



Full length Article

Effects of decarbonation on elemental behaviors during subduction-zone metamorphism: Evidence from a titanite-rich contact between eclogite-facies marble and omphacitite



Yuanyuan Xiao ^{a,b,c,*}, Yaoling Niu ^{a,b,d}, Hong-Fu Zhang ^{e,f}, Kuo-Lung Wang ^c, Yoshiyuki Iizuka ^c, Jinyan Lin ^e, Yulong Tan ^e, Yongjiang Xu ^e

^a Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

^b Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266061, China

^c Institute of Earth Sciences, Academia Sinica, Taipei 11529, Taiwan

^d Department of Earth Sciences, Durham University, Durham DH1 3LE, UK

^e Department of Geology, Northwest University, Xi'an 710069, China

^f State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

ARTICLE INFO

Article history:

Received 18 May 2016

Received in revised form 11 January 2017

Accepted 11 January 2017

Available online 12 January 2017

Keywords:

Marine carbonate subduction
Behaviors of chemical elements
Subduction-zone metamorphism
Subduction-zone magmatism
Mantle isotopic heterogeneity

ABSTRACT

In this paper, we show the effects of subducted carbonates on geochemical processes during subduction-zone metamorphism (SZM) through the study of an eclogite-facies marble coexisting with metabasite from the ultrahigh pressure metamorphic belt of the Chinese Western Tianshan orogen. Between the marble and metabasite is a titanite-rich contact resulting from fluid-facilitated metamorphic reactions between the two lithologies, and recording elemental changes of geodynamic significance. Because this titanite-rich contact is dominated by titanite (an important host for high field strength elements, HFSEs) without white micas (an important host for large ion lithophile elements, LILEs), HFSEs are largely conserved in titanite whereas LILEs are moved away. This observation emphasizes the potential significance of subducting carbonate in retaining HFSEs in the slab through the formation and stabilization of titanite, contributing to the characteristic “arc signature” unique to subduction-zone magmatism (i.e., high LILEs, low HFSEs). The implicit assumption in this interpretation is that the observed lithological assemblage represents residues of subducting oceanic crust that has undergone major episodes of dehydration. Subducted carbonates also have significant implications for the origin of mantle isotopic heterogeneity as revealed from oceanic basalts.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Arc magmas with characteristic “arc” signatures (i.e., high large ion lithophile elements, LILEs and low high field strength elements, HFSEs) have been interpreted as resulting from slab dehydration-induced mantle wedge peridotite melting (“fluid-flux melting”; McCulloch and Gamble, 1991). The released fluids are thought to selectively carry water-soluble (or mobile) elements (e.g., Ba, Rb, Cs, K, Sr, Pb, U, B, As, Sb) into the mantle wedge, while the water-insoluble (or immobile) elements (e.g., HFSEs, heavy rare earth elements [HREEs]) remain in the subducting slab carried further into the deep mantle (McCulloch and Gamble, 1991). Therefore, to understand behaviors of chemical elements during

subduction-zone metamorphism (SZM) is important for better understanding arc magmatism. We have a good understanding of elemental behaviors during SZM on hand-specimen and even meter-scales, which are largely controlled by the formation and stability of relevant element-hosted minerals (El Korh et al., 2009; Hermann and Rubatto, 2009; Beinlich et al., 2010; Xiao et al., 2012, 2013, 2014, 2016). The abundances of fluids and fluid properties (e.g., fluids with dissolved Na-Al silicates or halogen, supercritical fluids above the second critical point) can also control the elemental mobility (Gao and Klemd, 2001; Rubatto and Hermann, 2003; Gao et al., 2007; Zack and John, 2007; John et al., 2008).

Despite all these complexities, we cannot truly understand geochemical behaviors of chemical elements during SZM without evaluating the effects of subducting/subducted carbonate. Carbonate makes up to ~7 wt.% of the global subducting sediments (GLOSS; Plank and Langmuir, 1998), and can indeed subduct mixed with sil-

* Corresponding author at: Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.

E-mail address: yuanyuan_xiao@foxmail.com (Y. Xiao).

icate sediments and altered oceanic crust. As a result, carbonation and decarbonation readily happen during metamorphism (Niu and Lesher, 1991). Hence, subducting/subducted carbonate must participate in metamorphic reactions and is likely to influence geochemical processes during SZM most likely in the form of CO_2 . The significance of subducting/subducted carbonate has been discussed in the context of global carbon recycling (Kerrick and Connolly, 2001a,b; Caciagli and Manning, 2003; Hayes and Waldbauer, 2006; Huybers and Langmuir, 2009; Manning et al., 2013; Ague and Nicolescu, 2014; Flesia and Frezzotti, 2015; Liu et al., 2015; Thomson et al., 2016) and the petrogenesis of mantle carbonatite and related mantle metasomatism (Yaxley and Brey, 2004; Dasgupta and Hirschmann, 2006, 2010; Tsuno et al., 2012; Poli, 2015).

In this paper, we report our findings of a titanite-rich contact between the marble and metabasite formed as the result of reactions between the two lithologies during seafloor subduction recorded in the ultrahigh pressure (UHP) metamorphic assemblage of the Chinese Western Tianshan orogenic belt (Xiao et al., 2012; Lü et al., 2013). We discuss the geochemical significance of the titanite lithology in moderating elemental behaviors during SZM and the geodynamic implications of carbonate subduction.

2. Field geology and petrology

2.1. Field geology

The Chinese Western Tianshan orogenic belt has been confirmed to be a typical UHP metamorphic (UHPM) belt as evidenced by findings of coesite and coexisting magnesite and aragonite as the product of dolomite breakdown (Lü et al., 2008, 2009, 2013, 2014; Zhang et al., 2002a,b; Lü and Zhang, 2012). This UHPM belt represents a paleo-convergent margin associated with the successive northward subduction of the South Tianshan Silurian-Devonian-seafloor and the Tarim Plate in the Carboniferous (Fig. 1a; Gao et al., 1999; Gao and Klemd, 2003). In this UHPM belt,

both metasedimentary rocks and metabasite coexist, including pelitic schist, marble, blueschist, and eclogite (Zhang et al., 2002a,b; Lü and Zhang, 2012; Lü et al., 2014). The protoliths of metabasite are oceanic basalts, including ocean island basalts (OIB), normal (N)-type and enriched (E)-type mid-ocean ridge basalts (MORB) as well as volcanic arc basalts (Gao and Klemd, 2003; Ai et al., 2006; Xiao et al., 2012).

Our study area is along the Atantayi River (Fig. 1b; Gao et al., 1999; Lü et al., 2014). Abundant marble is closely associated with other metasedimentary rocks (Fig. 2a and b; Lü et al., 2013) and metabasite (Fig. 2c and d). The marble intercalates with the metabasite, mica schist and mica quartz schist, the protolith of which are basaltic rocks, pelite and sandstone respectively. The marble shows well-preserved rhythmical interbeds with mica schist and mica quartz schist (Fig. 2a and c), probably inherited from the protolith assemblage of pelite, sandstone and carbonate as part of turbidite flysch sequence in a deep marine environment despite the subduction-exhumation related deformation (Fig. 2c). The marble also occurs as lenses together with the metabasite (Fig. 2a–c) with their long axes parallel to the orientation of other lithologies of the sequence (e.g., mica schist, mica quartz schist; Fig. 2a and b). The discrete carbonate and basaltic lenses (Fig. 2a–c) reflect disruption of turbidites by within-trench landslides. The entire sequence has experienced SZM. Our sample in this study (12TS-AT-18) is from the contact between a metabasite enclave and the marble host (Fig. 2d).

2.2. Petrography

Between the marble (represented by circles 3 and 5–11 in Layer I; Fig. 3b–f) and metabasite (represented by circles 13–22 in Layer III–VI; Fig. 3i–l) is a titanite-rich contact (Fig. 3g and h; represented by circles 2, 4 and 12 in Layer II) with a large (~8 mm long) titanite crystal (Fig. 3a). The titanite-rich contact is dominated by well-crystallized titanite, clinozoisite (X_{Ps} ratios, $\text{Fe}^{3+}/[\text{Fe}^{3+}+\text{Al}]$, smaller than 0.05; Ps, pistacite; Supplementary Table S.1) and fine-

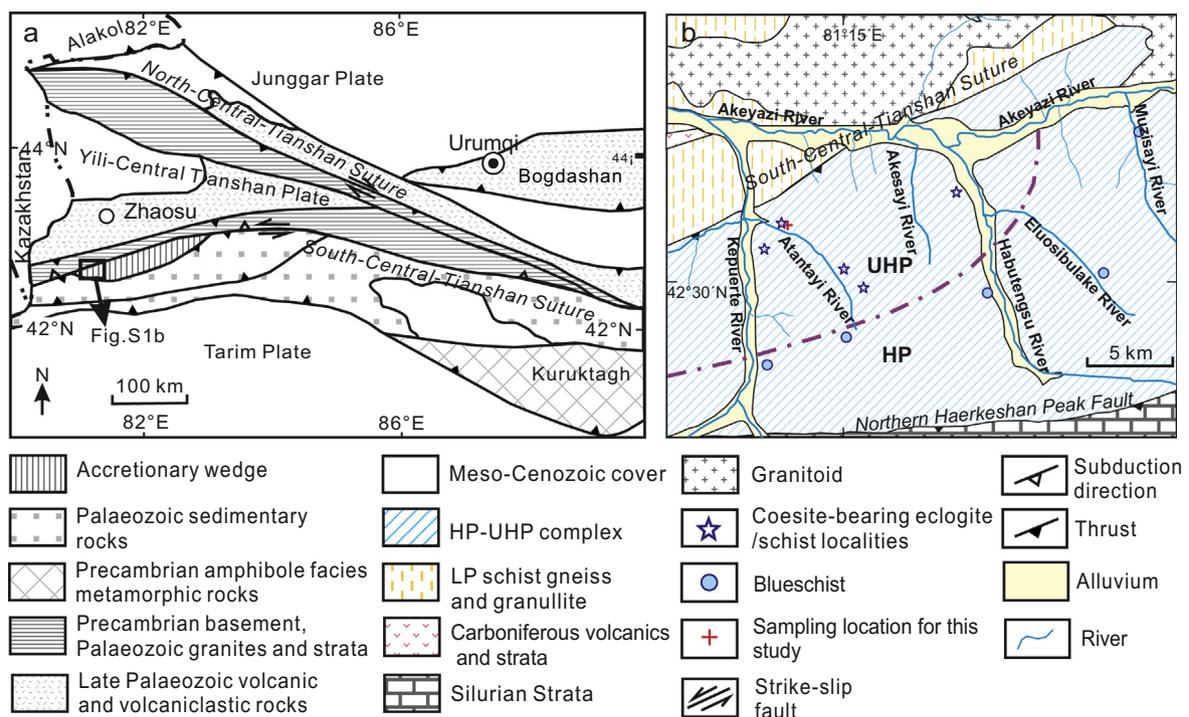


Fig. 1. Geological sketch of the Chinese Western Tianshan HP-UHP metamorphic terrane (Lü et al., 2013) and our sampling location for this study.

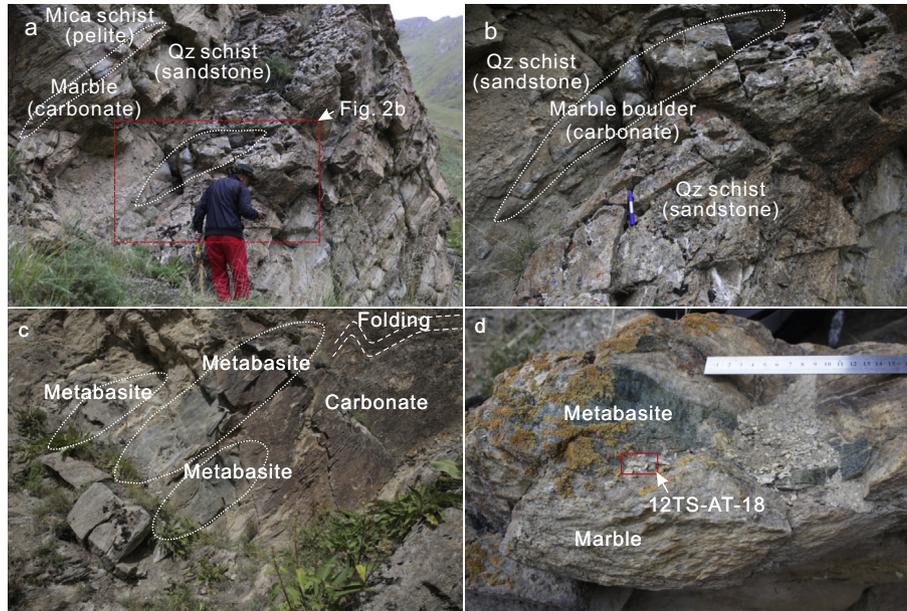


Fig. 2. Photos of field observations along the Atantayi River. (a and b) Intercalated marble, mica schist and mica quartz schist without obvious deformation, reflecting the well-preserved flysch structure. The protolith of marble, mica schist and quartz schist are carbonate, pelite and sandstone respectively. Marble can also occur as boulders (b), the long axis of which is consistent with the orientation of foliation in neighbouring rocks. (c) Metabasite boulders in marble. The dash lines represent the folding foliation of carbonate turbidites (including some pelitic materials) as a result of plastic deformation. (d) The metabasite occurs as enclaves in the marble host, the contact of which is sampled (12TS-AT-18) in this study.

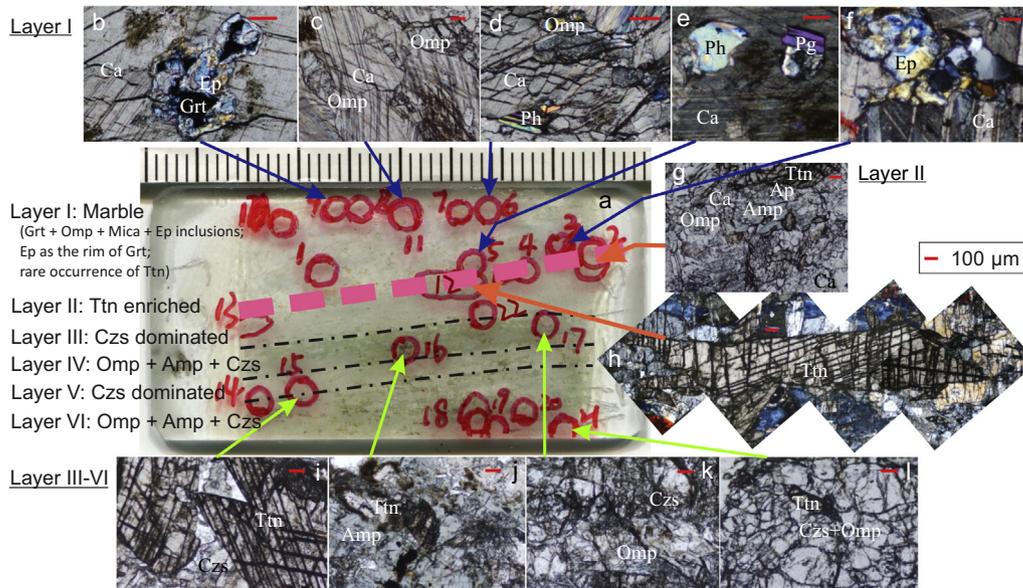


Fig. 3. Photomicrographs of sample 12TS-AT-18. The pink thick dash line represents the titanite-rich contact between the marble and metabasite. (b–f), (g and h) and (i–l) represent mineral assemblages in the marble, the titanite-rich contact and the metabasite respectively. The length of the red line marked in each photo is equivalent to 100 µm. Images (c, g, i–l) are taken under plane polarized light, and the others are taken under cross polarized light. Mineral abbreviations used in this study are as follows: Ab – albite; Ae – aegirine; Amp – amphibole; Ap – apatite; Arg – aragonite; Ca – carbonate; Cal – calcium carbonate; Coe – coesite; Czs – clinozoisite; Gln – glaucophane; Grt – garnet; Ep – epidote; Omp – omphacite; Pg – paragonite; Ph – phengite; Qz – quartz; Rt – rutile; Ttn – titanite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

grained aggregates of carbonate + omphacite + apatite (Fig. 3g; Layer II). (Sodic-)calcic amphibole is also occasionally present, replacing omphacite and clinozoisite. The elongation of titanite crystals is parallel to the contact between the marble and metabasite.

The marble (Layer I) is dominated by calcium carbonate (>90 vol.%) with minor omphacite, epidote (with X_{Ps} ratio from 0.09 to 0.23, see Supplementary Table S.1), phengite (with Si atom

per formula >3.3), and paragonite (Figs. 3b–f and 4a–c). There is no reaction rim of these accessory minerals. Garnet is also present rimmed with epidote overgrowth (Figs. 3b and 4a). Only several tiny titanite inclusions are found in paragonite (Fig. 4c).

The metabasite consists mainly of clinozoisite (X_{Ps} ratios smaller than 0.05; Supplementary Table S.1), omphacite, amphibole (mainly sodic-calcic and calcic amphiboles with $\text{Mg}/[\text{Mg} + \text{Fe}^{2+}]$ ratios of 0.69–0.83), and titanite plus minor fine-grained parago-

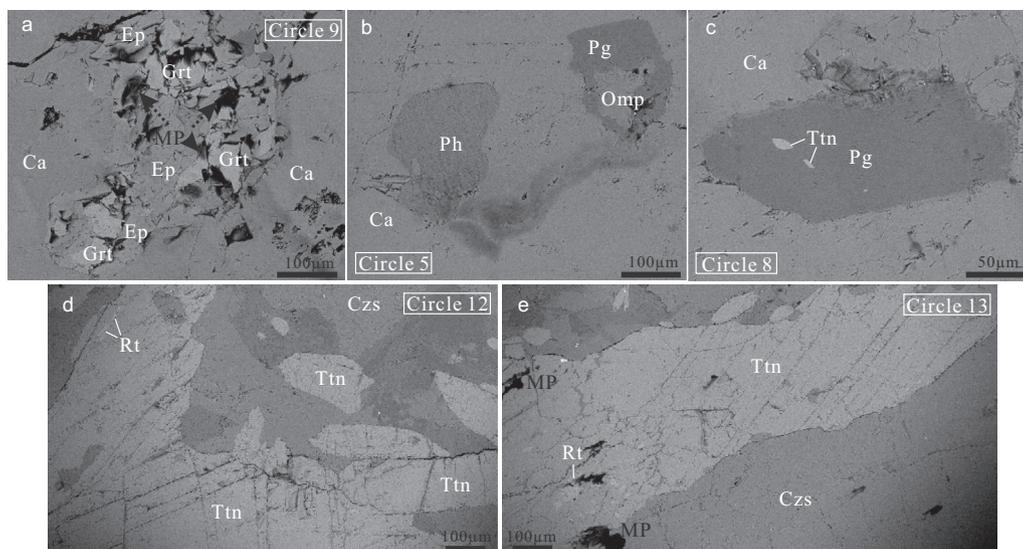


Fig. 4. Backscattered electron (BSE) images. (a–c) display the accessory minerals in the marble. (d–e) show residual rutile in big titanite crystals from the metabasite and the titanite-rich contact between the marble and metabasite. The thick black lines or dots as indicated (MP, marking pen) are stained by marking pen when label. See explanations of mineral abbreviations in the caption of Fig. 3.

nite and rare albite. Mineral modes (mainly omphacite and clinozoisite) vary significantly, and the metabasite can be further divided into omphacite-rich (Layers IV & VI; Fig. 3j–l) and clinozoisite-rich (Layers III & V; Fig. 3i) parts. (Sodic-)calcic amphibole is present, replacing clinozoisite and omphacite. No carbonate mineral is observed in the metabasite. Large titanite crystals both from the metabasite and the titanite-rich contact have very-fine-grained residual rutile (Fig. 4d and e).

The occurrence of omphacite and garnet in the marble indicates that the marble has experienced eclogite-facies metamorphism as also evidenced by the close relationship of the marble with the omphacite-bearing metabasite. Epidote overgrown on the rim of the residual garnet (Figs. 3b and 4a) results from the reaction between garnet and calcium carbonate during retrograde metamorphism.

3. Methods

Mineral compositions are analyzed in the Institute of Earth Sciences, Academia Sinica in Taipei. Mineral major elements are analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7100F) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford instruments Xmax 80) and a cathodoluminescence (CL) image detector (Deben Centaurus). The sample is carbon-coated and the analysis was done at an acceleration voltage of 15 kV with 0.1 nA current under the high vacuum environment ($<10^{-4}$ Pa) for 50 s in each run. The working distance is set at 10 mm. The X-ray intensities were corrected for using ZAF on synthetic mineral standards, i.e., wollastonite for Si and Ca, corundum for Al, fayalite for Fe, periclase for Mg, Cr oxide for Cr, InP (alloy) for P, rutile for Ti, Mn oxide (MnO_2) for Mn, albite for Na, and orthoclase for K. Analytical results of mineral major elements are given in Supplementary Table S.1, and representative backscattered electron images (BSE) are given in Fig. 4.

Mineral trace elements are analyzed using *in situ* Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS, a Thermo Finnigan Element XR equipped with Photon Machines Analyte G2 Excimer ArF 193 nm Laser sampler) on polished thick (100 μ m) “thin” sections. Si is chosen as the internal standard for trace element analysis for all the minerals, but Ca is used for apatite. The repetition rate of laser ablation is 5 Hz, and the spot

size is 40 μ m. In each run, acquisition times for the background (gas blank) and the sample ablation are 45 s and 75 s respectively. The energy fluence is 4.60 J/cm². The NIST (National Institute of Standards and Technology) glass standard SRM 612 and the USGS (United States Geological Survey) glass standard BCR-2G are analyzed as the reference materials. On the basis of repeated analyses of BCR-2G, the accuracy is estimated to be within $\pm 10\%$ for all the analyzed elements but $\sim 15\%$ for Gd and Tb. The precision for all the analyzed trace elements is better than 10% (Supplementary Table S.2). During the analysis, we purposely avoid mineral inclusions. Analytical results of mineral trace elements are given in Supplementary Table S.3.

4. Results

In chondrite normalized trace element diagram (Fig. 5), the residual **garnet** with epidote overgrowth (Figs. 3b and 4a) shows highest HREE contents (10 s ppm) with a $(HREE > LREE)_{\text{chondrite}}$ pattern for all the analyzed grains (Fig. 5a). **Epidote** group minerals show variably high contents of REEs ($\sim 1\text{--}10^3$ times the chondritic values; Fig. 5a). Epidote from the marble tends to show the highest REE contents than clinozoisite from the titanite-rich contact or from the metabasite, e.g., up to 407 ppm vs. 119 ppm for La (Supplementary Table S.3). The epidote overgrown on the rim of the residual garnet from the marble displays the lowest LREEs (e.g., only several ppm for La), Th and U (only 10 s ppb vs. up to 10 s ppm), but the highest HREEs (e.g., several ppm vs. mostly <1 ppm for Lu) among all the analyzed epidote group minerals (Fig. 5a).

All the **titanite** analyses show consistently high Nb and Ta contents, up to $\sim 10^3\text{--}10^4$ times the chondritic value (Fig. 5b). However, REE contents of titanite are highly variable (from hundreds of ppb to 10 s ppm), even within a single crystal grain (Supplementary Table S.3). All the titanite analyses can be divided into two groups: (1) Group I, with a $(HREE > LREE)_{\text{chondrite}}$ pattern, and (2) Group II, with a LREE-rich pattern (Fig. 5b). Compared with Group II, Group I also shows relatively lower Th (10 s of ppb vs. several to 10 s of ppm), U (several ppm vs. 10 s to 100 s of ppm), Pb (several ppm vs. ~ 10 s ppm), Sr (10 s ppm vs. ~ 100 s ppm) and L-MREE contents (several ppm vs. ~ 10 s ppm). Group I with a $(HREE > LREE)_{\text{chondrite}}$ pattern only represents the core composition

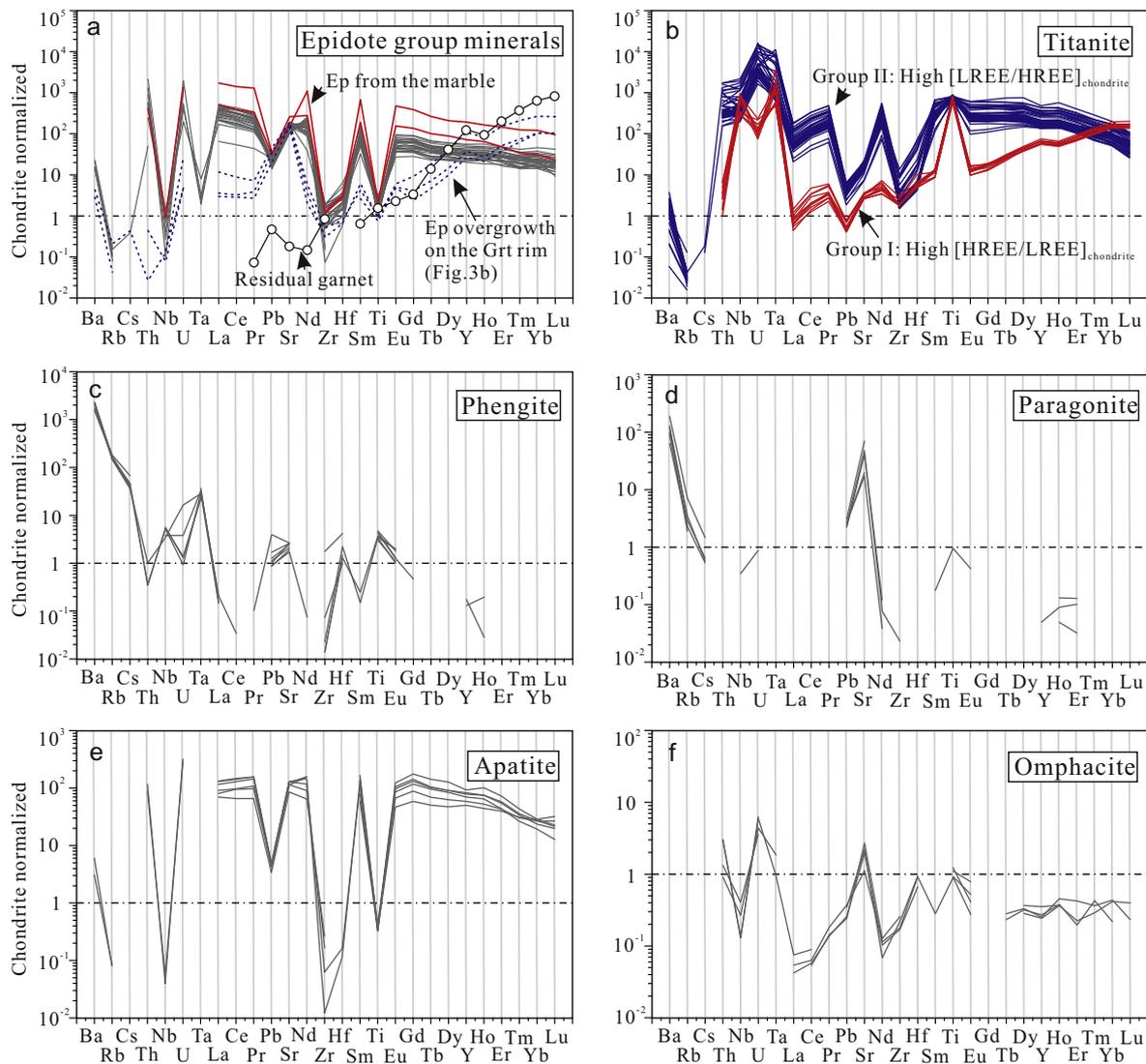


Fig. 5. Chondrite (Sun and McDonough, 1989) normalized mineral trace element abundances. (a) Epidote trace element pattern, with highly variable REEs contents. The red lines represent compositions of epidote from the marble (e.g., Fig. 3f), which contains the highest LREEs. It indicates the strongest preference of epidote for LREEs than other minerals. The dotted lines represent compositions of epidote overgrown on the rim of garnet from the marble (Fig. 3b). The trace element pattern of the residual garnet is also plotted for comparison, represented by the line with hollow circles. The similar trace element feature between the residual garnet and the epidote rim clearly indicates the significant inheritance of HREEs from garnet to epidote. (b) Two trace element patterns of titanite with different LREE/HREE ratios. The HREE-rich pattern mostly represent the core composition of big titanite crystals from the metabasite, while the LREE-rich pattern mostly represent titanite from the titanite-rich contact and the rim composition of those from the metabasite. (c and d) Phengite and paragonite trace element patterns, which are characterized by high LILEs. (e) Apatite trace element pattern, showing consistently high Th-U-Sr-REEs. (f) Omphacite trace element pattern, with only a little high U and Sr.

of the large titanite crystals from the metabasite, although some analyzed spots of titanite core from the metabasite can also show LREE-rich feature.

Phengite contains the highest Ba, Rb and Cs ($\sim 10^3$ ppm, 10^2 ppm and several ppm respectively) among all the analyzed minerals (Fig. 5c). **Paragonite** also contains high Ba-Rb-Pb-Sr, i.e., ~ 10 – 10^2 times the chondritic values to different extents (Fig. 5d). Paragonite from the marble shows the lowest Sr contents than other paragonite crystals (~ 100 ppm vs. ~ 300 – 500 ppm; Supplementary Table S.3). **Apatite** shows consistently high Th, U, REEs, and Sr ($\sim 10^2$ times the chondritic value) as well as some Pb (10 times the chondritic value; Fig. 5e). All the **omphacite** analyses show similarly low contents of all the analyzed trace elements, except for Th, U and Sr (no more than 10 times the chondritic values; Fig. 5f). The Sr contents of omphacite from the marble seem to be lower than those of other analyzed omphacite, 8.09–16.1 ppm vs. 19.7 ppm (Supplementary Table S.3).

5. Discussions

5.1. Controls on mineral compositional variations

All the above mineral trace element systematics (Fig. 5) generally confirm previous studies (e.g., Tribuzio et al., 1996; Sorensen et al., 1997; Spandler et al., 2003; El Korh et al., 2009; Hermann and Rubatto, 2009; Xiao et al., 2013, 2014). However, Sr contents of omphacite from the marble (e.g., Fig. 3c and d) are lower than those of omphacite from the metabasite and from subduction-zone metamorphosed rocks in our previous studies for the Chinese Western Tianshan orogenic belt (8.09–16.1 ppm vs. up to 135 ppm; Xiao et al., 2014). Paragonite from the marble (e.g., Fig. 3e) also shows the lowest Sr contents among all the analyzed paragonite grains in this study, which are as low as those of paragonite inclusions that together with clinozoisite occur as lawsonite pseudomorphs in our previous studies (Xiao et al., 2014). Given the

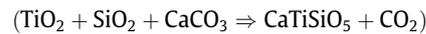
fact that calcite has the great potential to host Sr, e.g., $\sim 10^3$ ppm (Spandler et al., 2003), lower Sr contents of silicate minerals (omphacite and paragonite) from the marble is likely resulting from the strong partitioning of Sr to the host marble. REE contents of epidote from the marble (e.g., Figs. 3f and 5a) are significantly higher than those of (clino)zoisite from the metabasite. The higher REE contents of epidote from the marble likely reflect the stronger preference of REEs for epidote relative to calcium carbonate. In addition, unlike the high $(\text{LREE}/\text{HREE})_{\text{chondrite}}$ of analyzed clinozoisite from the metabasite and other epidote from the marble, the high $(\text{HREE}/\text{LREE})_{\text{chondrite}}$ of epidote overgrown on the rim of garnet from the marble (Fig. 3b) clearly reflects the inheritance of HREEs from garnet (Fig. 5a), indicating the significant redistribution of REEs between different mineral phases rather than their loss (Xiao et al., 2016).

As a major element for titanite, Ti contents of titanite are constrained by the stoichiometry (i.e., CaTiSiO_5), but trace element contents of titanite are highly heterogeneous, i.e., different spots show variable LREEs, Th, and U contents (Fig. 5b). The significant correlations of U with the immobile elements (e.g., Th; Fig. 6a) and the significant correlation of LREE (e.g., La) with the immobile elemental ratio (e.g., Th/Nb ratio; Fig. 6b) indicate that variations of LREEs, Th, and U in titanite are not caused by the mobilization of these elements. Given the consistent Nb-Ta contents in both of the two titanite groups, the obviously lower LREE-Th-U contents of the HREE-rich titanite group than those of the LREE-rich titanite group reflects less LREE-Th-U available for the growth of the HREE-rich titanite at the analyzed spots. Indeed, many trace elements are only redistributed locally among different mineral phases with metamorphic reactions (e.g., REEs redistributed from garnet to epidote group minerals as discussed above; Xiao et al., 2014); heterogeneous trace element contents of metamorphic minerals are controlled by the availability of their “compatible” trace elements (Xiao et al., 2016). Thus, the inherited both bulk rock and precursor mineral compositions and the competition between the adjacent growing minerals in contact can significantly affect trace element contents of metamorphic minerals. Because garnet prefers HREEs and epidote group minerals prefer LREEs, two different trace element patterns of titanite (Fig. 5b) reflect their inheritance from different precursor minerals (garnet vs. epidote). The inherited “garnet” trace element signature in high HREE group titanite offers evidence for complete transformation of garnet in the metabasite sample without garnet. Alternatively, considering the large

amounts of clinozoisite in the metabasite and its significance for LREE-Th-U budget (Xiao et al., 2014), the growth of clinozoisite may also strongly result in the LREE-Th-U depletion of the neighboring titanite in contact (shown as Group I titanite).

5.2. Formation of the titanite-rich contact

The large titanite crystals as well as other titanite crystals at the titanite-rich contact between the marble and metabasite contain Nb and Ta as high as rutile. Tiny residual rutile remains in some large titanite crystals (Fig. 4d and e), probably resulting from the following reaction (Niu and Lesher, 1991):



Furthermore, the lithological contact has been proposed to preferentially serve as the major conduit for the fluid flow (Breeding et al., 2003; Fig. 7). The orientation (i.e., parallel to the contact between the metabasite and marble), the large crystal size and the abundant titanite at the titanite-rich contact emphasize its formation through the metamorphic reaction between the two lithologies facilitated by SiO_2 -rich fluids. The absence of phengite and paragonite (the most important mineral hosts for highly water-soluble LILEs and fluids; Xiao et al., 2014) at the titanite-rich contact between the two lithologies suggests that highly water-soluble elements must have been largely transported away with the fluids, and only immobile elements like Ti-Nb-Ta remain stabilized in the form of titanite in the fluid conduit after dehydration and decarbonation. As no obvious change of hydrous mineral modal abundances in metabasite and the LILEs depletion in the titanite-rich contact, the fluids facilitating the reaction (1) are unlikely derived from the metabasite or externally from the metasedimentary rocks. The fluids externally derived from the subducting serpentinite (uppermost mantle section of the slab equivalent to the “abyssal peridotites”; Niu, 2004), which can continuously dehydrate to depths even up to ~ 250 km in cold subduction zones (depending on the thermal structure of the slab; Syracuse et al., 2010), is more likely responsible for this reaction.

The replacement of rutile by titanite is commonly thought to represent the retrograde metamorphic process during the slab exhumation (e.g., Chen and Zheng, 2015; Zhang et al., 2016). However, the replacement during the apparent “retrograde” metamor-

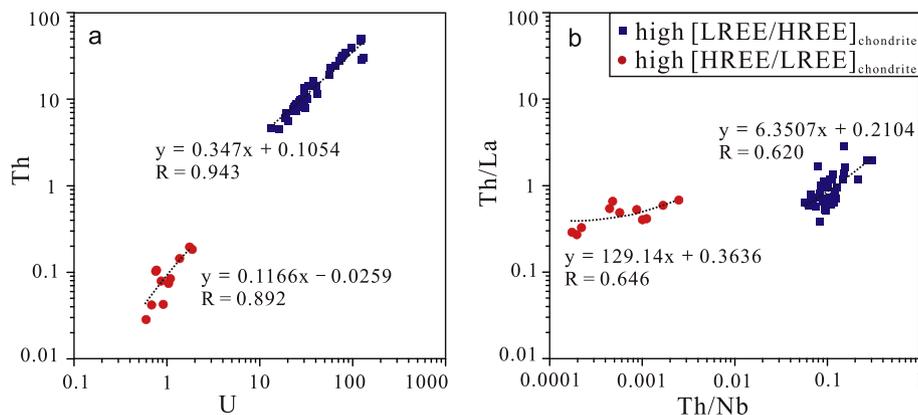


Fig. 6. Co-variation diagrams for titanite: (a) Th-U, (b) Th/La-Th/Nb. The two groups of titanite with different LREE/HREE ratio patterns as shown in Fig. 5b are also reflected as two groups in these figures, i.e., red solid circles (11 analyzed spots) for the HREE-rich group representing the core composition of titanite from the metabasite, while blue solid rectangles (49 analyzed spots) for the LREE-rich group mostly representing titanite from the titanite-rich contact and the rim composition of those from the metabasite. U (a) and LREE (represented by La; b) correlate with the immobile Th and Nb (the critical values of Pearson's correlation coefficient using one-tail test for 11 samples and 49 samples are 0.5214 and 0.2377 respectively at >95% confidence levels), indicating that the variation of LREE-U in titanite are not caused by the mobility of these elements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

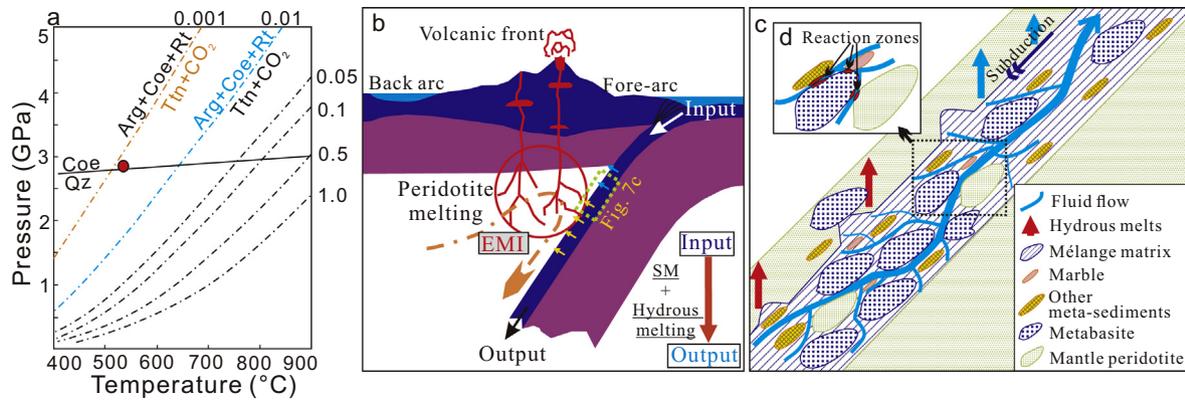


Fig. 7. (a) P-T diagram showing phase equilibria of the reaction: $Rt + Coe/Qz + Arg/Cal \Rightarrow Ttn + CO_2\uparrow$ (after Ye et al., 2002). Numbers at the end of the univariate curves are X_{CO_2} values. The red solid circle represents the peak metamorphic condition of the Chinese Western Tianshan, i.e., $\sim 520^\circ C$ at 2.7 GPa (Lü et al., 2009). It is below the univariate line with $X_{CO_2} = 0.001$ (in orange) but above the univariate line with $X_{CO_2} = 0.01$ (in blue), indicating titanite can become stable in the system with decreasing X_{CO_2} rather than with decreasing pressure or temperature. (b) The schematic diagram for the context of the slab subduction, modified from Niu (2009). The released fluids and the hydrous melts (including supercritical fluids) derived from the subducting slab can carry certain elements into the overlying mantle wedge, and contribute to the petrogenesis of IAB. As a result, the composition of the altered subducting slab after SZM and hydrous melting into the deep mantle cannot be equal to the inputting composition into the trench. (c) The schematic diagram showing diverse lithologies with different mineral assemblages in the subduction channel (marble, other meta-sediments like metapelite, metabasite, peridotite, mélange matrix) and the fluid flow as well as the hydrous melts from the subducting slab (modified from Xiao et al., 2016). (d) The schematic diagram showing reactions between different lithologies, which are facilitated by infiltrated fluids along the lithological contact. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

phism can actually happen with the change of geochemical composition of the system (Fig. 7a) rather than with the decrease of pressure or temperature. Considering the effects of CO_2 activity on the varying stability of titanite (Ye et al., 2002), titanite instead of rutile can become stable at higher pressures in the system with decreasing X_{CO_2} (Fig. 7a). In addition, the titanite-rich contact in this study represents an open system, possibly affected by externally derived fluids from the subducting serpentinite and releasing CO_2 as well as other water-soluble elements via the reaction 1 as discussed above. As a result, the release of CO_2 may further enhance the formation of titanite, which can be formed even up to UHPM conditions (Ye et al., 2002; Lü et al., 2013). In that case, carbonates (metamorphosed to eclogite-facies marble) participate in the reaction with the metabasite during SZM at the lithological contact facilitated by the fluid flow (Breeding et al., 2003). HFSEs can be hosted by and stabilized in the newly formed titanite, while the fluid-soluble LILEs are readily transported away (e.g., to the mantle wedge) during subduction-zone dehydration metamorphism. Therefore, it is important to emphasize that if the titanite can be formed and stable under UHPM conditions, possibly by fluid-facilitated decarbonation reactions, it can host and stabilize HFSEs in the oceanic crust passing through SZM, contributing to the characteristic “arc signature” unique to subduction-zone magmatism (i.e., high LILEs, low HFSEs).

5.3. Geodynamic significance

Globally, the distribution of subducting sedimentary carbonates is highly variable from one trench to another (Plank and Langmuir, 1998). As Morse et al. (2007) summarized, most sedimentary carbonate minerals deposited on the seafloor is of biogenic origin (e.g., skeletal organisms such as corals, calcareous algae), rather than of abiogenesis (mostly as sedimentary cements or through post-depositional reactions). Hence, the occurrence of marine sedimentary carbonates is always related to the growth of these organisms, which always prefer a warm environment, i.e., tropical and subtropical zones between $\sim 30^\circ N$ and $\sim 30^\circ S$. Correspondingly, subduction of marine carbonates is more likely restricted to relatively lower latitude.

The palaeogeographic distribution of the North Tianshan during the Early Carboniferous (~ 330 Ma) is located at the latitude of $\sim 30^\circ N$ or even lower as evidenced by palaeomagnetic studies (Kirscher et al., 2014; Kirscher, 2015), and the ancient South Tianshan Ocean was situated south of $\sim 30^\circ N$, which is also supported by the occurrence of abundant carbonates in the Chinese Western Tianshan orogenic belt (Lü et al., 2013). Furthermore, because calcium carbonate dissolves at depths deeper than the carbonate compensation depths (CCDs), and because all trenches are deeper than the CCDs, subduction of carbonates requires silicate mix to enable carbonate protected from the seawater. The forearc basin flysch caused by turbidity currents from shallower depths can result in the presence of deep sea carbonates to subduct (e.g., Ericson et al., 1952; Yamamoto et al., 1988; Tsuboi et al., 2014). Globally heterogeneous distribution of carbonates from one trench to another makes it not straightforward at present to quantify this process and geochemical consequences of carbonate subduction. However, the observations and analysis we present here points to the significance of subducting carbonates in moderating geochemical behaviors of chemical elements during SZM, hence in improved understanding of geochemical consequences of SZM, about which further research is warranted.

Recent studies (e.g., Castillo, 2015) have mentioned that as a result of precipitation from seawater with abundant U but low Pb (>1 ppm vs. 0.003 ppb), marine carbonates are expected to show high U/Pb ratios. Together with the lowest Rb/Sr ratio of marine carbonates among other crustal rocks, he proposed that the subduction of ancient marine carbonates can result in characteristically high $^{238}U/^{204}Pb$ ratio (μ ; HIMU) but unradiogenic $^{87}Sr/^{86}Sr$ isotopic signatures in OIB (Castillo, 2015). Based on significant correlations of U and Th with immobile elements (e.g., HFSEs) for subduction-zone metamorphosed rocks and IAB in our previous studies (Xiao et al., 2012, 2016), we think that U and Th are immobile or much less mobile than Pb during SZM. Although Sr and Rb are both mobilized during SZM as discussed in our previous studies (Xiao et al., 2012, 2016), Sr can be largely hosted by subducting carbonates. Hence, these different behaviors of radioactive parent and radiogenic daughter during SZM can result in the low U/Pb ratios but high Rb/Sr ratios of the released fluids. After being affected by these released fluids from the carbonate-bearing sub-

ducting slab during SZM, the mantle wedge as the source of IAB may also have lower U/Pb ratio and higher Rb/Sr ratio. This is consistent with the lower U/Pb but higher Rb/Sr ratios in IAB relative to MORB (e.g., the average values of U/Pb and Rb/Sr ratios for IAB are 0.1 and 0.04 compared with 0.19 and 0.02 in MORB; IAB data is referred to Elliott, 2003, and MORB data referred to Niu and Batiza, 1997). The high Rb/Sr but low U/Pb in the overlying mantle wedge can further evolve to high radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and unradiogenic Pb isotopic features of EMI with time.

In addition, based on the petrological and geochemical studies of subducted marble from the Eocene Cycladic subduction complex on Syros and Tinos islands, Greece, Ague and Nicolescu (2014) reported abundant CO_2 release at the lithological contact between metacarbonate and other lithologies (e.g., mantle rocks, blueschist or metapelites in the subduction channel along slab-mantle interfaces). However, instead of decarbonation reactions, these authors prefer a model of fluid-induced dissolution of calcium carbonate for CO_2 release, and they proposed that the water activity will be lowered by adding CO_2 to the fluids after the dissolution of CaCO_3 at high pressures. As a result, silicate minerals will precipitate owing to their lower solubility. Whether subducting carbonates undergo decarbonation or dissolution, the fluid infiltration along the lithological contact is crucial for the CO_2 release from the subducting slab. Considering the complex scenarios of the slab-mantle interface (Bebout, 2007a), i.e., different types of blocks with highly variable and hybridized compositions (including marble, other meta-sediments like metapelite, metabasite, and mantle peridotite), the decarbonation/dissolution of carbonate facilitated by fluids at the lithological contact during SZM (Fig. 7) is expected to be common (e.g., reaction 1 or see model of Ague and Nicolescu, 2014), and can release abundant CO_2 for global carbon cycling through arc volcanic degassing (e.g., Kerrick, 2001).

6. Conclusions

The titanite-rich contact between the marble and metabasite from the Chinese Western Tianshan UHPM belt provides important information on geochemical behaviors of chemical elements affected by subducting carbonates. The titanite-rich contact is formed as the result of decarbonation reaction between the two lithologies at the presence of SiO_2 -rich fluids. Such reactions and products are expected to be common in subduction zones, and the release of CO_2 during this process can contribute to the global carbon cycling. Importantly, this decarbonation reaction forms and stabilizes titanite that preferentially conserves HFSEs over LILEs. Although globally heterogeneous distribution of carbonates from one trench to another makes it not straightforward at present to quantify this process and geochemical consequences of SZM, serious effort is in urgent need because such processes may be fundamentally important towards our improved understanding of subduction-zone magmatism and the geochemical consequences of SZM.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant numbers: 41572047 to Yuanyuan Xiao; 9101400, 41130314 to Yaoling Niu) and the Excellent Young Project of Institute of Oceanology, Chinese Academy of Sciences (Y52221101Q) and the Special Research Program of the State Oceanic Administration of China (GASI-GEOGE-02) to Yuanyuan Xiao. We thank all the research staff in the Institute of Earth Sciences, Academia Sinica, Taiwan, especially people from well-communicated geochemical group for their great supports. We also thank Mr Yu-Shiang Wang, Ms Hui-Ho Hsieh, Mr Fulong Lin, and

Ms Xiaohui Lin for their great helps on geochemical analytical work. Professor M.F. Zhou, Professor J.H. Yang, Professor Y.L. Xiao and an anonymous reviewer are greatly appreciated for their handling and constructive suggestions. Detailed discussion with Dr. Guodong Wang is also helpful.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jseaeas.2017.01.006>.

References

- Ague, J.J., Nicolescu, S., 2014. Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nat. Geosci.* 7, 355–360.
- Ai, Y.L., Zhang, L.F., Li, X.P., Qu, J.F., 2006. Geochemical characteristics and tectonic implications of HP-UHP eclogites and blueschists in Southwestern Tianshan, China. *Prog. Nat. Sci.* 16, 624–632.
- Bebout, G.E., 2007a. Metamorphic chemical geodynamics of subduction zones. *Earth Planet. Sci. Lett.* 260, 373–393.
- Beinlich, A., Klemm, R., John, T., Gao, J., 2010. Trace-element mobilization during Ca-metasomatism along a major fluid conduit: eclogitization of blueschist as a consequence of fluid–rock interaction. *Geochimica et Cosmochimica Acta* 74, 1892–1922.
- Breeding, C.M., Ague, J.J., Bröcker, M., Bolton, E.W., 2003. Blueschist preservation in a retrograded, high-pressure, low-temperature metamorphic terrane, Tinos, Greece: implications for fluid flow paths in subduction zones. *Geochem. Geophys. Geosyst.* 4.
- Caciagli, N., Manning, C., 2003. The solubility of calcite in water at 6–16 kbar and 500–800 °C. *Contrib. Miner. Petrol.* 146, 275–285.
- Castillo, P.R., 2015. The recycling of marine carbonates and sources of HIMU and FOZO ocean island basalts. *Lithos* 216, 254–263.
- Chen, Y.-X., Zheng, Y.-F., 2015. Extreme Nb/Ta fractionation in metamorphic titanite from ultrahigh-pressure metagranite. *Geochim. Cosmochim. Acta* 150, 53–73.
- Dasgupta, R., Hirschmann, M.M., 2006. Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440, 659–662.
- Dasgupta, R., Hirschmann, M.M., 2010. The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.* 298, 1–13.
- El Korb, A., Schmidt, S.T., Ulianov, A., Potel, S., 2009. Trace element partitioning in HP-LT metamorphic assemblages during subduction-related metamorphism, Ile de Groix, France: a detailed LA-ICPMS study. *J. Petrol.* 50, 1107–1148.
- Ericson, D.B., Ewing, M., Heezen, B.C., 1952. Turbidity currents and sediments in North Atlantic. *AAPG Bulletin* 36 (3), 489–511.
- Flesia, C., Frezzotti, M.L., 2015. The dilemma of the dwarf Earth's CO_2 degassing: irrelevant or crucial? *J. Geochem. Explor.* 152, 118–122.
- Gao, J., John, T., Klemm, R., Xiong, X.M., 2007. Mobilization of Ti-Nb-Ta during subduction: evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. *Geochim. Cosmochim. Acta* 71, 4974–4996.
- Gao, J., Klemm, R., 2001. Primary fluids entrapped at blueschist to eclogite transition: evidence from the Tianshan meta-subduction complex in northwestern China. *Contrib. Miner. Petrol.* 142, 1–14.
- Gao, J., Klemm, R., 2003. Formation of HP-LT rocks and their tectonic implications in the western Tianshan Orogen, NW China: geochemical and age constraints. *Lithos* 66, 1–22.
- Gao, J., Klemm, R., Zhang, L., Wang, Z., Xiao, X., 1999. P-T path of high-pressure/low-temperature rocks and tectonic implications in the western Tianshan Mountains, NW China. *J. Metamorphic Geol.* 17, 621–636.
- Hayes, J.M., Waldbauer, J.R., 2006. The carbon cycle and associated redox processes through time. *Phil. Trans. R. Soc. B* 361, 931–950.
- Hermann, J., Rubatto, D., 2009. Accessory phase control on the trace element signature of sediment melts in subduction zones. *Chem. Geol.* 265, 512–526.
- Huybers, P., Langmuir, C., 2009. Feedback between deglaciation, volcanism, and atmospheric CO_2 . *Earth Planet. Sci. Lett.* 286, 479–491.
- John, T., Klemm, R., Gao, J., Garbe-Schonberg, C.D., 2008. Trace-element mobilization in slabs due to non steady-state fluid–rock interaction: constraints from an eclogite-facies transport vein in blueschist (Tianshan, China). *Lithos* 103, 1–24.
- Kerrick, D.M., 2001. Present and past nonanthropogenic CO_2 degassing from the solid earth. *Rev. Geophys.* 39, 565–585.
- Kerrick, D.M., Connolly, J.A.D., 2001a. Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* 411, 293–296.
- Kerrick, D.M., Connolly, J.A.D., 2001b. Metamorphic devolatilization of subducted oceanic metabasalts: implications for seismicity, arc magmatism and volatile recycling. *Earth Planet. Sci. Lett.* 189, 19–29.
- Kirscher, U., 2015. Paleozoic paleogeography of the south western part of the Central Asian Orogenic Belt – paleomagnetic constraints. *Ludwig-Maximilians-Universität München, München*, p. 142.
- Kirscher, U., Bilardello, D., Mikolajchuk, A., Bachtadse, V., 2014. Correcting for inclination shallowing of early Carboniferous sedimentary rocks from

- Kyrgyzstan—indication of stable subtropical position of the North Tianshan Zone in the mid-late Palaeozoic. *Geophys. J. Int.* 198, 1000–1015.
- Lü, Z., Bucher, K., Zhang, L., 2013. Omphacite-bearing calcite marble and associated coesite-bearing pelitic schist from the meta-ophiolitic belt of Chinese western Tianshan. *J. Asian Earth Sci.* 76, 37–47.
- Lü, Z., Zhang, L., 2012. Coesite in the eclogite and schist of the Atantayi Valley, southwestern Tianshan, China. *Chin. Sci. Bull.* 57, 1467–1472.
- Lü, Z., Zhang, L., Chen, Z., 2014. Jadeite- and dolomite-bearing coesite eclogite from western Tianshan, NW China. *Eur. J. Mineral.* 26, 245–256.
- Lü, Z., Zhang, L.F., Du, J.X., Bucher, K., 2008. Coesite inclusions in garnet from eclogitic rocks in western Tianshan, northwest China: convincing proof of UHP metamorphism. *Am. Mineral.* 93, 1845–1850.
- Lü, Z., Zhang, L.F., Du, J.X., Bucher, K., 2009. Petrology of coesite-bearing eclogite from Habutengsu Valley, western Tianshan, NW China and its tectonometamorphic implication. *J. Metamorph. Geol.* 27, 773–787.
- Liu, Y., He, D., Gao, C., Foley, S., Gao, S., Hu, Z., Zong, K., Chen, H., 2015. First direct evidence of sedimentary carbonate recycling in subduction-related xenoliths. *Scientific Reports* 5.
- Manning, C.E., Shock, E.L., Sverjensky, D.A., 2013. The chemistry of carbon in aqueous fluids at crustal and upper-mantle conditions: experimental and theoretical constraints. *Rev. Mineral. Geochem.* 75, 109–148.
- McCulloch, M.T., Gamble, J.A., 1991. Geochemical and geodynamical constraints on subduction. *Earth Planet. Sci. Lett.* 102, 358–374.
- Morse, J.W., Arvidson, R.S., Lüttge, A., 2007. Calcium carbonate formation and dissolution. *Chem. Rev.* 107, 342–381.
- Niu, Y.L., 2004. Bulk-rock major and trace element compositions of abyssal peridotites: implications for mantle melting, melt extraction and post-melting processes beneath mid-ocean ridges. *J. Petrol.* 45, 2423–2458.
- Niu, Y., 2009. Some basic concepts and problems on the petrogenesis of intra-plate ocean island basalts. *Chin. Sci. Bull.* 54, 4148–4160.
- Niu, Y.L., Batiza, R., 1997. Trace element evidence from seamounts for recycled oceanic crust in the Eastern Pacific mantle. *Earth Planet. Sci. Lett.* 148, 471–483.
- Niu, Y.L., Lesher, C.M., 1991. Hydrothermal alteration of mafic metavolcanic rocks and genesis of Fe-Zn-Cu sulfide deposits, Stone Hill district, Alabama. *Econ. Geol. Bull. Soc. Econ. Geol.* 86, 983–1001.
- Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* 145, 325–394.
- Poli, S., 2015. Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. *Nat. Geosci.* (advance online publication).
- Rubatto, D., Hermann, J., 2003. Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): implications for Zr and Hf budget in subduction zones. *Geochim. Cosmochim. Acta* 67, 2173–2187.
- Sorensen, S.S., Grossman, J.N., Perfit, M.R., 1997. Phengite-hosted LILE enrichment in eclogite and related rocks: implications for fluid-mediated mass transfer in subduction zones and arc magma genesis. *J. Petrol.* 38, 3–34.
- Spandler, C., Hermann, J., Arculus, R., Mavrogenes, J., 2003. Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contrib. Miner. Petrol.* 146, 205–222.
- Sun, S.-S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. Lond. Spec. Publ.* 42, 313–345.
- Syracuse, E.M., van Keken, P.E., Abers, G.A., 2010. The global range of subduction zone thermal models. *Phys. Earth Planet. Inter.* 183 (1–2), 73–90.
- Thomson, A.R., Walter, M.J., Kohn, S.C., Brooker, R.A., 2016. Slab melting as a barrier to deep carbon subduction. *Nature* 529, 76–79.
- Tribuzio, R., Messiga, B., Vannucci, R., Bottazzi, P., 1996. Rare earth element redistribution during high-pressure-low-temperature metamorphism in ophiolitic Fe-gabbros (Liguria, northwestern Italy): implications for light REE mobility in subduction zones. *Geology* 24, 711–714.
- Tsuboi, T., Wada, H., Nakamura, T., Hang, T.T., Matsuzaki, H., Otsuji, N., Fujioka, K., Oguri, K., Kitazato, H., 2014. Deep-sea limestone block as a source of 14C-depleted dissolved inorganic carbon at the Palau Trench. *Chem. Geol.* 364, 1–8.
- Tsuno, K., Dasgupta, R., Danielson, L., Righter, K., 2012. Flux of carbonate melt from deeply subducted pelitic sediments: geophysical and geochemical implications for the source of Central American volcanic arc. *Geophys. Res. Lett.* 39.
- Xiao, Y., Lavis, S., Niu, Y., Pearce, J.A., Li, H., Wang, H., Davidson, J., 2012. Trace-element transport during subduction-zone ultrahigh-pressure metamorphism: evidence from western Tianshan, China. *Geol. Soc. Am. Bull.* 124, 1113–1129.
- Xiao, Y., Niu, Y., Li, H., Wang, H., Liu, X., Davidson, J., 2014. Trace element budgets and (re-)distribution during subduction-zone ultrahigh pressure metamorphism: evidence from Western Tianshan, China. *Chem. Geol.* 365, 54–68.
- Xiao, Y., Niu, Y., Song, S., Davidson, J., Liu, X., 2013. Elemental responses to subduction-zone metamorphism: constraints from the North Qilian Mountain, NW China. *Lithos* 160–161, 55–67.
- Xiao, Y., Niu, Y., Wang, K.-L., Lee, D.-C., Iizuka, Y., 2016. Geochemical behaviours of chemical elements during subduction-zone metamorphism and geodynamic significance. *Int. Geol. Rev.* 58, 1253–1277.
- Yamamoto, S., Tokuyama, H., Fujioka, K., Takeuchi, A., Ujiie, H., 1988. Carbonate turbidites deposited on the floor of the Palau Trench. *Mar. Geol.* 82, 217–233.
- Yaxley, G., Brey, G., 2004. Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: implications for petrogenesis of carbonates. *Contrib. Miner. Petrol.* 146, 606–619.
- Ye, K., Liu, J.-B., Cong, B.-L., Ye, D.-N., Xu, P., Omori, S., Maruyama, S., 2002. Ultrahigh-pressure (UHP) low-Al titanites from carbonate-bearing rocks in Dabieshan-Sulu UHP terrane, eastern China. *Am. Mineral.* 87, 875–881.
- Zack, T., John, T., 2007. An evaluation of reactive fluid flow and trace element mobility in subducting slabs. *Chem. Geol.* 239, 199–216.
- Zhang, L.F., Ellis, D.J., Jiang, W.B., 2002a. Ultrahigh-pressure metamorphism in western Tianshan, China: Part I. Evidence from inclusions of coesite pseudomorphs in garnet and from quartz exsolution lamellae in omphacite in eclogites. *Am. Mineral.* 87, 853–860.
- Zhang, L.F., Ellis, D.J., Williams, S., Jiang, W.B., 2002b. Ultra-high pressure metamorphism in western Tianshan, China: Part II. Evidence from magnesite in eclogite. *Am. Mineral.* 87, 861–866.
- Zhang, L.J., Zhang, L.F., Lü, Z., Bader, T., Chen, Z., 2016. Nb-Ta mobility and fractionation during exhumation of UHP eclogite from southwestern Tianshan, China. *J. Asian Earth Sci.* 122, 136–157.