun and McDonough 1989) normalized mineral trace element diagrams mainly based on mineral trace element data for subducted HP–UHP metamorphic rocks from the Chinese Western Tianshan (Xiao *et al.* 2014; represented by the hatched area) and the North Qilian Mountain (Xiao *et al.* 2013; represented by light grey curves). Mineral data published in other authors' studies are also presented (represented by dark grey curves), i.e. Spandler (2003) for New Caledonia, Usui *et al.* (2007) for Colorado Plateau, Herms *et al.* (2012) for Ecuador (Raspas Complex), El Korh *et al.* (2009) for Ile de Groix, Miller *et al.* (2007) for Austroalpine basement. Metamorphic minerals from different localities generally share similar geochemical characteristics. Amphibole, omphacite, chlorite, and chloritoid (m–o) show low contents of most trace elements, except the residual magmatic augite for REEs (n).

Recent studies have also proposed that serpentines may act as an important carrier for halogens, Li, B, As, Sb, Pb, Sr, K–Ba–Rb–Cs, and U, whose dehydration may further enhance the arc signature of the subduction-zone magmatism (Niu 2004; Scambelluri *et al.* 2004, 2014, 2015; Deschamps *et al.* 2010, 2012, 2013; John *et al.* 2011). However, these serpentine-hosted elements could largely result from intense reactions of serpentines with subducting sediments and/or ocean crust that are the most significant hosts for these elements (e.g. Deschamps *et al.* 2013; Barnes *et al.* 2014; Cannà *et al.* 2015). Therefore, to understand elemental behaviours controlled by ocean crust and sediments is still the key for understanding elemental behaviours during

seafloor SZM (e.g. Herms *et al.* 2012), which is the focus of this study. The potential effects of serpentines on geochemical processes and consequences of SZM have been discussed by others (e.g. Deschamps *et al.* 2011, 2013; Cannà *et al.* 2015; Scambelluri *et al.* 2015).

2.2. Controls on mineral compositional heterogeneity

Metamorphic minerals from subduction-zone metamorphosed rocks always display a more heterogeneous composition than magmatic minerals (e.g. El Korh *et al.* 2009; Xiao *et al.* 2014). The reason for this is straightforward, but not explicitly discussed in the

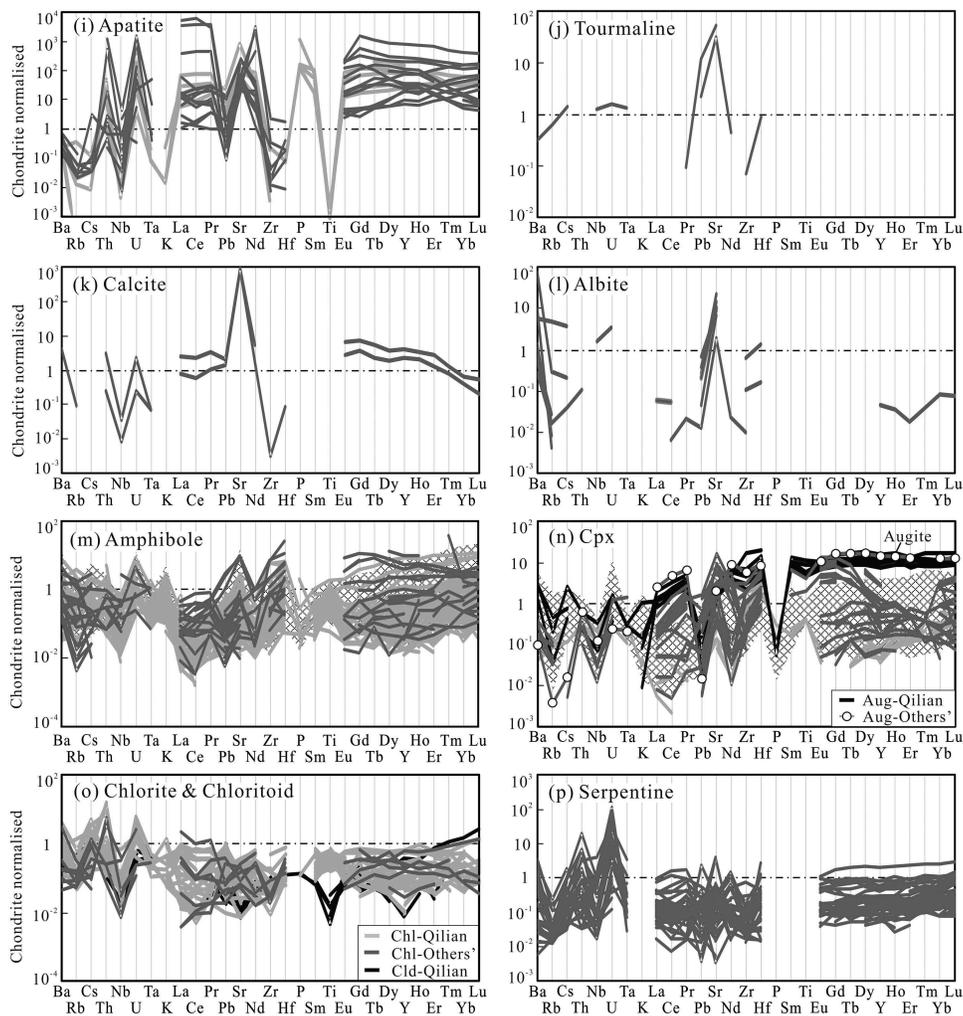


Figure 4. (continued).

literature. Under magmatic conditions, trace elements diffuse readily facilitated by the melt phase. Therefore, the elemental behaviour is strictly governed by partitioning between minerals and melts (e.g. Beattie 1994). Whereas under sub-solidus metamorphic conditions, like SZM, elemental diffusion is much more difficult even in the presence of fluids (e.g. Lee *et al.* 1997). Furthermore, trace elements only substitute geochemically similar major elements in crystal lattices without forming new phases. As a result, trace element distribution in metamorphic minerals is more heterogeneous than in magmatic minerals. For example, HREEs are strongly preferred by garnet. In magmatic systems, HREEs diffuse readily in the melt to supply garnet, but this is not the case for metamorphic garnet. Therefore, the abundances of 'compatible' elements in metamorphic minerals actually depend on the availability of these elements for the growing minerals. Specifically, the two major controls are: (1) the

inherited compositions, both the protolith bulk-rock composition and the precursor mineral composition; and (2) the competition between neighbouring growing mineral phases. All of these controls, as illustrated in Figure 6, are manifested in our studied rocks from the Chinese Western Tianshan, for which a lot of petrological and geochemical works have been done (Xiao *et al.* 2014).

As the bulk-rock composition of metamorphic rocks inherits from the protolith composition, the metamorphic mineral composition is thus determined accordingly by the protolith composition at a given metamorphic condition. In our studies of metamorphic rocks from the Chinese Western Tianshan, epidote group minerals with depleted LREEs (Figure 6a) are all from rocks with relatively depleted protolith composition (i.e. Group 2 resembling normal [N]-type MORB affected by arc materials and Group 3 N-MORB-like as shown in Figure 6b; see Xiao *et al.*

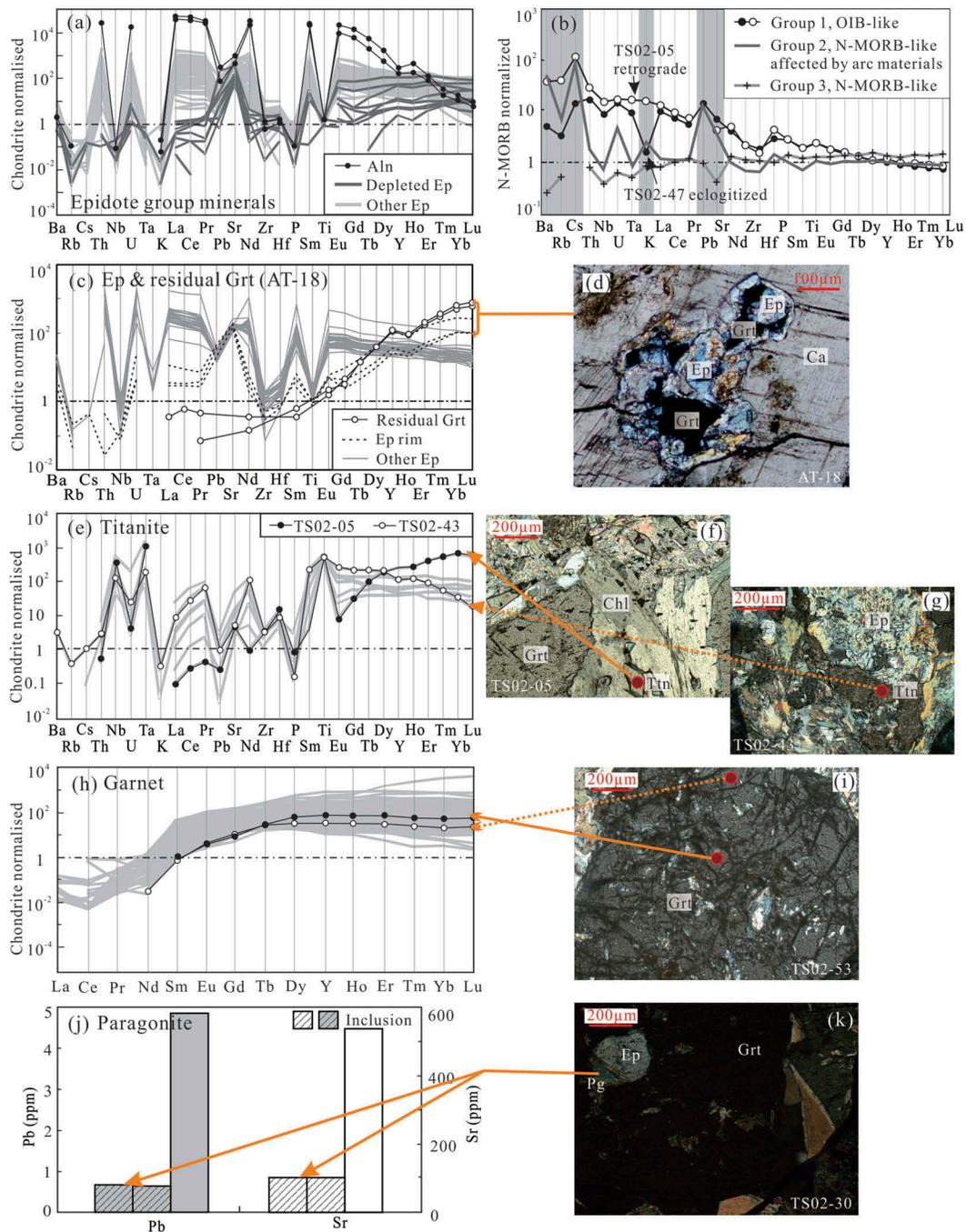


Figure 6. Different controls on mineral compositional heterogeneity, evidenced by those in metamorphic rocks from the Chinese Western Tianshan (Xiao *et al.* 2014 and unpublished data). (a, b) Controls of variable bulk-rock compositions, e.g. no depleted epidote group minerals (a) are from rocks of Group 1 with an enriched protolith composition (OIB-like; b). In (b), sample TS02-47 is highly eclogitized, while sample TS02-05 has been largely overprinted by retrograde metamorphism. Correspondingly, these two rock samples from the co-genetic group display great difference in the abundances of mobile elements (which are plotted in grey areas). (c–g) Controls of precursor mineral composition. The epidote replacing garnet (d) also displays a correspondingly high HREE/LREE pattern like garnet, different from other analysed epidote group minerals from the same rock (c). The variable REE content of titanite is also determined by its precursor mineral, garnet (f) vs. clinozoisite (g). (h–i) Accumulation and sequestering of HREEs by already present host minerals, resulting in a rim-ward decrease of HREEs in a garnet porphyroblast. (j–k) Competition of the neighboring mineral in equilibrium. The hatched bars in (j) represent the paragonite inclusion coexisting with clinozoisite, present as lawsonite pseudomorph in the garnet porphyroblast (k). The much lower Pb and Sr content of paragonite inclusions than those of the paragonite matrix from the same rock may reflect the competition of neighbouring clinozoisite for these elements.

2014). Therefore, UHP metamorphic hydrous minerals (even as accessory minerals, e.g. Klimm *et al.* 2008; Hermann and Rubatto 2009) can accommodate their preferred elements after the breakdown of amphibole, and transport these elements to a greater depth until their breakdown as subduction continues. On the other hand, the physicochemical properties of fluids as well as fluid contents and flow mechanism (channels/veins vs. porous fluids) have been argued to be important for determining elemental behaviours during SZM, e.g. highly water-insoluble elements (e.g. HREEs and HFSEs) could be mobilized under some circumstances (e.g. Gao *et al.* 2007; Zack and John 2007; John *et al.* 2008; Putnis and John 2010; Pirard and Hermann 2015). More importantly, recent studies have proposed that the slab–mantle interface between the subducting slab and the mantle wedge may be characterized by a complex ‘mix’ of highly deformed lithologies, i.e. ocean crust, sediments and hydrated and metasomatized mantle wedge peridotites (Bebout 2007). This complex interface may benefit fluid flow, influence the fluid composition, and facilitate mass transfer through intense fluid–rock interactions (e.g. Bebout 2007, 2013; Ague and Nicolescu, 2014). Reaction kinetics may also be important for affecting elemental behaviours during SZM, including: (1) element transport/diffusion rate (Carlson 1989, 2002; Schmidt and Poli 2003; King *et al.* 2004; Lucassen *et al.* 2010; Cruz-Uribe *et al.* 2014); (2) compositional differences between fluids and wall rocks (Breeding *et al.* 2004); and (3) the rate of the appearance of a new phase relative to the breakdown of the older one or the relative rate of precipitation to dissolution (Zack and John 2007; John *et al.* 2008; van der Straaten *et al.* 2008; Beinlich *et al.* 2010; Putnis and John 2010). The oxidation state may affect SZM in terms of mineral assemblages (Rebay *et al.* 2010). As the effect of fluid physicochemical properties and flow mechanisms during SZM has been thoroughly discussed in the literature (e.g. Philippot 1993; Gao and Klemd 2001; Walker *et al.* 2003; Manning 2004; Schmidt *et al.* 2004; Kessel *et al.* 2005; Hermann *et al.* 2006; Stern *et al.* 2006; John *et al.* 2008, 2012; Beinlich *et al.* 2010; Mibe *et al.* 2011), here we focus on elemental behaviours during SZM of ocean crust and sediments controlled by subduction-zone metamorphosed rocks and metamorphic minerals.

3.1. ‘Forward’ and ‘reverse’ modelling in geochemistry

The ‘traditional’ method to deduce the possible contributions of subducting/subducted rocks to arc magmas is

based on the geochemical studies of IAB (e.g. Tatsumi and Kogiso 1997; Churikova *et al.* 2001; Morris and Ryan 2003; Tamura *et al.* 2007; Regelous *et al.* 2010; Cai *et al.* 2014; Haase *et al.* 2015) or their melt inclusions in mineral phenocrysts (e.g. Schiano *et al.* 1995; Cervantes and Wallace 2003; Walker *et al.* 2003) through ‘reverse modelling’. On the other hand, this can be studied more directly from experimental studies and field-based studies on exhumed HP–UHP metamorphic rocks through ‘forward modelling’ (e.g. Becker *et al.* 2000; Spandler *et al.* 2003; Konrad-Schmolke *et al.* 2008, 2011; Hermann and Rubatto 2009; Xiao *et al.* 2012).

For ‘forward modelling’, three methods are commonly used to characterize elemental behaviours in response to SZM. (1) To compare the composition of HP veins/segregations formed during eclogitization with unaltered host rocks (Becker *et al.* 1999; Brunsmann *et al.* 2000; Spandler and Hermann 2006; Gao *et al.* 2007; John *et al.* 2008; Herms *et al.* 2012) by using mass balance calculations (e.g. Konrad-Schmolke *et al.* 2008, 2011; van der Straaten *et al.* 2008; Beinlich *et al.* 2010). Alternatively, the composition of HP–UHP metamorphic rocks is compared with that of unaltered equivalent protoliths (Breeding *et al.* 2004; John *et al.* 2004; Spandler *et al.* 2004), or with averaged composition of MORB/altere ocean crust (AOC; e.g. Becker *et al.* 2000; Bebout 2007). This method can help directly identify and quantitatively evaluate the specific chemical changes during SZM, but may be affected by bulk-rock compositional heterogeneity. (2) Through analysing the composition of each constituent mineral phase and mineral modal abundances to evaluate trace element budgets in the bulk-rock composition. As SZM is a time-evolved process, the understanding of trace element budgets should be combined with detailed studies of petrography and potential metamorphic reactions to reveal the elemental behaviours in response to the progressive SZM (Figure 5; e.g. Tribuzio *et al.* 1996; Becker *et al.* 2000; Zack *et al.* 2001; Spandler *et al.* 2003; El Korh *et al.* 2009; Bebout *et al.* 2013; Xiao *et al.* 2013, 2014). However, metamorphic mineral compositions can be highly heterogeneous as discussed above, and the mineral modal abundances may not be precisely estimated, especially for some accessory minerals, which may accommodate significant amounts of certain trace elements (e.g. zircon for Zr and Hf). As a result, the trace element budgets may not be well reconstructed using this method. (3) The analysis of fluid inclusions from HP–UHP metamorphic rocks can also be useful in helping understand the contribution of the subducting seafloor to arc magmatism, especially the fluid information during seafloor SZM (i.e. fluid physicochemical features; e.g. Philippot and Selverstone 1991; Scambelluri

et al. 1997, 2015; Scambelluri and Philippot 2001; Spandler *et al.* 2014).

Because the bulk-rock composition of protoliths exerts the key control on metamorphic mineral assemblages (e.g. Spandler *et al.* 2004) and thus on the behaviours of chemical elements (Xiao *et al.* 2012), it is important to reveal the protolith compositions so as not to be confused with the effect of SZM (e.g. Spandler *et al.* 2004; Xiao *et al.* 2012). In the following sections, we discuss the geochemical processes and consequences of SZM of ocean crust and sediments by considering both the literature results and the data on (1) the Chinese Western Tianshan UHP metamorphic rocks exhumed from a cold oceanic subduction zone (Gao and Klemd 2003; Ai *et al.* 2006; John *et al.* 2008; van der Straaten *et al.* 2008; Beinlich *et al.* 2010; Xiao *et al.* 2012), (2) HP metamorphic rocks exhumed from the New Caledonia warm subduction zone (Spandler *et al.* 2004) and the Raspas Complex in Southwest of Ecuador (John *et al.* 2010), and (3) HP metamorphic rocks exhumed from the Cabo Ortegal hot subduction zone in Spain (Halama *et al.* 2010). Supplementary Table 1 gives the general information; Supplementary Table 3 gives bulk-rock compositional data; and Figures 2 and 3a give sample locations and metamorphic conditions.

By using Nb/Y–Zr/Ti and Nb/Yb–Th/Yb diagrams considering the common immobility of these elements (Pearce 2008), all the selected meta-mafic rocks can be classified into three groups, i.e. OIB-like, enriched (E)-MORB-like, and N-MORB-like (Figure 7a and b). Geochemical behaviours of elements in meta-mafic rocks during SZM will be discussed within these co-genetic groups.

3.2. Mobility of LILEs

Because of the relatively high LILEs relative to HFSEs in IAB compared with the ocean crust (Figure 1a), this characteristic arc signature indicates that LILEs may have been transferred from the subducting seafloor through dehydration during SZM (e.g. Kay *et al.* 1978; Cervantes and Wallace 2003; Tamura *et al.* 2007; Regelous *et al.* 2010). On the other hand, however, the strong conservation of LILEs by phengite and its wide stability range can result in the immobility of LILEs during SZM, which contradicts the earlier inference but has been observed in natural HP–UHP metamorphic rocks (e.g. Busigny *et al.* 2003; Chalot-Prat *et al.* 2003; Miller *et al.* 2007).

For those selected meta-mafic rock samples from global HP–UHP metamorphic belts, at a given Nb/Zr within a co-genetic group, Ba/Nb ratios vary significantly (Figure 7c). Because HFSEs are commonly immobile, the highly variable Ba/Nb ratios reflect the mobility of Ba in meta-mafic rocks since the formation of their

magmatic protoliths (e.g. seafloor alterations before subduction and/or SZM). Furthermore, the mobility of LILEs in meta-mafic rocks is also supported by highly variable LILE contents compared with REEs and HFSEs for meta-mafic rocks of the same protolith composition in our recent studies of the Chinese Western Tianshan sample suites (e.g. TS02-05 and TS02-47 from a co-genetic group in Figure 6b). Among others, highly eclogitized rocks (e.g. TS02-47) have lower LILEs, while highly retrograde metamorphic rocks (e.g. TS02-05) have very high LILEs (Figure 6b). Given the different metamorphic histories based on our detailed petrological studies, we interpret that the low LILEs in eclogitic rocks but the high LILEs in retrograde metamorphic rocks reflect the loss of these elements during prograde metamorphism, but possible re-enrichment during retrograde metamorphism respectively (Xiao *et al.* 2012, 2014). On the other hand, meta-sedimentary rocks from the Chinese Western Tianshan show significant correlations of Ba–Rb–Cs with HFSEs (Xiao *et al.* 2012), indicating the similar immobility of these elements with HFSEs. By comparing Cs contents of meta-sedimentary rocks from different subduction zones with varied metamorphic conditions (i.e. Schistes Lustrés, Lago di Cignana and Catalina Schist; see Supplementary Table 1 and Figure 3a for their metamorphic conditions), Bebout *et al.* (2013) also found the retention of Cs (which was thought to be a highly fluid-mobile element) by subducting sediments during SZM to depths of >90 km (~3 GPa) in a cold subduction zone (represented by Lago di Cignana). The above analysis indicates that the geochemical behaviour of the same LILEs during SZM may differ between different protolith types, i.e. mobile in meta-mafic rocks vs. immobile in meta-sedimentary rocks, controlled by the stability of the host mineral phases.

Because the mineral compositional heterogeneity is controlled by the availability of their preferential elements as discussed above, white micas as the important LILE-hosts also display different LILE features in different lithologies, e.g. variable LILE contents of white micas from meta-sedimentary rocks vs. relatively constant LILE contents (with some 'exotic' data points) for those from meta-mafic rocks (e.g. the inset of Figure 7c; Xiao *et al.* 2014). This is attributed to different origins of white micas, i.e. those inherited from the protolith of meta-sedimentary rocks, and those of metamorphic origin in meta-mafic rocks. As a result, LILEs can be well conserved in meta-sedimentary rocks throughout the SZM, but will be liberated before the formation of white micas in meta-mafic rocks, resulting in the relatively homogeneous composition of white micas and the mobility of LILEs during SZM. The 'exotic' LILE enrichment in some retrograde white

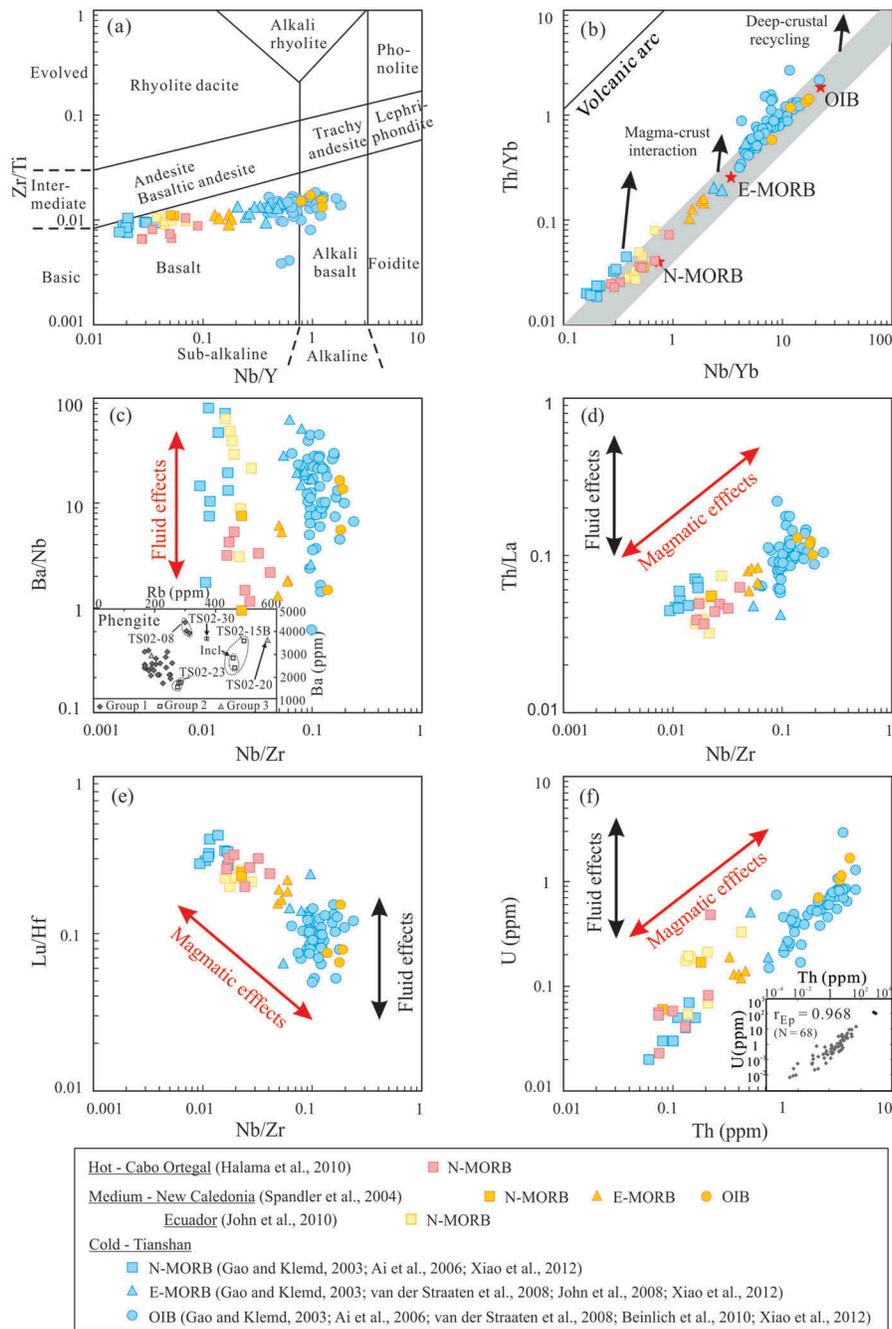


Figure 7. Correlation diagrams of element ratios for HP-UHP metamorphic rocks. Data for rock samples from the Chinese Western Tianshan (a cold subduction zone, blue symbols) are from: Ai *et al.* (2006), Gao and Klemd (2003), van der Straaten *et al.* (2008), John *et al.* (2008), Beinlich *et al.* (2010), Xiao *et al.* (2012). Other data used are: Spandler *et al.* (2004; Type I, Type III, and Type IV used) for New Caledonia and John *et al.* (2010) for Raspas Complex in Southwest of Ecuador as representatives of subduction zones experienced medium temperature paths (orange symbols), Halama *et al.* (2010) for Cabo Ortegal in Spain representing for hot subduction zones (red symbols). Nb/Y vs. Zr/Ti (a) and Nb/Yb vs. Th/Yb (b) diagrams (Pearce 2008) are used for distinguishing the protolith composition of HP-UHP metamorphic rocks. Three groups are generally classified: OIB-like (represented by circles), E-MORB-like (represented by triangles), N-MORB-like (represented by rectangles). Except the obvious fractionation of Ba from HFSEs (c), LREEs (d), HREEs (e) and U-Th (f) are all significantly correlated with HFSEs and reflect their similar immobility during prograde SZM. The inset in (c) and the inset in (f) display the relationship of Rb and Ba in phengite and the significant correlation of U-Th in epidote group minerals from meta-mafic rocks of the Chinese Western Tianshan respectively (after Xiao *et al.* 2014). The latter is consistent with the significant U-Th correlation in the bulk-rock composition.

micas from meta-mafic rocks also indicates the mobility of these elements during retrograde metamorphism of originally basaltic protolith. Therefore, both the timing of the appearance and the stability of white micas control the geochemical behaviour of LILEs, resulting in different geochemical behaviours of LILEs in different lithologies.

Once phengite has been formed, LILEs can be efficiently transported to a greater depth until this mineral is dissolved or melted in the presence of supercritical fluids (at temperature and pressure above its second critical point like a 'hydrous melt' or a 'silicate-rich fluid' without distinguishable properties; e.g. Schmidt *et al.* 2004) or hydrous melts (e.g. Sorensen *et al.* 1997; Hermann *et al.* 2006; Hermann and Spandler 2008). Moreover, because of the high permeability and the heterogeneously distributed lithologies along the slab–mantle interface (e.g. Bebout 2007), recent studies also proposed that there may be intense fluid–rock interactions and metasomatism controlled by the channelized fluids and the compositional difference between fluids and surrounding wall rocks in this region, which can facilitate the destabilization of phengite and enhance the mobility of LILEs (e.g. Breeding *et al.* 2004; John *et al.* 2008; van der Straaten *et al.* 2008). In addition, varied thermal structures of subducting seafloor may lead to different geochemical behaviours of LILEs (Bebout *et al.* 1999, 2007, 2013; Spandler *et al.* 2003). For example, LILEs have been found to be mobilized in meta-sedimentary rocks from the high grade unit (amphibolite facies) of Catalina Schist with a high thermal gradient (Bebout *et al.* 1999, 2007).

3.3. Ambiguous mobility/immobility of LREEs and immobility of HREEs

Niu (2004) showed that in highly and variably serpentinized (also weathered on the seafloor) abyssal peridotites, LREEs exhibit significantly correlated variations with HFSEs, which is a preserved magmatic signature. This clearly reflects the immobile nature of LREEs during serpentinization processes. For rock samples from global HP–UHP metamorphic belts, Th/La ratio is significantly correlated with Nb/Zr ratio; no obvious fractionation of these two ratios within a co-genetic group or obvious differences caused by different thermal structures of the subducting slab (Figure 7d). These indicate that La, as the representative of LREEs, is as immobile as HFSEs during SZM (Xiao *et al.* 2014). As discussed in Section 2.1, the important LREE-hosts in subduction-zone metamorphosed rocks are lawsonite and epidote group minerals including allanite (Figures 4c and 5; Tribuzio *et al.* 1996; Spandler *et al.* 2003; Miller *et al.* 2007; Martin *et al.* 2014; Xiao *et al.* 2014), which are also verified experimentally (Hermann 2002; Feineman *et al.* 2007; Hermann and Rubatto 2009; Martin *et al.* 2011). As subduction advances,

LREEs can be re-distributed among lawsonite, epidote, (clino)zoisite, and allanite, covering much of the subduction-zone metamorphic pressure–temperature (P–T) range (Supplementary Table 2), e.g. lawsonite in a cold subduction zone (e.g. Usui *et al.* 2007; Martin *et al.* 2014), allanite in a relatively warm subduction zone (e.g. Martin *et al.* 2014). Therefore, these minerals can be responsible for the retention of LREEs and their immobility on a bulk-rock scale (Figure 7d), even up to UHP metamorphic conditions in a cold subduction zone (e.g. the Chinese Western Tianshan, Xiao *et al.* 2012, 2014; Colorado Plateau, Usui *et al.* 2007) or in a warm subduction zone (e.g. eclogites of gabbroic protoliths from Austroalpine basement, Miller *et al.* 2007).

Figure 7e shows that Lu/Hf ratio and Nb/Zr ratio of rock samples from global HP–UHP metamorphic belts are also significantly correlated, and these two ratios remain nearly constant within a co-genetic group. This indicates that Lu, as a HREE, is also immobile like HFSEs during SZM. As discussed above, it has been recognized that pumpellyite and lawsonite are important HREE-hosts at low-grade metamorphic conditions (Xiao *et al.* 2013; Figure 5c). During eclogitization, HREEs are re-distributed into the newly formed garnet (Figure 5d), which becomes the most important host of HREEs (e.g. Spandler *et al.* 2003; El Korh *et al.* 2009; Xiao *et al.* 2013, 2014). Titanite can also accommodate significant amounts of HREEs throughout SZM (Figure 5c and g). Therefore, HREEs are largely re-distributed among these minerals and show their immobility on a bulk-rock scale during SZM.

3.4. Immobile Th and U

Different from the insolubility/immobility of Th in aqueous fluids, U can be readily mobilized in aqueous fluids in the form of U^{6+} (vs. U^{4+}) under oxidized conditions (Bailey and Vala Ragnarsdottir 1994). Hence, aqueous fluids derived from the subducting seafloor are characterized by high U/Th ratios with relatively low Th. However, during partial melting of crustal rocks, Th is slightly more incompatible than U (Beattie 1993; LaTourrette *et al.* 1993; Hawkesworth *et al.* 1997; Niu and Batiza 1997; Niu *et al.* 1999; Klemme *et al.* 2005; Elkins *et al.* 2008). As a consequence, the melts derived from subducting seafloor should have low U/Th ratios with relatively high Th. Therefore, the U/Th ratio of IAB has often been used to distinguish different subducted components involved in the source of IAB, i.e. melts vs. aqueous fluids from the subducting seafloor (e.g. Gill and Williams 1990; Hawkesworth *et al.* 1993, 1997). However, Th shows a statistically significant correlation with U for global arc basalts (Figure 8a; Elliott 2003), similar to that of global MORB (MORB glass data refer to

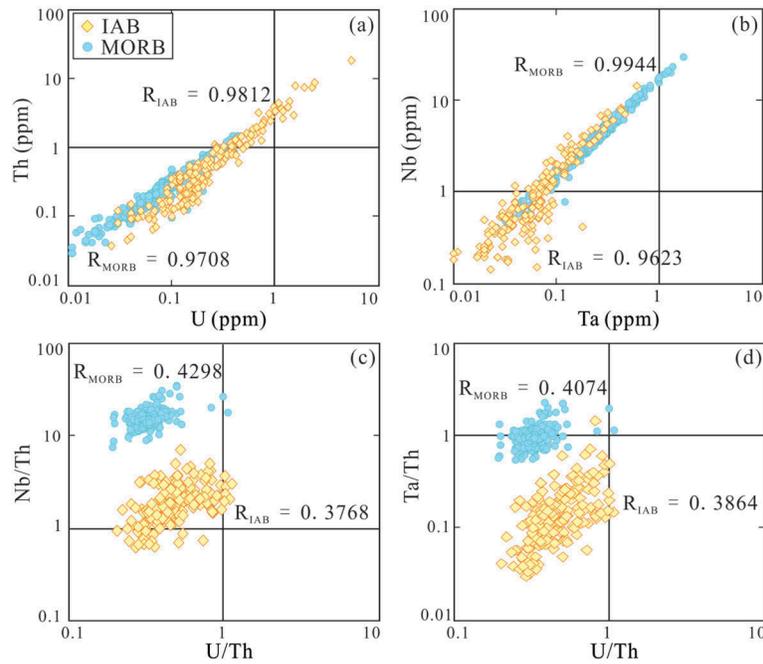


Figure 8. Comparison between global IAB (Elliott 2003; $n = 205$) and MORB (refer to PetDB, <http://beta.www.petdb.org/>, $n = 351$). We choose MORB glass samples with data for contents of major elements and commonly used trace elements (Rb, Sr, Y, Zr, Nb, Cs, Ba, REEs, Hf, Ta, Pb, Th, U), and exclude those glass samples with $\text{SiO}_2 > 53$ wt% and $\text{MgO} < 7$ wt% to avoid higher extents of magma evolution in this study. (a,b) show linear correlations between Th and U, Nb and Ta in arc magmas, which are similar to those in MORB lavas. It suggests that U is as immobile as Th during arc magmatism, although their geometric averages of Th/U ratio are different, i.e. 3.39 in IAB vs. 3.17 in MORB (through reading the slope of their linear correlations in [a]). In (c, d), U/Th ratios of IAB significantly correlate with Nb/Th and Ta/Th ratios, like their correlations in MORB. It indicates that U shows similar immobility like HFSEs and Th, which are controlled by magmatic processes (including supercritical fluids) for the petrogenesis of IAB, rather than the distinctive mobility of U caused by the dehydration during SZM.

PetDB, <http://beta.www.petdb.org/>), with only slightly different Th/U ratios (Figure 8a). Furthermore, together with the similar correlation of Nb and Ta (Figure 8b), the similar correlation between U/Th and Nb/Th (Figure 8c) or Ta/Th (Figure 8d) in arc magmas with that of MORB, indicates that U, Th, Nb, and Ta do show the same geochemical behaviour without being significantly fractionated for the petrogenesis of IAB as is the case for MORB although IAB have on average lower Nb and Ta abundances (hence lower Nb/Th and Ta/Th ratios) than in MORB (Figure 8c and d).

On the other hand, based on our studies for HP metamorphic rocks from North Qilian Mountain (Xiao *et al.* 2013), we found the alteration of U since the formation of the protolith. However, this change is more likely caused by heterogeneous seafloor alterations before subduction, rather than by SZM. Becker *et al.* (2000) also attributed the mobility of U to its addition during seafloor alteration with only limited or negligible loss during SZM, based on their studies of global HP–UHP metamorphic rocks. Furthermore, the significant correlation of Th–U–LREE with HFSEs for global subduction-zone metamorphosed rocks (Figure 7d

and f) may reflect that U, Th, and LREEs are largely hosted by the same carrier, i.e. epidote group minerals (see discussion in Section 2.1). This is also consistent with the significant U–Th correlation in epidote group minerals in subduction-zone metamorphosed rocks from the Chinese Western Tianshan (the inset of Figure 7f), resulting in the similar immobility of these elements during SZM. Based on the studies of a series of blueschist–eclogite–facies rocks in a vein-infiltrated system (composed of unaltered blueschist host – blueschist–eclogite transition zone – eclogitic selvage – vein), Beinlich *et al.* (2010) also reached the similar conclusion that U–Th–LREEs share the same carrier and ‘no major net loss occurred’ during SZM.

3.5. The immobility of HFSEs

Considering that rutile, titanite, and zircon accommodate almost all the HFSEs in subduction-zone metamorphosed rocks, the discussion on the mobility/immobility of HFSEs is always related to the possible mechanism and the extent of dissolution of these minerals. Although HFSEs were widely considered to be water-

insoluble during SZM (Brenan *et al.* 1995; Kogiso *et al.* 1997; Audétat and Keppler 2005; Tropper and Manning 2005; Baier *et al.* 2008), the mobility of HFSEs has been suggested (Philippot and Selverstone 1991; Van Baalen 1993; Rubatto and Hermann 2003; Tomaschek *et al.* 2003; Gao *et al.* 2007; Woodhead *et al.* 2001 for Hf mobility). The mobility of HFSEs on local scales is thought to be closely related to the distinctive fluid physicochemical properties, e.g. supercritical fluids (Ayers and Watson 1993), fluids with dissolved Na–Al silicates (Tropper and Manning 2005; Gao *et al.* 2007; Antignano and Manning 2008), fluids with halogen (especially fluoride brines; Bright and Readey 1987; Rapp *et al.* 2010), which can enhance the solubility of rutile; the alkali zircono–silicate complex that is able to enhance the solubility of zircon (Wilke *et al.* 2012). However, all these studies agree that pure H₂O fluids have poor capability to dissolve HFSE-hosted mineral phases (e.g. rutile and zircon).

Some recent studies have found the presence of zircon, garnet, and rutile in eclogite–facies veins (Rubatto and Hermann 2003; Spandler and Hermann 2006; Gao *et al.* 2007), and proposed that the relevant elements of these minerals (i.e. HREEs in garnet, Ti–Nb–Ta in rutile, Zr–Hf in zircon; see Section 2.1) could be mobilized in a large fluid flux system (Spandler and Hermann 2006; Gao *et al.* 2007; Zack and John 2007; John *et al.* 2008). However, the heterogeneous distribution of metamorphic minerals (especially accessory minerals) can lead to the heterogeneous distribution of relevant mineral components. Therefore, the vein composition cannot be taken directly as the fluid composition (Spandler and Hermann 2006), but may also include the effect of bulk-rock compositional heterogeneity. In addition, as HREEs and HFSEs are rarely available to aqueous fluids in the first place, no matter how large the amount of fluids may be, aqueous fluids cannot result in the significant mobility of HREEs and HFSEs (e.g. Ryerson and Watson 1987). When fluids pass through variable lithologies in subduction zones, especially along the slab–mantle interface with varying lithologies (e.g. Marschall and Schumacher 2012; Zheng 2012; Bebout 2013), the physicochemical properties and the composition of fluids will change accordingly through intense fluid–rock reactions (Bebout 2013). As a result, this change may lead to HFSE reprecipitation (Gao *et al.* 2007; Rapp *et al.* 2010; Wilke *et al.* 2012) because of the very low solubility of HFSEs in most fluids (e.g. aqueous fluids), while highly water-soluble LILEs may travel some distance along a fluid channel manifested by veins. Therefore, the mobility of HFSEs may be only a local phenomenon (e.g. Rubatto and Hermann 2003; Wilke *et al.* 2012).

4. Implications for subduction-zone magmatism and mantle compositional heterogeneity

With a series of subduction-zone alterations (i.e. alterations by SZM, hydrous melting and supercritical fluids), we have found that some elements could be removed from the subducting seafloor and further responsible for the enrichment of relevant elements in arc magmas, while the slab carrying the residual materials will continue to subduct into the deep mantle. Hence, the enrichment manifested by IAB should be complementary to the depletion of the residual slab rocks relative to their original compositions input into subduction zones (Figure 1b). Therefore, both the arc signatures caused by the elemental removal from the subducting slab and the deep mantle compositional heterogeneity as the consequence of subduction of the residual slab materials should be considered together (e.g. Niu and O'Hara 2003; Ryan and Chauvel 2014). In the following, we discuss the contribution of subduction-zone alterations to subduction-zone magmatism and mantle compositional heterogeneity.

4.1. For subduction-zone magmatism

The exposed HP–UHP metamorphic rocks of seafloor protolith always recorded geochemical consequences of SZM without showing melting phenomenon. However, LREEs and U did not fractionate from Th or HFSEs in HP–UHP metamorphic rocks (Figure 7d and f), suggesting that these elements were not liberated significantly through dehydration. Considering higher partitioning coefficients of LREEs and U into supercritical fluids/hydrous melts than aqueous fluids, the derivation of supercritical fluids or hydrous melts from the subducting slab formed at greater depths rather than simple metamorphic dehydration of aqueous fluids is required for the elevated abundances of LREEs and U in arc lavas (e.g. Kessel *et al.* 2005; Hermann and Rubatto 2009).

On the other hand, melting or derivation of supercritical fluids from the subducting slab for arc lavas is also consistent with evidence from arc lavas. In arc lavas, U shows significant correlation with Th (Figure 8a) and HFSEs (Figure 8c and d), similar to the case of MORB, which is all consistent with a magmatic signature, rather than a fluid effect. Furthermore, as Ryan and Chauvel (2014) summarized, Nd and Hf isotopic compositions of arc lavas are different from those of MORB, which may be attributed to the contribution of the subducting slab. However, arc lavas also show significant correlations between Nd and Hf isotopes similar to those in MORB, which clearly indicates that Sm/Nd and Lu/Hf (ratios of radioactive parent over

radiogenic daughter elements) are not greatly altered by fluids derived from the subducting slab. Hence, the difference in Nd–Hf isotopic composition of arc lavas from those of MORB may be caused by the melting or the derivation of supercritical fluids from the subducting slab. Therefore, we proposed here with emphasis that the traditionally accepted ‘fluid flux induced-melting’ model requires revision in order to explain the geochemical signatures of arc magmas produced through subduction-zone magmatism (see also Gerya and Yuen 2003; Behn *et al.* 2011; Marschall and Schumacher 2012). Wet melting at the top of the subducting slab or derivation of supercritical fluids from the subducting slab become widely accepted to be responsible for the petrogenesis of IAB and arc geochemical signatures in recent studies (e.g. Schmidt *et al.* 2004; Kessel *et al.* 2005; Stern *et al.* 2006; Gómez-Tuena *et al.* 2011; Mibe *et al.* 2011; Xiao *et al.* 2012).

During seafloor subduction, hydrous minerals like amphibole, serpentine and chlorite formed in the overlying mantle wedge by the dehydration of subducting seafloor at shallower depths, can be dragged downwards by the subducting slab until they are no longer stable at the sub-arc depth (process 1 in Figure 9b). Together with the possible breakdown of serpentine in the subducting slab at deeper depths (process 2 in Figure 9b; Syracuse *et al.* 2010; Deschamps *et al.* 2013), fluids released from the hydrous minerals in the mantle wedge are also likely to enhance the melting of subducting sediments and ocean crust (process 3 in Figure 9b). Moreover, because some subducting rocks could be peeled off to the mantle wedge (process 4 in Figure 9b), these peeled-off rocks can also melt in the mantle wedge because the conditions are above their solidus.

Furthermore, the partial melts in equilibrium with garnet (a residual phase as an important host of HREEs) should correspondingly show low HREEs and HREE/LREE ratios, which have only been observed in adakites (Defant and Drummond 1990) but not in IAB (Figure 1a). As Kelemen *et al.* (2003) proposed, the reaction of slab melts with mantle peridotite at low melt/rock ratios (probably $< \sim 0.1$) can compensate the low HREEs in slab-derived melts, but with little alteration of highly incompatible elements (Kelemen *et al.* 1993; Kelemen 1995). Therefore, the extensive reaction of slab-derived melts with mantle peridotite during ascent of slab melts is also required for the common occurrence of IAB but rare occurrence of adakites in the field. Moreover, within the similar U/Th ratio range, Nb/Th and Ta/Th ratios of arc magmas are obviously lower than those in MORB (Figure 8c and d), suggesting lower Nb–Ta contents in the source of arc magmas (also an important arc signature). As Ryerson and Watson (1987) mentioned, the partial melts through hydrous melting of subducting

oceanic basaltic rocks are rutile-saturated. Therefore, these slab-derived melts with depleted Nb and Ta relative to Th may further impart this depleted feature to arc magmas. In addition, recent studies reported that Ti–clinohumite and Ti–chondrodite in ultramafic rocks from mantle wedge may also sequester HFSEs (Arai *et al.* 2012) and be responsible for the HFSE depletions in arc magmas (Shen *et al.* 2015).

4.2. For mantle compositional heterogeneity

After pervasive seafloor alteration, the mobile incompatible elements (e.g. LILEs and LREEs) can be largely released with the subduction-zone alterations (alterations by SZM, hydrous melting, and supercritical fluids) for the petrogenesis of IAB. Correspondingly, the residual subducted materials should be relatively highly depleted in these mobile elements compared with immobile incompatible elements (e.g. HFSEs; Niu and O’Hara 2003; Xiao *et al.* 2012, 2014). Hence, these residual subducted materials cannot contribute to the enrichment of these mobile elements in the deep mantle supplying OIB.

Our recent studies have found that with SZM, elemental ratios (e.g. Rb/Sr, Sm/Nd, Lu/Hf, U/Pb, and Th/Pb) of subducting rocks may have also been significantly changed (Figure 10) because of different elemental mobility of radioactive parents (e.g. Rb, Sm, Lu, U, and Th) and radiogenic daughters (e.g. Sr, Nd, Hf, Pb; Xiao *et al.* 2012). Considering the influences of hydrous melting and supercritical fluids after SZM, these ratios of the residual slab rocks may be further modified, which will be greatly more different from the original materials entering subduction zones (Figure 1b). This should have implications for mantle isotopic compositions when the residual slab materials enter mantle source of oceanic basalts (Niu and O’Hara 2003; Xiao *et al.* 2012, 2014). For example, during SZM, Rb/Sr ratio has been altered, because of different mobility of Rb (stabilized in phengite) and Sr (stabilized by epidote group minerals) while the Sm/Nd ratio remains constant because of the relative immobility of LREEs (sharing the same host mineral, e.g. epidote group minerals); the Lu/Hf ratio also remains constant owing to highly insolubility/immobility of HREEs and HFSEs, although they are hosted by different minerals (Lu by garnet and zircon, but Hf by zircon only; Xiao *et al.* 2014). Hence, the ratio of mobile radioactive parent to radiogenic daughter (Rb/Sr) decouples from ratios of immobile radioactive parent to radiogenic daughter (Lu/Hf, Sm/Nd; Figure 10a), the latter of which are inter-correlated (Figure 10b). Significant Th/Pb and U/Pb fractionations are also anticipated. Such differential P/D ratio fractionation during SZM is expected to lead to uncorrelated radiogenic isotope correlations in the residual slab materials, which, when entering mantle source of oceanic basalts, will impart such uncorrelated

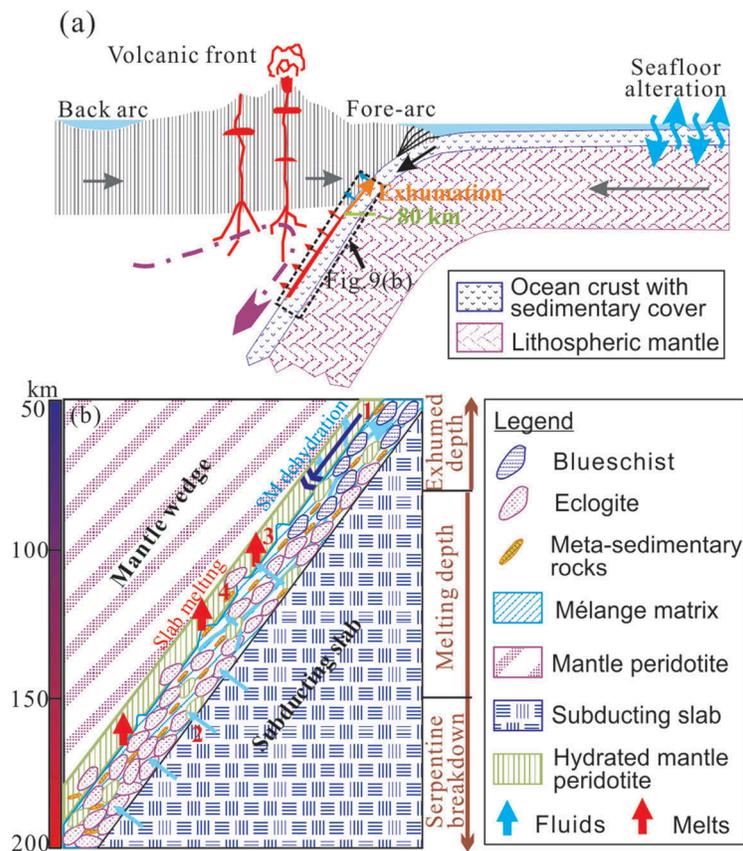


Figure 9. Schematic diagrams for the formation of arc magmatism. (a) shows the preferential sampling, i.e. ~80 km may represent the deepest depth for exhumation of subduction-zone metamorphosed rocks. Four processes are highlighted in (b). 1 – Hydrous minerals like amphibole, chlorite and serpentine in mantle wedge formed by metamorphic dehydration of subducting seafloor at shallow depths, could be dragged downwards until it is no longer stable. 2 – Large amounts of fluids liberated by the breakdown of serpentine at deeper depths (even greater than 250 km in cold subduction zones; Syracuse *et al.* 2010). 3 – Hydrous melting at the subducting slab top. 4 – Some subducting rocks may have been peeled off to the mantle wedge and melted. Through these four processes in subduction zones, it produced slab melts, which further interacted with the overlying mantle wedge to variable extents during its ascent and ultimately formed arc magmas.

isotopic signature (i.e. $^{87}\text{Sr}/^{86}\text{Sr}$ should be uncorrelated with $^{143}\text{Nd}/^{144}\text{Nd}$ or $^{176}\text{Hf}/^{177}\text{Hf}$) in OIB and other oceanic basalts (Xiao *et al.* 2014). However, this is not the case because these isotopic ratios are correlated in oceanic basalts (see Niu and O'Hara 2003). Therefore, the residual subducted ocean crust cannot be the major source material for OIB although they could contribute to the deep mantle compositional heterogeneity (Xiao *et al.* 2012, 2014; see also Niu and O'Hara 2003; Niu 2009 for other evidence, also Zheng 2012 for the alternative mechanism for the formation of OIB).

5. Cautions and future works

With increased quantity of high quality trace element data on constituent mineral phases of subduction-zone metamorphosed rocks as a result of advanced analytical techniques, significant advances have been made concerning

the trace element (re-)distribution in various metamorphic minerals in response to SZM (e.g. El Korh *et al.* 2009; Xiao *et al.* 2014). We have found that the behaviours of chemical elements during SZM are rather complex because of many controlling factors, e.g. varied thermal structures of subducting slab, physicochemical properties of fluids, and variable protolith compositions reflected by different mineral assemblages. To further improve the understanding of SZM, it needs to combine field observations, detailed petrography and well-designed analytical work, aided with experimental petrology. Several important issues need addressing in future investigations.

5.1. To distinguish different contributions of various geological processes

The exposed HP–UHP metamorphic rocks in the field are net products of complex processes, including (1) seafloor

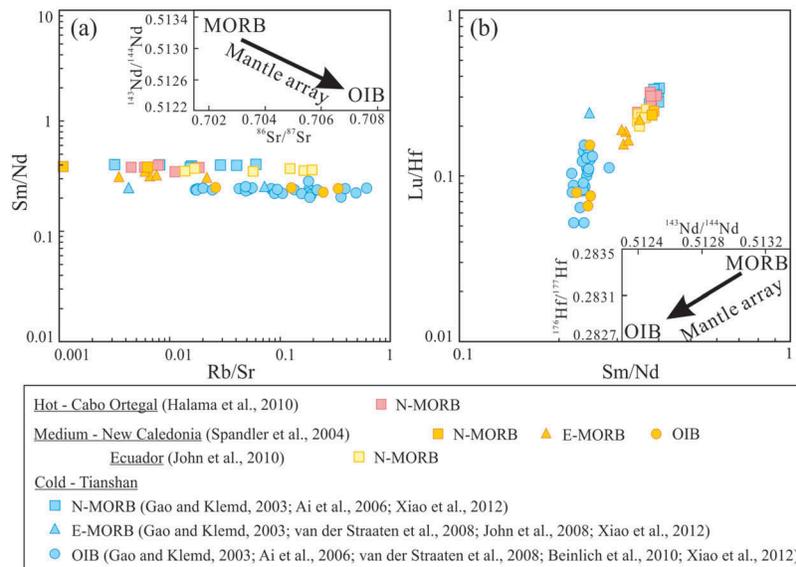


Figure 10. Comparison of radioactive parent/daughter element ratios (P/D) in the residual subducted materials with radiogenic isotopic ratios of OIB (after Xiao *et al.* 2012). Two insets are adapted from Hofmann (1997) and White and Patchett (1984). Highly eclogitized rock samples are used as the representative residual materials of subducted ocean crust (see compiled data in bold in Supplementary Table 3). The symbols used are the same to those in Figure 7. The positive Sm/Nd–Lu/Hf correlation of highly eclogitized rocks is consistent with these rocks being potential source materials for OIB when subducted with a positive Hf–Nd isotopic relationship (b), but the lack of Rb/Sr–Sm/Nd (and Lu/Hf) correlation is inconsistent with the rocks being the major source materials for OIB that show significant inverse Sr–Nd (a) and Sr–Hf correlations.

alteration (e.g. variable enrichment of U [5×], Rb [9×], and Cs [7×]; Kelley *et al.* 2003), (2) SZM, and (3) overprints in subduction channels (not only during exhumation processes, but also prograde processes of multiple subduction–exhumation cycles, e.g. Rubatto *et al.* 2011). Hence, it is difficult to clearly distinguish or estimate the effect of each geological process, but this task is essential towards a genuine understanding of elemental behaviours during SZM. To better constrain the elemental behaviours, it is important to understand each metamorphic stage along the subduction-zone metamorphic history through detailed petrological studies (Xiao *et al.* 2014). Moreover, different lithologies and various protolith compositions also complicate the mineral assemblages of subducting rocks. As elemental behaviours can be largely affected by the presence and stability of their hosted minerals, variable mineral assemblages may lead to different geochemical processes during SZM, which should also be considered in future studies.

5.2. Difference of seafloor subduction and resultant subduction of continental materials

Owing to common findings of the close relationship between the occurrence of UHP metamorphic belts and the distribution of subducted continental materials, the latter has attracted popular attention for studying UHP metamorphism and related geochemical processes (e.g.

Ye *et al.* 2000). Actually, because of low density, the continental materials are reluctant to subduct although they can be dragged down by previous seafloor subduction. As a result, the occurrence of subducted continental materials seem to be common in the HP–UHP metamorphic belts. However, it is the seafloor subduction and its geochemical processes, *not* ‘continental subduction’, that are responsible for the formation of arc magmas and the arc geochemical signatures as well as the mantle compositional heterogeneity. Studies of subducted seafloor rocks are key to understanding the petrogenesis of IAB and mantle compositional heterogeneity, although studies of subducted continental materials are significant for understanding UHP metamorphism.

5.3. Representativeness of studied HP–UHP metamorphic rocks

When we attempt to use HP–UHP metamorphic rocks to discuss SZM and subduction-zone magmatism, it is important to consider the representativeness of these rock samples. As Bebout (2013) suggested, the scale of studied rock samples determined our evaluation of the scale of mass transfer. We have obtained some basic understandings of elemental behaviours during SZM on hand-specimen scale and even metre scales. However, the contribution of the subducting slab to arc

signatures should be discussed in the context of a large-scale mass transfer from the subducting slab, which is expected to offer more general understanding of elemental behaviours of SZM than studies on discrete and localized samples.

On the other hand, the low density of serpentines relative to peridotite minerals (e.g. olivine and pyroxenes) can also facilitate exhumation of subducting/subducted rocks through overcoming the negative buoyancy (Agard *et al.* 2009). Agard *et al.* (2009) summarized that exhumed seafloor rocks from global subduction zones may be 'preferentially' sampled and always record metamorphic pressures <2.0–2.3 GPa (corresponding to depths less than ~70–80 km, the 'maximum depths' for sampling subducted seafloor rocks; Agard *et al.* 2009), while UHP metamorphism is only occasionally recorded, possibly as a result of serpentine dehydration and thus imbalanced negative buoyancy of ocean crust beyond this depth. The exposed HP–UHP metamorphic rocks may only record metamorphic histories for seafloor subduction before reaching the actual sub-arc depth, where the slab may be relatively hotter than these HP–UHP metamorphic rocks recorded (Figure 3a; Spandler and Pirard 2013). The occurrence of UHP metamorphic rocks of seafloor protolith in the Chinese Western Tianshan (Zhang *et al.* 2002a, 2002b, 2005; Lü *et al.* 2008, 2009, 2013, 2014; Lü and Zhang 2012) demonstrates that the maximum depth for exhumation of subduction-zone metamorphosed rocks may be up to 80–120 km.

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Disclosure statement

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