Geochimica et Cosmochimica Acta 343 (2023) 272–285

Contents lists available at ScienceDirect

Geochimica et Cosmochimica Acta

journal homepage: www.elsevier.com/locate/gca

Barium isotope fractionation during slab dehydration: Records from an eclogite-quartz vein system in Dabie orogen

Juan Xu[a], Wang-Ye Li[a,b], Xiao-Feng Gu[a,*], Hui-Min Yu[a,b,c], Xiao-Yun Nan[a], Yi-Xiang Chen[a,b], Fang Huang[a,b]

[a] *CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China*
[b] *CAS Center for Excellence in Comparative Planetology, University of Science and Technology of China, Hefei 230026, China*
[c] *State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*

ARTICLE INFO

Article history:
Received 2 July 2022
Accepted 30 November 2022
Available online 2 December 2022
Associate editor: Julie Prytulak

Keywords:
Barium isotopes
Metamorphic fluid
Quartz vein
Phengite breakdown
Eclogite

ABSTRACT

Barium isotopes are a potential tracer of fluid-mediated recycling of subducted crustal materials into the mantle wedge. However, the behavior of Ba isotopes during metamorphic breakdown of Ba-rich hydrous minerals is not well understood. High-pressure (HP) and ultrahigh-pressure (UHP) metamorphic rocks and associated veins in convergent orogens can provide important insight into Ba transport and Ba isotope fractionation during metasomatic fluid activities. This study reports Ba isotope data for whole rocks and mineral separates of a HP-UHP eclogite-quartz vein system from Bixiling in the Dabie orogen. The samples include epidote-phengite-bearing quartz veins and two types of eclogites. The Type I eclogites are the host of the quartz veins and were not affected by the metasomatic fluids, whereas the Type II eclogites are hosted in the veins and were strongly modified by the fluids. The results show that the Type I eclogites have relatively homogeneous $\delta^{138/134}$Ba ranging from −0.12 to −0.04‰. In contrast, the quartz veins have highly variable $\delta^{138/134}$Ba ranging from 0.16 to 0.51‰. The Type II eclogites have $\delta^{138/134}$Ba from 0.32 to 0.40‰, similar to those from 0.25 to 0.35‰ of the quartz separates within the veins, which may represent the average Ba isotopic composition of the fluid inclusions trapped in the quartz during vein formation.

These results demonstrate that the vein-forming fluid has much higher $\delta^{138/134}$Ba than the host eclogites, indicating significant Ba isotope fractionation during dehydration of eclogites. Mineralogical evidence suggests that the fluid was probably derived from the breakdown of phengite at the HP eclogite-facies to amphibolite-facies stage during slab exhumation. The higher $\delta^{138/134}$Ba of the phengite separates (from −0.16 to −0.05‰) than those of the coexisting biotite separates (from −0.34 to −0.22‰) in the Type I eclogites indicate that the fluid released from the breakdown of phengite to biotite would be enriched in heavy Ba isotopes. This explains well the observed heavier Ba isotopic compositions of the quartz veins relative to the host eclogites. In summary, our results reveal that the breakdown of phengite during continental slab exhumation could produce Ba-rich fluids with remarkably higher $\delta^{138/134}$Ba than that of the host rocks, and thus might potentially influence the Ba isotopic systematics at convergent plate margins.

1. Introduction

As a fluid mobile element, Ba can be transported from slabs into the overlying mantle wedge by fluids during subduction (Kessel et al., 2005), enriching Ba in global arc magmas. Recently, significant Ba isotopic variations among the terrestrial reservoirs related to subduction recycling have been revealed (Fig. 1), suggesting that the Ba isotope system could be a potential new tool to track recycled crustal materials in the mantle (Nielsen et al., 2020; Wu et al., 2020; Zhao et al., 2021; Bai et al., 2022; Hao et al., 2022; Xu et al., 2022; Yu et al., 2022). For example, the observed $\delta^{138/134}$Ba variations in arc lavas (from −0.38 to 0.31‰) have been attributed to the different Ba isotopic compositions of subducted crustal materials, including altered oceanic crust (AOC; from −0.09 to 0.33‰) and marine sediments (from −0.11 to 0.11‰) (Nielsen et al., 2018, 2020; Wu et al., 2020). Besides the slab inputs, the potential Ba isotope fractionation during slab dehydration may also influence the Ba isotopic compositions of the mantle wedge and arc lavas through fluid metasomatism (Gu et al., 2021). However, the behavior of Ba isotopes during slab dehydration and the Ba isotope characteristics of slab-derived fluids are poorly understood.

---

[*] Corresponding author.
E-mail address: xfgu@ustc.edu.cn (X.-F. Gu).

https://doi.org/10.1016/j.gca.2022.11.030
0016-7037/

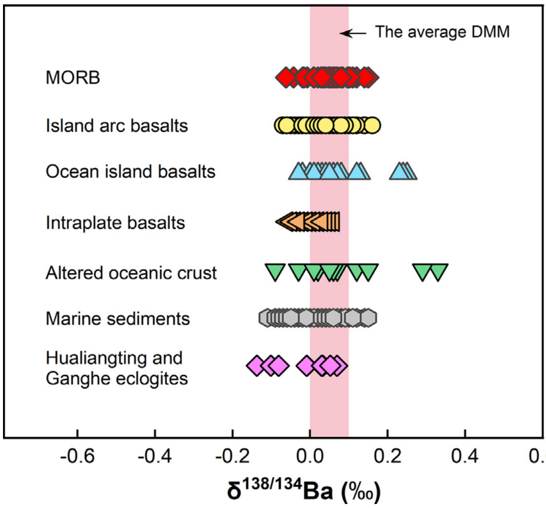

Fig. 1. Barium isotopic compositions ($\delta^{138/134}$Ba = [($^{138/134}$Ba$_{sample}$)/($^{138/134}$Ba$_{SRM3104a}$) − 1] × 1000) of the terrestrial reservoirs related to subduction recycling. The vertical light red area represents the estimated average $\delta^{138/134}$Ba of the depleted MORB mantle (DMM; 0.05 ± 0.05‰; Nan et al., 2022). Data sources: MORB (Nielsen et al., 2018; Nan et al., 2022), island arc basalts (Nielsen et al., 2020; Wu et al., 2020), ocean island basalts (Yu et al., 2022), intraplate basalts (Zhao et al., 2021; Xu et al., 2022), altered oceanic crust (Nielsen et al., 2018), and marine sediments (Bridgestock et al., 2018; Nielsen et al., 2018, 2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Exhumed high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic rocks, such as eclogites, represent fragments of the previously subducted crust. Metamorphic veins commonly occur in orogenic eclogites. They result from dehydration reactions in eclogites and are direct records of slab-derived fluids (Zheng et al., 2007). Hence the HP-UHP eclogite-vein system could provide useful information on the behaviors of element migration and isotope fractionation in subduction zones (e.g., Becker et al., 1999; Spandler and Hermann, 2006; Guo et al., 2015, 2019; Huang et al., 2020; Li et al., 2020). For instance, Gu et al. (2021) recently studied the eclogite-vein systems from Ganghe and Hualiangting in the Dabie orogen and found that lawsonite breakdown and subsequent fluid-rock interactions could produce metasomatic fluids with heavy Ba isotopic compositions. In order to further constrain the Ba isotope characteristics of subduction-zone fluids, the behavior of Ba isotopes during metamorphic breakdown of other Ba-rich hydrous minerals also needs to be investigated. Among them, phengite in metabasites and metapelites usually contains >90% of the bulk Ba budget (Sorensen et al., 1997; Zack et al., 2001; Spandler et al., 2003), thus is the most important source that could deliver Ba and water to depth (Bebout, 2007). Despite the experimental results indicate that phengite has a large stability range and can be stable up to very high-pressure conditions in a relatively cold subducted slab (e.g., Schmidt et al., 2004), it can readily break down during slab exhumation, resulting in remarkable fluid release with abundant Ba budget at convergent plate margins (e.g., Franz et al., 1986; Zheng, 2009). Therefore, the direction and magnitude of Ba isotope fractionation during this decomposition process are crucial to understand the influence on the Ba isotopic systematics at convergent plate margins and the potential contribution to Ba budget of the mantle wedge.

This study provides major-trace element and Sr-Nd-Ba isotope data for an eclogite-quartz vein system from the Bixiling area in the Dabie orogen. The samples include the epidote-phengite-bearing quartz veins and two types of eclogites. Field observations and Sr-Nd isotope data indicate that the quartz veins were precipitated from the internal fluids derived from the host eclogites (termed below as the Type I eclogites), hence are ideal for investigating the behavior of Ba isotopes during slab dehydration. Petrological observations and Ba isotope data show that the fluids were probably derived from the retrograde breakdown of phengite to biotite in the host eclogites during exhumation and were characterized by heavy Ba isotopic compositions, as evidenced by the quartz vein whole-rocks, the vein-hosted eclogites (termed below as the Type II eclogites), and the quartz separates from the veins. The significant Ba isotope fractionation during phengite breakdown revealed in this study is important for understanding the Ba isotopic systematics of the subduction zones.

2. Geological background and sample descriptions

2.1. Geological background

The Dabie–Sulu UHP metamorphic belt in east-central China is a Triassic continental collision zone between the North China and South China Blocks (Fig. 2a) (e.g., Ames et al., 1993; Li et al., 1993; Zheng, 2008). The occurrence of coesite- and diamond-bearing eclogites in the Dabie orogen indicates the subduction of continental crust to the upper mantle depths (Wang et al., 1989; Xu et al., 1992; Okay, 1993). Studies on the cooling history and O isotope characteristics of the Dabie UHP metamorphic rocks further indicate that they experienced processes of rapid subduction, a short residence within the mantle, and rapid exhumation during the continental collision (Li et al., 2000; Zheng et al., 2003; Liu et al., 2011). As records of metamorphic fluid activities during slab subduction and exhumation, metamorphic veins are common within eclogites from the Dabie orogen. These veins were formed by fluids derived from the breakdown of hydrous minerals (Li et al., 2004; Guo et al., 2012; Huang et al., 2012) and/or from the exsolution of structural hydroxyl dissolved in nominally anhydrous minerals (Zheng et al., 1999; Chen et al., 2007). Petrological and chronological studies show that the metamorphic veins in the Dabie orogen were mainly formed at the HP eclogite-facies stage to the amphibolite-facies stage during the rapid exhumation at about 220 Ma (Zheng et al., 2007; Chen et al., 2012, 2022).

This study focuses on an eclogite-quartz vein system from the Bixiling meta-mafic–ultramafic complex, which occurs as a tectonic block within orthogneisses (Fig. 2b). As the largest outcrop of eclogites in the Dabie orogen, the Bixiling body has been well investigated in previous studies (e.g., Zhang et al., 1995; Chavagnac and Jahn, 1996; Xiao et al., 2000; Liu et al., 2006; Li et al., 2011; Huang et al., 2012; Chen et al., 2022). Petrological and geochemical studies show that the Bixiling eclogites have gabbroic protoliths differentiated from mantle-derived magma with slight crustal contamination (Zhang et al., 1995; Chavagnac and Jahn, 1996). The presence of coesite relicts in minerals (e.g., Zhang et al., 1995; Chavagnac and Jahn, 1996; Xiao et al., 2000; Chen et al., 2022) indicates that the Bixiling eclogites were subducted to the mantle depths, and zircon U-Pb dating (Liu et al., 2006; Chen et al., 2022) suggests that they experienced UHP metamorphism at 240–225 Ma. The subsequent exhumation imparted by HP eclogite-facies recrystallization was dated at 225–215 Ma and amphibolite-facies retrogression at 215–205 Ma (Liu and Liou, 2011; Zheng et al., 2011), respectively.

2.2. Sample description and petrography

The eclogite and quartz vein samples were collected from an outcrop along a north–south road across the Bixiling complex (Fig. 2b), whose GPS coordinates are 30°43.57′N and 116°16.97′E. Eclogites occur as blocks of several to tens of meters within foliated quartzofeldspathic gneiss, while the irregular-shaped HP quartz

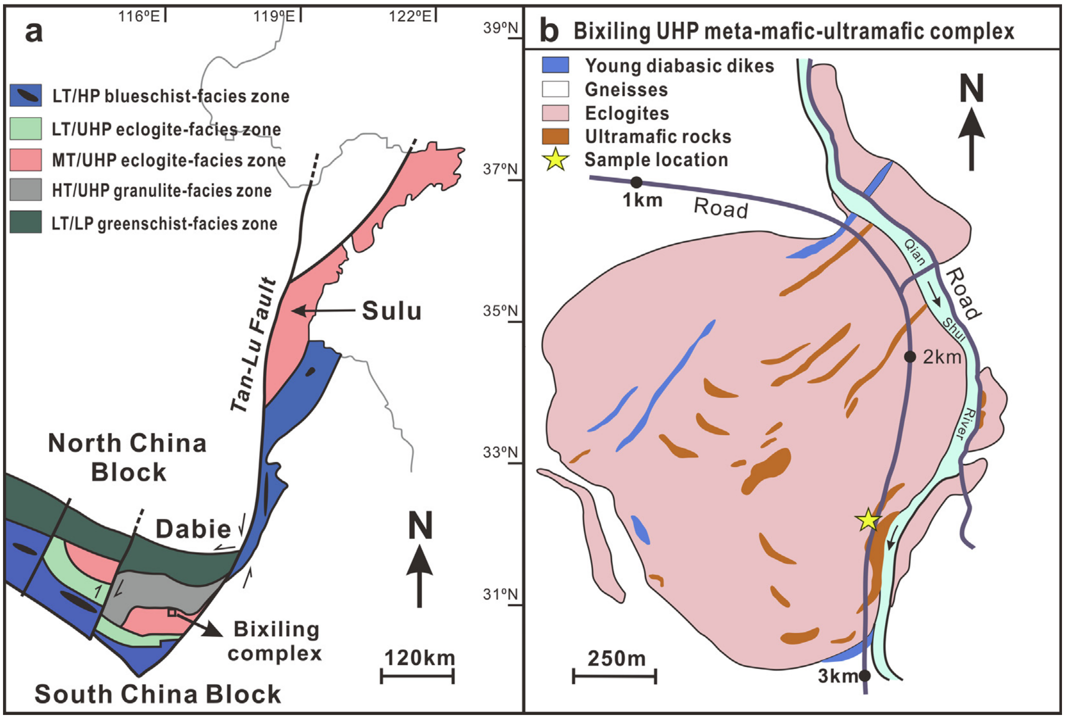

Fig. 2. (a) Simplified map of the Dabie–Sulu UHP metamorphic zone in east-central China. (b) Geological sketch map of the Bixiling UHP meta-mafic–ultramafic complex. The yellow star shows the location of the sampling site. Maps are from Li et al. (2011) and modified after Zhang et al. (1995). Acronyms: LT, low temperature; MT, middle temperature; HT, high temperature; LP, low pressure; HP, high pressure; UHP, ultrahigh pressure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

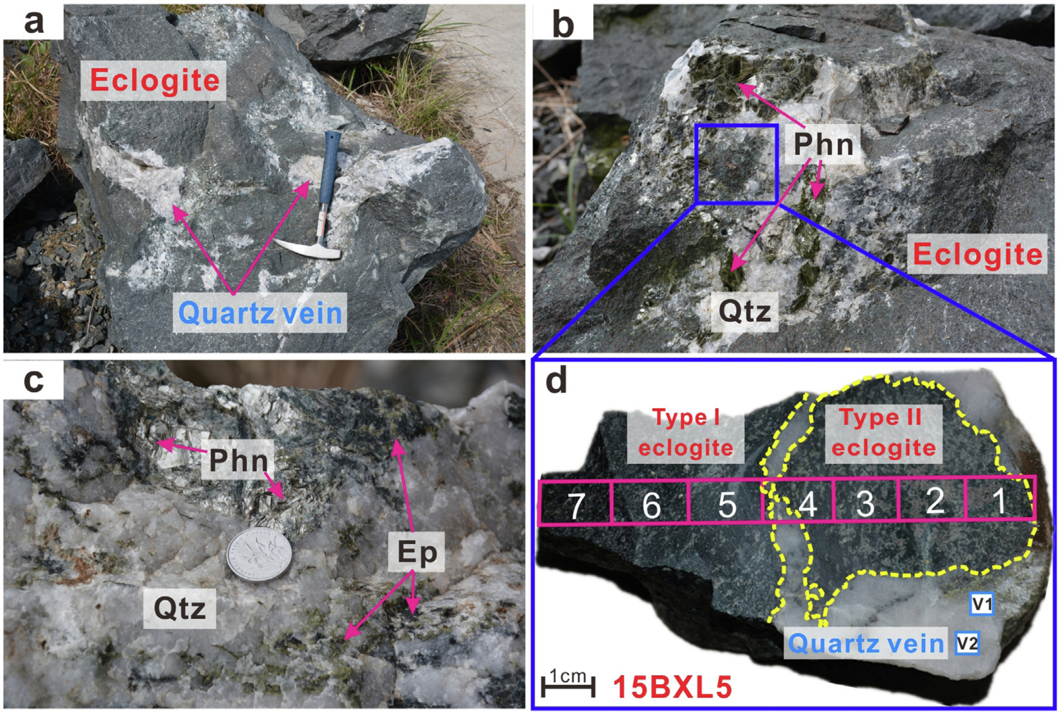

Fig. 3. Field photographs of the Bixiling UHP eclogites and HP quartz veins. (a) Epidote-phengite-bearing quartz veins enclosed in an eclogite block. (b) A typical quartz vein hosting a small eclogite fragment. (c) Heterogeneous distribution of minerals in the quartz vein. Phengite and epidote are mostly aggregated near the vein-eclogite boundary. (d) A representative hand specimen (sample 15BXL5) from partial enlarged of (b), containing the Type I eclogite, Type II eclogite, and quartz vein. This hand specimen was segmented into nine samples along with the lithologic changes, with 2 samples from the quartz vein (15BXL5-V1 and 15BXL5-V2), 4 from the Type II eclogite (15BXL5-1 to 15BXL5-4), and 3 from the Type I eclogite (15BXL5-5 to 15BXL5-7). The yellow dashed lines show the boundaries between the quartz vein and eclogites. Acronyms: Ep, epidote; Phn, phengite; Qtz, quartz. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

veins with a length of several decimeters and a width of several centimeters to decimeters are totally enclosed in the interior of eclogite blocks (Fig. 3a and b). In particular, some small eclogite fragments are encased in the quartz veins (Fig. 3b). No obvious reaction selvages occur between the quartz veins and their host eclogites. According to the field occurrences and petrological observations, the studied eclogites can be divided into two types, with the Type I being the host eclogites, and the Type II being the vein-hosted eclogites (Fig. 3d).

A representative hand specimen (15BXL5, with a length of ca. 10 cm) containing quartz veins and both types of eclogites was collected and separated into nine samples (Fig. 3b and d). Specifically, four samples (15BXL5-1 to 15BXL5-4) belong to the Type II eclogites, three (15BXL5-5 to 15BXL5-7) belong to the Type I eclogites, and the other two (15BXL5-V1 and 15BXL5-V2) are the quartz veins. Additionally, nine quartz vein bands nearby and six Type I eclogites far away from the quartz veins (>50 cm) were also sampled for investigation (Tables 1 and S1).

The Type I eclogites are composed of garnet, omphacite, clinopyroxene/diopside, phengite, quartz, and amphibole, with minor biotite, plagioclase, epidote, rutile, pyrite, and zircon (Fig. 4a–d; Table S1). These eclogites exhibit strong retrograde alteration and partial transformation to garnet amphibolites. Garnet mainly occurs as idioblastic crystals with kelyphitic rims of amphibole. Most omphacites have been replaced by symplectite of amphibole, plagioclase, and diopside, and phengite is partially replaced by symplectite of biotite + plagioclase along margins and cleavages (Fig. 4d).

The Type II eclogites are entirely encased in the quartz veins with a volume of 4 cm × 4 cm × 5 cm (Fig. 3b), and mainly consist of garnet, clinopyroxene, amphibole, plagioclase, epidote, and pyrite (Fig. 4e). Omphacite is absent and has been totally replaced by symplectite of amphibole, epidote, and plagioclase. Notably, the Type II eclogites have a higher volume abundance (~60 vol%) and bigger phenocryst (2–4 mm) of garnet but lack rutile and phengite, different from the Type I eclogites (Table S1).

The quartz veins generally show sharp contacts to the host eclogites with irregular shapes, and contain large amounts of quartz (>90 vol%) and variable amounts of phengite and epidote (Fig. 3c), thus are called epidote-phengite-bearing quartz veins. The distribution of these minerals is heterogeneous in different portions, with phengite and epidote mostly aggregated near the vein-eclogite boundary (Fig. 3b and c). A lot of fluid inclusions occur in quartz from the veins (Fig. 4f), whereas no visible mineral inclusions are observed. The fluid inclusions occur isolated or in groups and clusters, and range in size from 1 to 10 μm.

A total of 19 samples were analyzed for whole-rock major and trace element and Ba isotopic compositions. Among them, 14 samples were also analyzed for Sr-Nd isotopic compositions. Besides whole-rock samples, 23 mineral separates (phengite, biotite, epidote, amphibole, and quartz) from both the Type I eclogites and the quartz veins were analyzed for Ba concentrations and isotopic compositions.

3. Analytical methods

3.1. Major and trace element analyses

Fresh eclogite and quartz vein samples were carefully prepared to avoid any visual alteration, then crushed in a corundum jaw crusher and powdered in an agate mortar to 200 mesh for whole-rock element and isotope analyses. Analyses of major elements were carried out using an X-ray fluorescence spectrometer (XRF) at the ALS Chemex (Guangzhou) Co., Ltd., with the relative standard deviation (RSD) better than 5%. Trace elements were analyzed by a Perkin-Elmer Elan DRC II inductively coupled plasma mass spectrometry (ICP–MS) at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC), Hefei. The procedures were described in Hou and Wang (2007). Two USGS reference materials (AGV-2 and BHVO-2) were processed with the investigated samples to evaluate the accuracy of trace element data. The results show that the RSD of most elements is better than 10% and the RSD of Ba is better than 5% (Table S2).

3.2. Whole-rock Sr-Nd isotope analyses

Sr-Nd isotope analyses were performed at the CAS Key Laboratory of Crust-Mantle Materials and Environments, USTC, Hefei, following the procedures described in Chen et al. (2002). The chemical procedures were performed in an ISOclass 6 clean laboratory, with Sr and Nd being separated from the matrix elements by two-step ion-exchange chromatography. Total procedural blanks were <200 pg for Sr and <50 pg for Nd. The isotopic compositions were measured by a Thermo Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC–ICP–MS). To correct for instrumental mass bias, the Sr and Nd isotopic ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively. During this study, the reference material NBS987 yielded $^{87}Sr/^{86}Sr$ of 0.710248 ± 13 (2 s) and the reference material JNdi-1 yielded $^{143}Nd/^{144}Nd$ of 0.512115 ± 13 (2 s). The USGS reference material BHVO-2 was processed with the investigated samples and the measured Sr-Nd isotope ratios agree with literature values (Table S3).

3.3. Barium isotope analyses

Barium isotope analyses were performed at the CAS Key Laboratory of Crust-Mantle Materials and Environments, USTC, Hefei, following the established methods of Nan et al. (2015, 2018). Whole-rock samples were dissolved with a combination of concentrated $HF–HNO_3–HCl$ in pre-cleaned screw-top Teflon beakers. After evaporation to dryness, the whole-rock samples were dissolved in 3 mol/L HCl. For mineral Ba concentration and Ba isotope analyses, fresh phengite, biotite, epidote, amphibole, and quartz grains that separated from the Type I eclogites and the quartz veins were hand-picked under a binocular microscope before dissolution. After the same dissolution procedures as whole-rock samples, the solution of the mineral separates was divided into two parts. One of which was evaporated to dryness and dissolved in 2% HNO_3, and then analyzed for Ba concentration by ICP-MS. The other was evaporated to dryness and diluted with 3 mol/L HCl in preparation for Ba purification. One milliliter of the 3 mol/L HCl solution of the whole-rock samples or mineral separates that containing ca. 2 μg Ba was loaded onto the pre-cleaned Bio-Rad AG 50 W–X12 (200–400 mesh) cation resin, and Ba was separated from the matrix elements by two-step ion-exchange chromatography. The Ba recoveries through column chemistry were >99% and the total procedure blank was <2 ng.

Barium isotopic measurements were performed with a Thermo Scientific Neptune Plus MC–ICP–MS at USTC, following the established methods of Deng et al. (2021). A double-spike ($^{135}Ba–^{136}Ba$) technique was used to correct the instrumental mass bias, with the optimal range of the proportion of double spike relative to the total Ba being 0.43 to 0.60. The samples were introduced into an Aridus II desolvating nebulizer system to obtain a sensitivity of ~30 V/100 ng/g for ^{138}Ba. In a low-resolution mode, ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, and ^{138}Ba were collected on the L2, L1, C-cup, H1, and H2 Faraday cups, respectively. ^{131}Xe and ^{140}Ce were also monitored by the L4 and H3 Faraday cups, to deduct the isobaric interferences of Xe and Ce. The signal of ^{138}Ba of the 2% HNO_3 was lower

Table 1
Barium concentrations and isotopic compositions of the Bixiling UHP eclogite and HP quartz vein whole-rock samples and mineral separates.

Sample No.	Rock type	Whole rock/mineral[a]	Ba (μg/g)	$\delta^{137/134}$Ba (‰)	2SD[b]	$\delta^{138/134}$Ba (‰)	2SD[b]	N[c]
16BXL3	Type I eclogite	Wr[*]	453	−0.04	0.04	−0.05	0.05	2
		Phn	2978	−0.08	0.01	−0.09	0.01	2
16BXL5	Type I eclogite	Wr[*]	360	−0.09	0.03	−0.12	0.05	2
		Amp	80.9	0.04	0.05	0.08	0.03	2
		Phn	1946	−0.07	0.02	−0.10	0.05	2
		Bt	3347	−0.19	0.01	−0.25	0.02	2
		Bt[#]	4815	−0.17	0.02	−0.24	0.03	2
16BXL10-1	Type I eclogite	Wr[*]	1144	−0.06	0.01	−0.09	0.05	2
		Replicate[d,*]		−0.05	0.01	−0.07	0.05	2
		Average		−0.06	0.02	−0.08	0.03	
18BXL2	Type I eclogite	Wr	213	−0.07	0.03	−0.08	0.05	2
		Phn	2748	−0.12	0.02	−0.16	0.01	2
		Phn[#]	2072	−0.11	0.01	−0.14	0.02	2
		Bt	5366	−0.23	0.01	−0.28	0.01	2
		Bt[#]	5856	−0.17	0.01	−0.22	0.03	2
18BXL3	Type I eclogite	Wr	242	−0.07	0.03	−0.09	0.05	4
		Amp	68.8	−0.05	0.05	−0.06	0.05	4
		Ep	144	0.09	0.04	0.12	0.04	2
		Phn	3891	−0.10	0.01	−0.12	0.02	2
		Bt	4748	−0.25	0.02	−0.34	0.05	4
18BXL5	Type I eclogite	Wr	419	−0.02	0.01	−0.04	0.05	2
		Phn	1829	−0.08	0.05	−0.10	0.01	2
		Phn[#]	2964	−0.04	0.02	−0.05	0.04	2
15BXL5-5	Type I eclogite	Wr	1040	−0.07	0.01	−0.09	0.01	2
15BXL5-6	Type I eclogite	Wr	1043	−0.06	0.02	−0.09	0.02	2
15BXL5-7	Type I eclogite	Wr	1026	−0.07	0.02	−0.10	0.01	2
15BXL5-1	Type II eclogite	Wr	911	0.24	0.01	0.32	0.01	2
15BXL5-2	Type II eclogite	Wr	916	0.27	0.01	0.37	0.01	2
15BXL5-3	Type II eclogite	Wr	914	0.30	0.01	0.40	0.04	2
15BXL5-4	Type II eclogite	Wr	879	0.25	0.03	0.34	0.05	2
15BXL5-V1	Quartz vein	Wr	2128	0.34	0.02	0.46	0.01	2
		Phn[*]	758	−0.19	0.04	−0.25	0.05	3
		Ep	7557	0.28	0.03	0.35	0.02	5
		Ep[#]	7359	0.30	0.01	0.40	0.02	4
		Qtz	22.1	0.26	0.02	0.35	0.01	2
15BXL5-V2	Quartz vein	Wr[*]	1021	0.36	0.01	0.48	0.05	2
		Phn	1193	−0.17	0.02	−0.22	0.01	2
		Qtz	19.0	0.20	0.01	0.25	0.03	2
16BXL1	Quartz vein	Wr[*]	192	0.12	0.01	0.16	0.05	2
		Qtz	22.1	0.24	0.03	0.32	0.05	3
16BXL6	Quartz vein	Wr[*]	1030	0.30	0.04	0.39	0.05	2
16BXL7	Quartz vein	Wr[*]	240	0.26	0.04	0.35	0.05	2
16BXL10-2	Quartz vein	Wr[*]	2952	0.39	0.02	0.51	0.05	2
		Qtz	27.5	0.22	0.02	0.32	0.04	2
15BXL3	Quartz vein	Phn	2000	0.07	0.01	0.09	0.04	2
		Phn[#]	2299	0.04	0.01	0.06	0.03	4
16BXL2	Quartz vein	Phn	1905	0.01	0.03	0.01	0.01	2
16BXL4	Quartz vein	Phn	1580	−0.17	0.01	−0.24	0.01	2
18BXL1	Quartz vein	Ep	8082	0.64	0.04	0.85	0.05	4
		Ep[#]	9331	0.51	0.01	0.67	0.04	2
18BXL4	Quartz vein	Qtz	28.8	0.21	0.02	0.27	0.01	2
USGS Reference materials								
AGV-1	Andesite	This study	1230	0.03	0.04	0.04	0.05	3
		van Zuilen et al. (2016)		0.06	0.04			4
		Nan et al. (2018)		0.05	0.03			4
		An et al. (2019)		0.04	0.04	0.06	0.05	2
BCR-2	Basalt	This study	683	0.04	0.03	0.05	0.04	9
		Nan et al. (2018)		0.05	0.03			12
		An et al. (2019)		0.05	0.03	0.06	0.06	6
BHVO-2	Basalt	This study	130	0.02	0.04	0.03	0.05	2
		Nan et al. (2015)		0.05	0.03			22
		An et al. (2019)		0.01	0.04	0.02	0.03	6
		Gu et al. (2021)		0.02	0.01			4

Notes:

[a] Wr = Whole rock, Phn = Phengite, Amp = Amphibole, Ep = Epidote, Bt = Biotite, Qtz = Quartz.

[b] 2SD indicates twice the standard deviation of the population of N repeated measurements of the same sample. Especially, the 2SD of the $\delta^{138/134}$Ba that calculated from the measured $\delta^{137/134}$Ba was set as 0.05‰, based on the long-term measurements of the in-house standards.

[c] N represents the number of mass spectrometry analyses for the same sample.

[d] Replicate denotes repeated sample dissolution, column chemistry, and instrumental analysis.

[*] Only the ^{137}Ba signals of these samples were measured, and their $\delta^{138/134}$Ba values were calculated by $\delta^{138/134}\text{Ba} = 1.33 \times \delta^{137/134}\text{Ba}$.

[#] This is the replicate for the corresponding mineral.

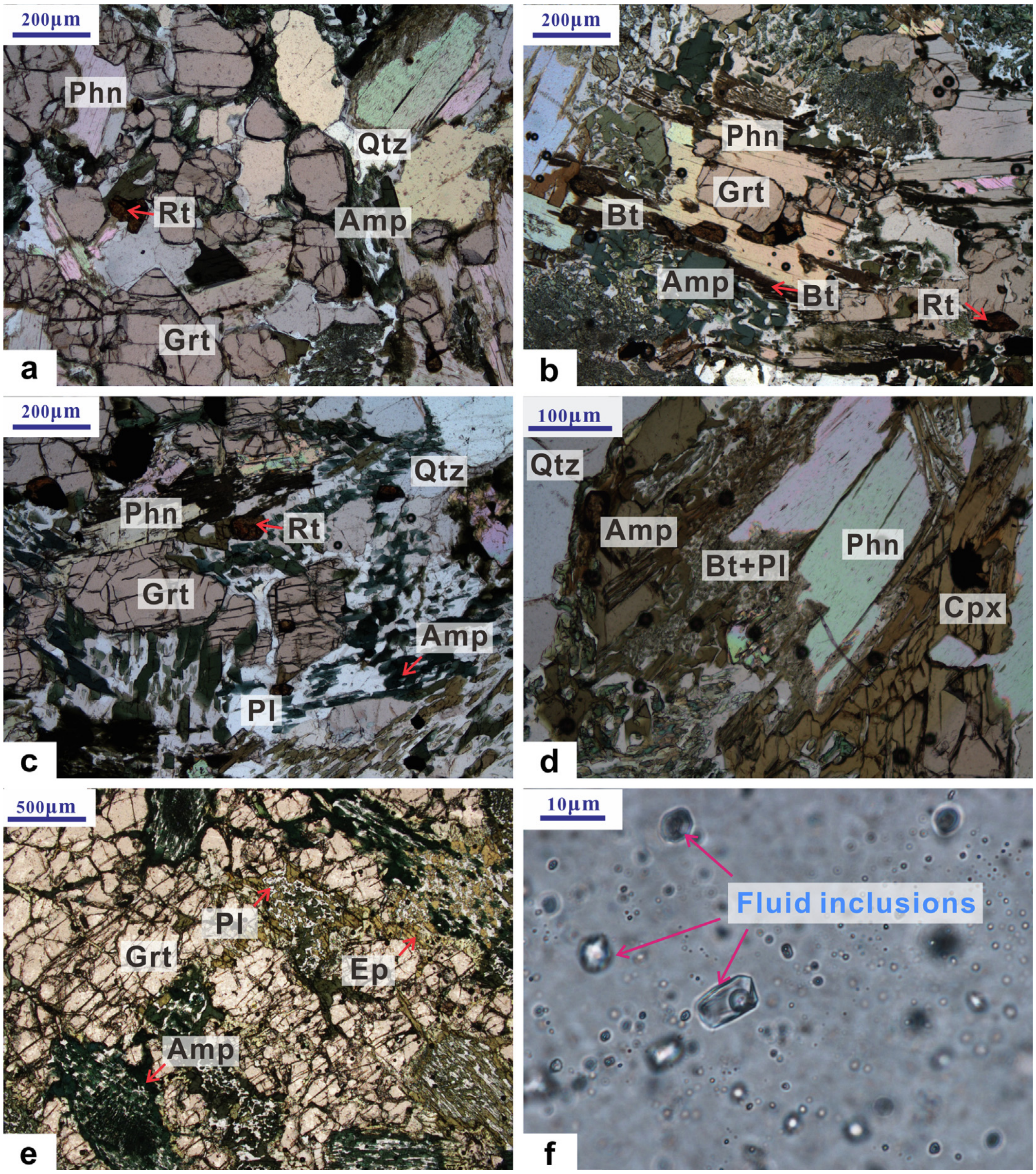

Fig. 4. Photomicrographs showing the textural characteristics of the Bixiling UHP eclogites and HP quartz veins. (a) Representative mineral assemblage of the Type I eclogite, sample 16BXL5. (b) Phengite rimmed by biotite in the Type I eclogite, sample 16BXL5. (c) Symplectite of fine-grained amphibolite and plagioclase after omphacite in the Type I eclogite, sample 16BXL3. (d) Biotite + plagioclase symplectite alongside the edge of phengite in the Type I eclogite, sample 16BXL5. (e) Large-grained porphyroblastic garnet in the Type II eclogite, sample 15BXL5-2. (f) Fluid inclusions in quartz from the quartz vein, sample 15BXL5-V2. Acronyms: Amp, amphibole; Bt, biotite; Cpx, clinopyroxene; Ep, epidote; Grt, garnet; Phn, phengite; Pl, plagioclase; Qtz, quartz; Rt, rutile.

than 0.02 V, which was much lower than the sample signals (~30 V).

Ba isotope ratios are reported in the delta notation relative to NIST SRM3104a and expressed in per mil (‰): $\delta^{x/134}Ba = [(^{x/134}Ba_{sample})/(^{x/134}Ba_{SRM3104a}) - 1] \times 1000$, where x represents 137 or 138. Both the $\delta^{137/134}Ba$ and $\delta^{138/134}Ba$ for most of the studied samples were directly obtained. For some samples analyzed at an earlier time, the ^{138}Ba signals were not simultaneously collected, and the reported $\delta^{138/134}Ba$ for these samples were calculated by multiplying the measured $\delta^{137/134}Ba$ by a factor of 1.33 (Deng et al., 2021). Based on replicate analyses of two in-house standards USTC-Ba and ICPUS-Ba, the long-term precision for $\delta^{138/134}Ba$ is better than 0.05‰ (2 s). The $\delta^{138/134}Ba$ of three USGS reference materials (AGV-1, BCR-2, and BHVO-2) obtained in this study agree with previously published values, and the results of all replicated samples agree with each other within error (Table 1).

4. Results

4.1. Major and trace element compositions

Whole-rock major and trace element compositions of the studied samples are listed in Supplementary Table S2 and shown in Figs. 5–7. Both the Type I eclogites near and far away from the veins have similar major and trace element compositions (Figs. 5 and 7), with SiO_2 from 50.57 to 54.47 wt%, Al_2O_3 from 13.55 to 14.50 wt%, TFe_2O_3 from 11.98 to 13.13 wt%, MgO from 3.37 to 3.95 wt%, CaO from 6.87 to 9.12 wt%, Na_2O from 3.34 to 4.99 wt %, and K_2O from 0.58 to 1.04 wt%, respectively. These eclogites have nearly flat rare earth element (REE) patterns in the chondrite-normalized REE diagram (Fig. 6a), with no or slight negative anomalies of Nb, Ta, and Zr in the spider diagram (Fig. 6b). In contrast, the Type II eclogites have much lower contents of TiO_2

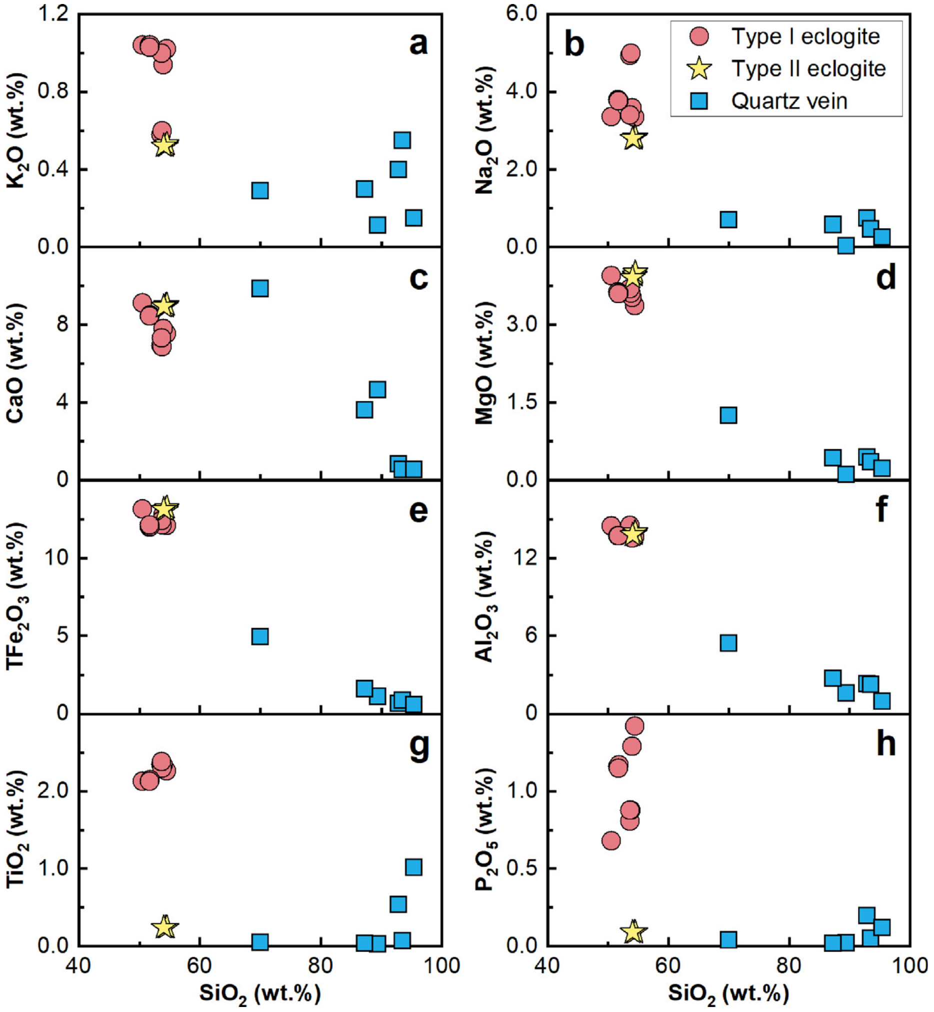

Fig. 5. Major element characteristics of the Bixiling UHP eclogites and HP quartz veins.

(0.24 wt%), Na_2O (2.79–2.83 wt%), and K_2O (0.52–0.53 wt%) but slightly higher contents of SiO_2 (54.06–54.53 wt%), Fe_2O_3 (13.08–13.22 wt%) and CaO (8.95–9.02 wt%) than the Type I eclogites (Figs. 5 and 7). They have dish-shaped REE distribution patterns (Fig. 6a) and high Sr, Y, light rare earth element (LREE), and heavy rare earth element (HREE) contents (Fig. 6b), which are possibly attributable to the high modal amount of garnet and epidote in the Type II eclogites.

The quartz veins show large variations in major and trace element compositions, corresponding to the heterogeneous distribution of constituent minerals (quartz, phengite, and epidote). Generally, these veins have very high SiO_2 contents from 70.00 to 95.37 wt%, together with strongly varying contents of TiO_2 (0.03–1.02 wt%), Al_2O_3 (0.94–5.43 wt%), Fe_2O_3 (0.58–4.94 wt%), MgO (0.10–1.25 wt%), CaO (0.53–9.88 wt%), and K_2O (0.11–0.55 wt%) (Figs. 5 and 7). Likewise, trace element concentrations vary by up to two orders-of-magnitude among the vein samples, mostly characterized by the enrichment of LREE and large ion lithophile element (LILE) relative to HREE (Fig. 6). An average of all the quartz vein samples was calculated (Table S2) to represent the credible element composition of the entire vein body, which is difficult to be obtained directly. The result shows that it has comparable LILE and LREE concentrations to the Type II eclogites, but is depleted in HREE, Nb, and Ta (Fig. 6), consistent with the absence of garnet and rutile in the quartz veins.

4.2. Sr-Nd isotopic compositions

The whole-rock Sr-Nd isotope data are presented in Supplementary Table S3. The $^{87}Sr/^{86}Sr$ of the Type I eclogites, the Type II eclogites, and the quartz veins are from 0.707251 to 0.708579, from 0.707145 to 0.707146, and from 0.707145 to 0.708903, respectively. Their $^{143}Nd/^{144}Nd$ ratios vary from 0.512433 to 0.512486, from 0.512440 to 0.512453, and from 0.512311 to 0.512483, respectively. When calculated to the formation age of the quartz veins (t = 220 Ma; Chen et al., 2022), the initial Sr-Nd isotopic compositions of these three types of rocks are 0.70656–0.70712 and −2.8 to −2.3, 0.70712 and −2.9 to −2.6, and 0.70659–0.70720 and −3.3 to −2.0, respectively, displaying a limited range (Fig. 8).

4.3. Ba concentrations and isotopic compositions of the whole rocks and mineral separates

Ba concentrations and isotopic compositions of the whole rocks and mineral separates are reported in Table 1 and shown in Figs. 7 and 9. The Type I eclogites in the profile have relatively high Ba concentrations (1026–1043 μg/g), while those far away from the veins have a broad variation from 213 to 1144 μg/g. However, the $\delta^{138/134}Ba$ of all these eclogites display a narrow range from −0.12 to −0.04‰, with an average of −0.09 ± 0.01‰ (2SE, n = 9),

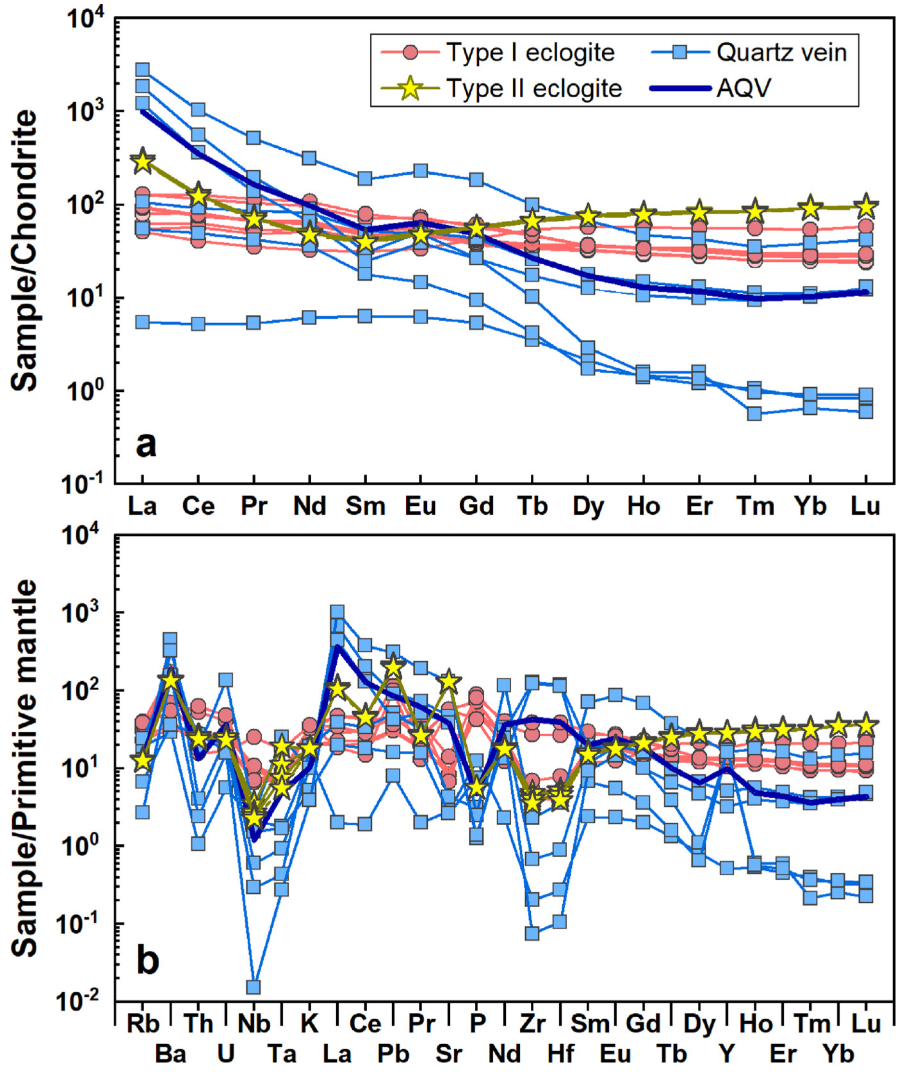

Fig. 6. Trace element characteristics of the Bixiling UHP eclogites and HP quartz veins. (a) Chondrite-normalized REE patterns. (b) Primitive mantle-normalized trace element patterns. The average of all quartz vein samples (AQV) is also plotted. The normalization values of (a) and (b) are from Sun and McDonough (1989) and from Mcdonough and Sun (1995), respectively.

which is somewhat lower than that of the MORB average (0.05 ± 0.09‰; Nan et al., 2022). The quartz veins also exhibit a large variation in Ba concentrations from 192 to 2952 μg/g and their $\delta^{138/134}$Ba significantly varies from 0.16 to 0.51‰, with an average of 0.39 ± 0.11‰ (2SE, $n = 6$). By contrast, the Type II eclogites have relatively homogeneous Ba concentrations from 879 to 916 μg/g and $\delta^{138/134}$Ba from 0.32 to 0.40‰, with an average $\delta^{138/134}$Ba of 0.35 ± 0.04‰ (2SE, $n = 4$). Their $\delta^{138/134}$Ba values are much higher than those of the Type I eclogites, but fall in the range of the quartz veins (Fig. 9).

The Ba concentrations and isotopic compositions of mineral separates from the Type I eclogites and the quartz veins are remarkably different (Fig. 9). In the Type I eclogites, biotite has the highest Ba concentrations from 3347 to 5856 μg/g and the lowest $\delta^{138/134}$Ba from −0.34 to −0.22‰. Phengite has the second-highest Ba concentrations from 1829 to 3891 μg/g, with $\delta^{138/134}$Ba ranging from −0.16 to −0.05‰, which are similar to those of their host rocks (Fig. 9a). Compared to biotite and phengite, epidote and amphibole in the Type I eclogites have much lower Ba concentrations of 144 μg/g and 68.8–80.9 μg/g, but higher $\delta^{138/134}$Ba of 0.12‰ and −0.06 to 0.08‰, respectively (Fig. 9a). In the quartz veins, phengite and epidote control the Ba budget, whose Ba concentrations are 758–2299 μg/g and 7359–9331 μg/g, respectively. The $\delta^{138/134}$Ba of the vein phengite varies from −0.25 to 0.09‰, obviously lower than those of the quartz vein whole-rock samples (Fig. 9b). In contrast, the vein epidote has much higher $\delta^{138/134}$Ba from 0.35 to 0.85‰. Especially, the vein quartz has unexpectedly high Ba concentrations of 19.0 to 28.8 μg/g, and relatively homogeneous $\delta^{138/134}$Ba from 0.25 to 0.35‰ with an average of 0.31 ± 0.04‰ (2SE, $n = 5$), similar to that of the Type II eclogites (Fig. 9b).

5. Discussion

5.1. Fluid sources for the quartz veins

In the Dabie-Sulu orogen, it is generally accepted that fluid flow was very limited during the peak UHP stage when the continental crust was subducted to the mantle depths, whereas significant amounts of aqueous fluid became active during slab exhumation (Zheng et al., 2003, 2007,2011; Chen et al., 2007, 2012; Zheng, 2009; Guo et al., 2015). The big drop in pressure from the peak UHP stage (>4.5 GPa) to the retrograde HP eclogite-facies stage

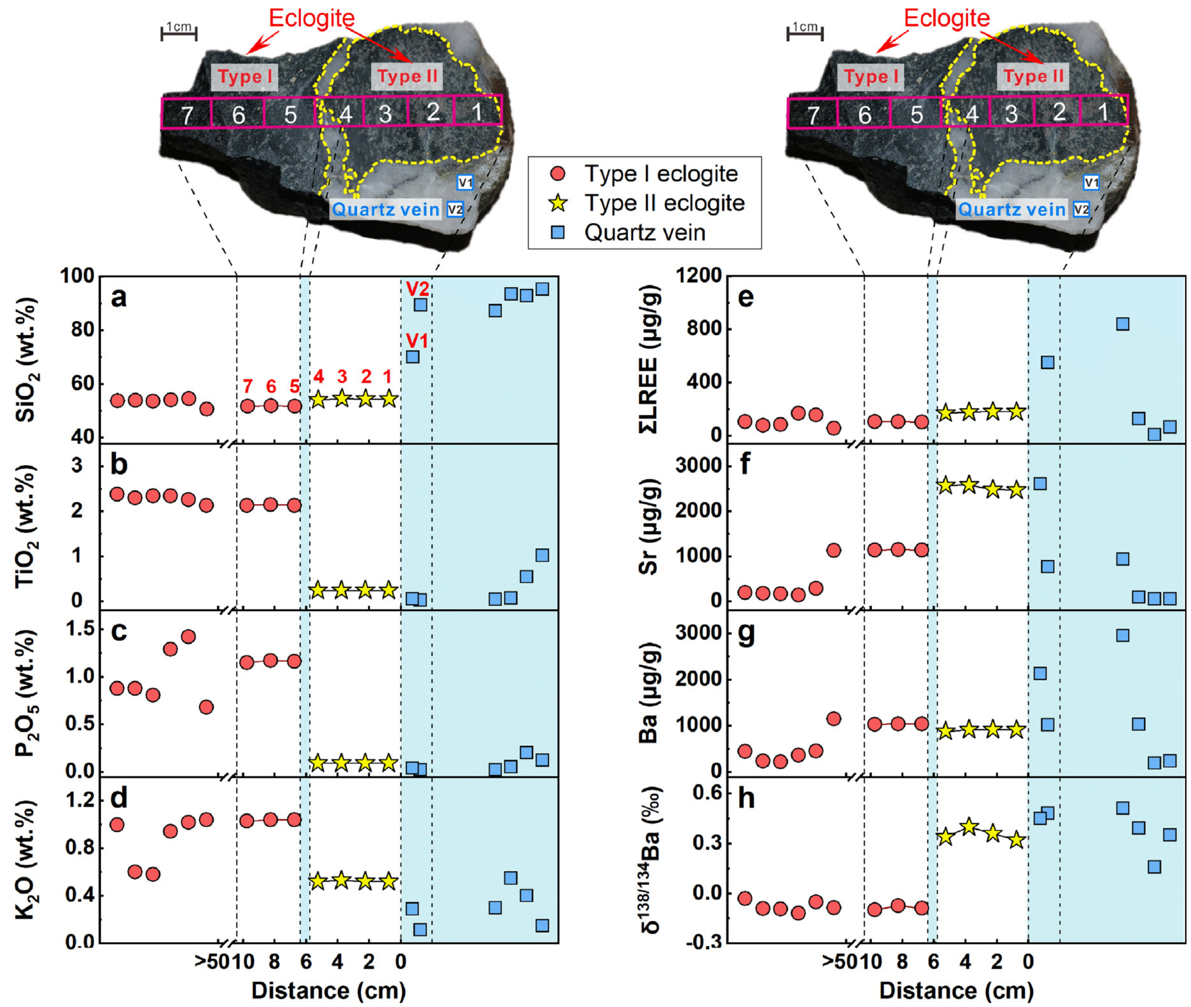

Fig. 7. Variations of selected major and trace element contents and $\delta^{138/134}$Ba of the Bixiling eclogite-vein system, including the comprehensive profile across the selected hand specimen sample 15BXL5 (shown at the top). The vertical light cyan areas denote the quartz veins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

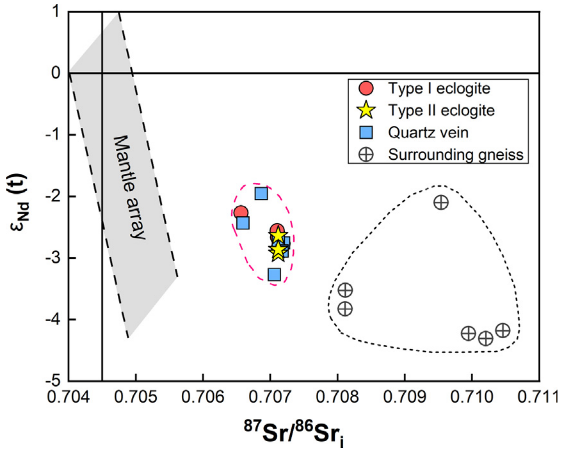

Fig. 8. Correlative diagram of $\varepsilon_{Nd}(t)$ versus $^{87}Sr/^{86}Sr_i$ (t = 220 Ma) for the eclogites, quartz veins, and surrounding gneisses at Bixiling. Data for the mantle array are from Hart et al. (1986), and for the surrounding gneisses are from Chavagnac and Jahn (1996) and Chavagnac et al. (2001), respectively.

(∼2.0 GPa) caused a significant release of aqueous fluid, due to the breakdown of hydrous minerals (e.g., lawsonite, phengite, zoisite, glaucophane, chloritoid, and paragonite; Li et al., 2004; Zheng, 2009; Guo et al., 2015) and/or the exsolution of structural hydroxyl and molecular H_2O in nominally anhydrous minerals (e.g., omphacite, garnet, and rutile; Zheng et al., 2003, 2007; Chen et al., 2007). The dehydrated fluid can dissolve fluid-mobile elements in the country rocks and transport them over short distances (Rubatto and Hermann, 2003; Zack and John, 2007), eventually resulting in metamorphic veins by precipitation of various minerals. While some fluids were derived from the surrounding gneisses, most fluids were probably derived from internal dehydration of the host eclogites (e.g., Li et al., 2004; El Korh et al., 2011; Chen et al., 2012; Guo et al., 2012).

Field observations and geochemical data may provide evidence for whether the metamorphic fluids responsible for the studied quartz veins were locally sourced or not. The quartz veins at Bixiling are well-enclosed in eclogites (Fig. 3a) and are not apparently in contact with the surrounding gneisses. The main mineral assemblage of the quartz veins is quartz, phengite, and epidote (Fig. 3c), within the subassemblage of the host eclogites with no trace of exotic minerals. Moreover, the quartz veins have $^{87}Sr/^{86}Sr_i$ ratios and $\varepsilon_{Nd}(t)$ values of 0.70659–0.70720 and −3.3 to −2.0, respectively, which are similar to those of the Type I eclogites (0.70656–0.70712 and −2.8 to −2.3, respectively) but obviously different from those of the surrounding gneisses (Fig. 8). The above evidences indicate an internal source from the host eclogites and localized fluid transport for veining.

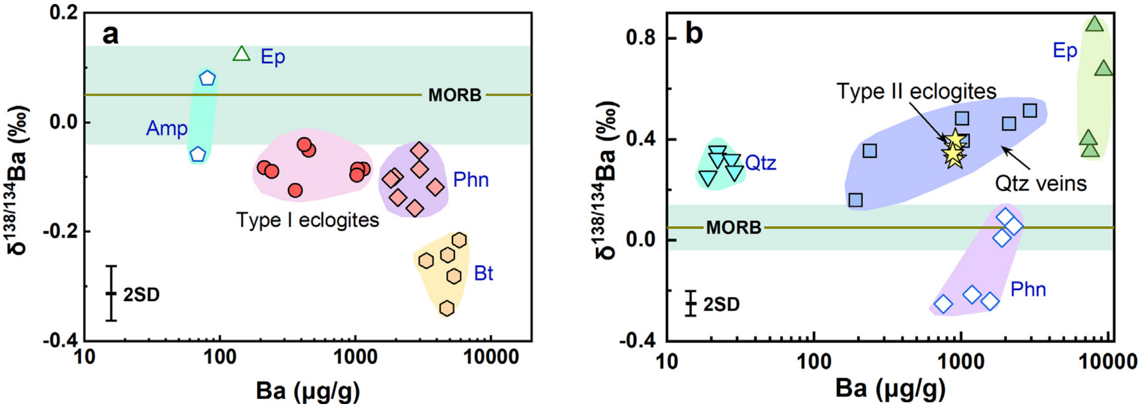

Fig. 9. Ba concentration (μg/g) and $\delta^{138/134}$Ba (‰) for whole rocks and Ba-bearing minerals of the Type I eclogites at Bixiling (a), and for whole rocks of the Type II eclogites and whole rocks and Ba-bearing minerals of the quartz veins at Bixiling (b). The horizontal lines and light green areas represent the average $\delta^{138/134}$Ba of MORB (0.05 ± 0.09‰; Nan et al., 2022). Acronyms: Amp, amphibole; Bt, biotite; Ep, epidote; Phn, phengite; Qtz, quartz. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In terms of the specific process(es) accounting for the origin of metamorphic fluid at Bixiling, the breakdown of lawsonite in eclogites can be ruled out due to the lack of lawsonite in the peak UHP stage (Wei et al., 2013). Instead, the occurrence of abundant symplectitic coronas of biotite + plagioclase around phengite in the Type I eclogites (Fig. 4d) is the direct evidence of phengite decomposition, suggesting that the vein-forming fluid may be derived from the breakdown of phengite. The calculations by Heinrich (1982) and You et al. (2000) both suggested that such a breakdown reaction could produce sufficient fluids to form metamorphic veins and/or to metasomatize adjacent eclogites. Besides, Sheng et al. (2007) found that garnet and omphacite grains in the Bixiling eclogites contained structural water occurring as hydroxyl (OH), with the H_2O contents up to 1915 μg/g and 695 μg/g, respectively, implying that the exsolution of structural hydroxyl from garnet and omphacite can also liberate significant amounts of water. Therefore, the vein-forming fluid of the Bixiling HP quartz veins was most likely derived from the host eclogites, and probably originated from the decomposition of phengite and/or the exsolution of structural water in garnet and omphacite during exhumation of the deeply subducted continental crust.

5.2. Ba isotopic composition of the vein-forming fluid

5.2.1. Constraint from whole rocks of the quartz veins

Petrological observations and geochemical data of metamorphic vein whole-rock samples can provide direct constraints on the fluid composition in metamorphic terranes (e.g., Rubatto and Hermann, 2003; Chen et al., 2012; Bebout, 2014; Guo et al., 2015). The majority of the mineral phase of the studied veins is quartz, suggesting that the vein-forming fluids should be aqueous fluids rather than hydrous melts, as the latter usually form metamorphic veins with granitic components (Hermann et al., 2006; Zheng and Hermann, 2014). Additionally, the presence of abundant phengite in the veins indicates significant amounts of LILE in the vein-forming fluid, while the presence of epidote suggests high mobility of REE during the fluid flow as epidote is strongly enriched in LREE (Frei et al., 2004; Chen et al., 2012). These observations, together with the average composition of the quartz veins (Fig. 6), indicate that the vein-forming fluid of the Bixiling quartz veins was aqueous fluid enriched in LILE and LREE.

The $\delta^{138/134}$Ba of the Bixiling quartz vein whole-rock samples significantly varies from 0.16 to 0.51‰, which is probably due to the extreme heterogeneity of vein mineralogy. Phengite and epidote are the two main dominant Ba-hosting minerals in these veins, and they have remarkably different Ba concentrations and isotopic compositions (Fig. 9b). Notably, the Ba content of vein epidote is up to 9331 μg/g, nearly-two orders-of-magnitude higher than that of epidote in the type I eclogite and several times higher than that of vein phengite (Table 1). Such a high Ba content is rarely observed in common epidote, as with its large cation radius Ba normally substitutes for Ca within epidote only in trace or minor amounts (Franz and Liebscher, 2004). It may be attributed to the high degrees of (Mn^{3+}, Fe^{3+}) substitution for Al in the lattice, similar to the Sr piemontite (with up to 2.7–6.7% BaO) from the Sanbagawa belt, Japan (Enami and Banno, 2001; Franz and Liebscher, 2004). The vein epidote also has much higher $\delta^{138/134}$Ba than the vein phengite (Fig. 9b), suggesting significant inter-mineral Ba isotope fractionation, with heavy Ba isotopes preferentially enriched in epidote than in phengite during vein formation. The direction of Ba isotope fractionation between phengite and epidote observed here is in agreement with that reported by Gu et al. (2021). However, the Ba isotopic compositions of the vein epidote and phengite are both highly variable (Fig. 9b), which is in contrast to the expectation of equilibrium isotope fractionation. Alternatively, this feature may reflect a dynamic crystallization process of the vein epidote and phengite over a long period in a closed system, which is similar to the occurrence of compositional differences of the same mineral pair within multi-stage metamorphic veins (Guo et al., 2015).

The heterogeneous spatial distribution of phengite and epidote and the remarkable inter-mineral Ba isotope fractionation between them result in the observed large Ba isotopic variation of the quartz vein whole-rock samples (Fig. 9b). Nonetheless, the bulk vein samples may still provide useful constraints on the Ba isotope characteristic of the vein-forming fluid. The experiment by Green and Adam (2003) indicated that the *D*phengite/fluid Ba value could be up to 131. Moreover, the vein epidote has higher Ba concentration than the vein phengite (Fig. 9b), implying that the *D*epidote/fluid Ba value could be even higher. Therefore, when abundant phengite and epidote are present in the veins, most of the Ba would be hosted in these two minerals. In this regard, the average $\delta^{138/134}$Ba (0.39 ± 0.11‰) of the bulk quartz vein samples may reflect the Ba isotopic composition of the vein-forming fluid. This average value is significantly higher than that of the Type I eclogites (−0.09 ± 0.01‰), indicating that metamorphic dehydration of the host eclogites at Bixiling produced fluids with much heavier Ba isotopic composition than the eclogites.

5.2.2. Constraint from whole rocks of the vein-hosted eclogites

Compared with the type I eclogites, the Type II eclogites have distinct differences in mineral constituents and element compositions (Figs. 4–7). Petrological observations show that the Type II eclogites are devoid of phengite and rutile, but enriched in garnet (Table S1). Moreover, the garnet grains in the type II eclogites are significantly coarser than those in the Type I eclogites (Fig. 4a and e), reflecting mineral recrystallization during fluid metasomatism (Chen et al., 2015). In terms of element features, the Type II eclogites show slightly higher contents of SiO_2, Fe_2O_3, and MgO, but obviously lower contents of Na_2O, TiO_2, P_2O_5, and K_2O than the type I eclogites in the sampling profile (Figs. 5 and 7). Besides, the Type II eclogites also have higher concentrations of LREE, HREE, Sr, and Pb, but lower concentrations of Ti, Nb, and Zr (Fig. 6). These results indicate that the Type II eclogites have been well modified by the vein-forming fluid, and thus may also record the fluid composition. For instance, the high contents of LILE and LREE in the Type II eclogites suggest that the vein-forming fluid was strongly enriched in LILE and LREE, consistent with the conclusion from the discussion on the quartz vein whole-rock samples in the above section.

With the modification of mineral constituents and element compositions, the Ba isotopic compositions of the Type II eclogites were also reset during fluid metasomatism. This is indicated by the observation that their $\delta^{138/134}$Ba values (from 0.32 to 0.40‰) are significantly higher than those of the Type I eclogites (from −0.12 to −0.04‰) but within the range of the quartz veins (Fig. 10). Furthermore, the relatively small volume of the Type II eclogites compared to the quartz veins (Fig. 3) and the homogeneous Ba isotopic compositions of the Type II eclogites suggest that their Ba isotopes may have been effectively homogenized by the vein-forming fluid during metasomatism. Consequently, the average Ba isotopic composition of the Type II eclogites ($\delta^{138/134}$Ba = 0.35 ± 0.04‰) is more representative of the vein-forming fluid than whole rocks of the quartz veins, which further confirms that the vein-forming fluid had a significantly heavier Ba isotopic composition compared to the host eclogites.

5.2.3. Constraint from the quartz separates from the veins

Besides the common ways to constrain chemical compositions of the vein-forming fluid directly by whole rocks of the metamorphic veins or indirectly by the metasomatic products strongly modified by the fluid (e.g., the Type II eclogites studied here), the Ba concentration and isotope data of the quartz separates from the Bixiling HP veins suggest that the vein quartz may provide an additional way to infer the Ba isotopic composition of the vein-forming fluid. It is noteworthy that the vein quartz studied here has unexpectedly high Ba concentration of 19–29 μg/g (Fig. 9b), whereas pure quartz itself should have Ba concentration far below 1 μg/g (Larsen et al., 2004; Götze et al., 2021) because LILE are difficult to enter the quartz crystal lattice (Larsen et al., 2000). Since Ba is a fluid mobile LILE and there are a lot of fluid inclusions but no visible mineral inclusions in the vein quartz at Bixiling (Fig. 4f), it is reasonable to assume that the measured Ba of the vein quartz is likely to be hosted in the fluid inclusions, although the in-situ Ba concentration analyses of the inclusions are unavailable because they are too small (1–10 μm). Moreover, petrological observations show that the fluid inclusions in the vein quartz occur isolated and have negative crystal morphologies (Fig. 4f), suggesting that they are primary inclusions (Xiao et al., 2000, 2002). Therefore, these inclusions could represent the contemporaneous fluid captured during crystallization of the vein quartz, and hence the Ba isotope data of the quartz separates from the Bixiling HP veins may reflect the Ba isotopic composition of the vein-forming fluid.

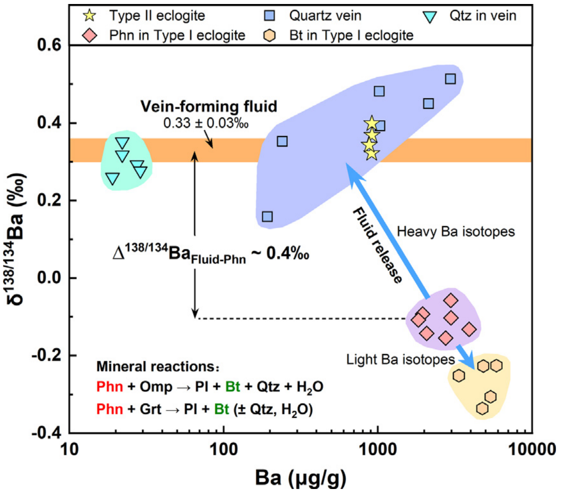

Fig. 10. Mechanism of Ba isotope fractionation during dehydration of eclogites at Bixiling. The higher Ba contents and lower $\delta^{138/134}$Ba of biotite than those of phengite in the Type I eclogites imply that the fluid released by phengite breakdown in the host eclogites would have high $\delta^{138/134}$Ba. The $\delta^{138/134}$Ba of the vein-forming fluid is estimated to be 0.33 ± 0.03‰ and $\Delta^{138/134}Ba_{Fluid-Phn}$ (=$\delta^{138/134}Ba_{Fluid}$ − $\delta^{138/134}Ba_{Phn}$) is estimate to be about 0.40‰, see text for details. The horizontal line and light green area represent the average $\delta^{138/134}$Ba of the MORB (0.05 ± 0.09‰, Nan et al., 2022). Acronyms: Bt, biotite; Grt, garnet; Omp, omphacite; Phn, phengite; Pl, plagioclase; Qtz, quartz. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The quartz separates from five different positions of the Bixiling quartz veins display relatively homogeneous $\delta^{138/134}$Ba from 0.25 to 0.35‰ (Fig. 9b), with an average of 0.31 ± 0.04‰. This average value is different from the $\delta^{138/134}$Ba of the phengite and epidote separates in the quartz veins (Fig. 9b), but agrees well with that of the Type II eclogites (0.35 ± 0.04‰), demonstrating that the vein quartz reliably records the Ba isotopic composition of the vein-forming fluid. In summary, combining the Ba isotope data of the Type II eclogites and the vein quartz, the average $\delta^{138/134}$Ba of the vein-forming fluid at Bixiling is estimated to be 0.33 ± 0.03‰ (2SE, n = 9; Fig. 10).

5.3. Mechanism of Ba isotope fractionation during metamorphic dehydration

The $\delta^{138/134}$Ba of the type I eclogites at Bixiling (from −0.12 to −0.05‰) is lower than that of the Ganghe and Hualiangting eclogites from the Dabie orogen (from −0.01 to 0.03‰; Fig. 1) and the MORB average (Fig. 9a), but similar to that of some Hualiangting amphibolites (from −0.11 to −0.04‰; Gu et al., 2021). Since the Type I eclogites had experienced strong amphibolite-facies retrograde metamorphism and some of them have been partially transformed to garnet amphibolites, it is necessary to first assess whether their low $\delta^{138/134}$Ba is the result of amphibolite-facies overprinting. However, different from the Hualiangting amphibolites that do not contain phengite (Guo et al., 2017) and were formed by metasomatism of the external fluids from country gneisses with low $\delta^{138/134}$Ba (<-0.11‰; Gu et al., 2021), the type I eclogites at Bixiling contain phengite (Table S1) and the fluid responsible for amphibolite-facies retrogression may probably originate from the eclogites themselves (see section 5.1). As phengite, when it exists, dominates the whole-rock Ba budget and Ba isotopic compositions of the host eclogites (Gu et al., 2021), the consistent $\delta^{138/134}$Ba of the phengite separate and its host eclogite (Table 1) suggests that the amphibolite-facies retrograde metamorphism had limited effect on the whole-rock Ba isotopic compositions of the Bilixing eclogites. Consequently, the behavior of Ba isotope fractionation during dehydration of eclogites can be constrained by direct comparison between the Ba isotopic composition of the Type I eclogites and that of the vein-forming fluid.

The higher average $\delta^{138/134}$Ba of the vein-forming fluid (0.33 ± 0.03‰) than that of the Type I eclogites (−0.09 ± 0.01‰) suggests that Ba isotopes were significantly fractionated during metamorphic dehydration of the host eclogites at Bixiling, with the fluid preferentially enriched in heavy Ba isotopes. Generally, the chemical compositions of metamorphic fluids are strongly controlled by the dissolved minerals in the reacting eclogites during fluid-rock interaction (Zheng and Hermann, 2014; Guo et al., 2015). For instance, Gu et al. (2021) found that the high $\delta^{138/134}$Ba of the initial vein-forming fluids in the Ganghe and Hualiangting areas in the Dabie orogen were derived from the dissolved epidote in the host eclogites with heavy Ba isotopes. However, all of the Ba-rich minerals in the host eclogites at Bixiling, including phengite, biotite, epidote, and amphibole, display much lower $\delta^{138/134}$Ba than the vein-forming fluid (Fig. 9), indicating that the high $\delta^{138/134}$Ba of the vein-forming fluid cannot be directly inherited from dissolution of these minerals in the type I eclogites.

Alternatively, as the most important host mineral of LILE in metabasite, phengite dominates the Ba budget of eclogites, and thus its decomposition may release considerable amounts of both fluid and LILE (Schmidt and Poli, 1998; Guo et al., 2022) and account for the observed Ba isotope fractionation during dehydration of eclogites at Bixiling. The symplectitic coronas of biotite + plagioclase around phengite in the type I eclogites (Fig. 4d) demonstrate the occurrence of phengite breakdown during slab exhumation, possibly through the metamorphic reactions of phengite + omphacite → plagioclase + biotite + quartz + H_2O and/or phengite + garnet → plagioclase + biotite (±quartz, H_2O) (Heinrich, 1982; Franz et al., 1986; You et al., 2000; Zheng, 2009). Noteworthily, the $\delta^{138/134}$Ba of the biotite separates in the Type I eclogites ranges from −0.34 to −0.22‰, obviously lower than that of the phengite separates, which ranges from −0.16 to −0.05‰ (Fig. 10). Such a difference reveals that biotite, the major Ba-hosting decomposed product, prefers to take up light Ba isotopes during the breakdown reaction of phengite. This is consistent with theoretical expectations as Dahl (1996) indicated that white mica generally has a shorter Ba—O bond length and relatively stronger Ba—O bonding compared to biotite. Hence, light Ba isotopes will be preferentially enriched in biotite versus the coexisting phengite at thermal equilibrium. Additionally, the Ba concentration of biotite is higher than that of phengite (Fig. 10), while plagioclase after phengite in eclogites usually has a low Ba concentration (i.e., from 85 to 111 μg/g; Guo et al., 2022). Therefore, a mass balance estimate implies that the breakdown of phengite to biotite will release significant amounts of isotopically heavy Ba into the vein-forming fluid, with a large $\Delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid\text{-}Phn}}$ ($=\delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid}} - \delta^{138/134}\mathrm{Ba}_{\mathrm{Phn}}$) of about 0.40‰ (Fig. 10).

Despite the occurrence of significant Ba isotope fractionation during fluid release within the Bixiling eclogites, both the type I eclogites near and far away from the quartz veins have similar $\delta^{138/134}$Ba from −0.16 to −0.05‰ (Fig. 7h). This observation demonstrates that metamorphic dehydration did not significantly affect the whole-rock $\delta^{138/134}$Ba of the Bixiling eclogites. A similar phenomenon has been observed in the Ganghe and Hualiangting eclogites (Gu et al., 2021). The reason for such observations may be that phengite is still the dominant Ba-hosting mineral in eclogites, and hence phengite always controls the Ba isotopic composition of the whole rocks as long as it exists. Therefore, although a certain amount of isotopically heavy Ba was released from the eclogites into the vein-forming fluid during phengite breakdown, the residual phengite still dominates the whole-rock Ba isotopic composition of the host eclogites, so $\Delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid\text{-}eclogite}}$ ($=\delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid}} - \delta^{138/134}\mathrm{Ba}_{\mathrm{eclogite}}$) is approximately equal to $\Delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid\text{-}Phn}}$ (i.e., about 0.40‰). Considering the limited effect of both metamorphic dehydration and amphibolite-facies retrograde metamorphism on the whole-rock Ba isotopic compositions of the type I eclogites at Bixiling, their low $\delta^{138/134}$Ba values are most likely inherited from the protoliths.

5.4. Implication for the Ba isotopic systematics of subduction zones

Knowledge on the behavior of Ba isotope fractionation during dehydration processes provide important constraints on the Ba isotope characteristics of metamorphic fluids in subduction zones. Metamorphic fluids derived from subducted slabs are generally produced by the breakdown of a series of hydrous minerals such as serpentine, lawsonite, epidote, phengite, and talc. These dehydration reactions occur at different P-T conditions during prograde or retrograde metamorphism, releasing fluids with various element and isotopic compositions (Hermann et al., 2006; Zheng et al., 2011). For example, Gu et al. (2021) reported heavy Ba isotope characteristics of fluids derived from lawsonite breakdown in eclogites occurred at 2.8–3.0 GPa and 650–720 °C during the early stage of slab exhumation, which were probably inherited from the dissolved epidote with heavy Ba isotopes during strong fluid-eclogite interaction. Comparatively, this study reveals the behavior of Ba isotope fractionation during decomposition of phengite, which usually contains Ba budget several orders-of-magnitude higher than lawsonite and other hydrous minerals (Spandler et al., 2003), thus can further the understanding of the Ba isotopic systematics in subduction zones. Notably, phengite has a large stability range and can be stable up to very high-pressure conditions (i.e., 8.5 and 9.5 GPa in metapelites and metabasalts, respectively) during slab subduction (Schmidt et al., 2004). In contrast, numerous studies have shown that phengite breakdown commonly occurs during HP eclogite-facies to amphibolite-facies retrograde metamorphism at about 0.8–2.0 GPa and 600–700 °C (e.g., Gu et al., 2002; Zheng, 2009; McDonald et al., 2018). Besides the eclogites we investigated, the decomposition reactions of phengite can also be observed in many other exhumed HP-UHP rocks, such as metabasite, metapelite, impure marbles and felsic gneiss (e.g., Zhang et al., 2011; McDonald et al., 2018; Guo et al., 2019, 2022). Therefore, it is expected that a significant amount of isotopically heavy Ba can be released from various lithologies in exhumed slabs, which potentially influences the Ba budget and Ba isotopic compositions at convergent plate margins.

Moreover, although the fluids derived from phengite breakdown and from lawsonite breakdown both have heavy Ba isotopic compositions, they can be distinguished by the Ba/Th and $\delta^{138/134}$Ba. The fluid derived from phengite breakdown will be characterized by high Ba/Th as phengite dominates the Ba budget in eclogites (Zack et al., 2001), whereas the fluid derived from lawsonite breakdown may have low Ba/Th because lawsonite and its decomposed product, i.e., epidote, are both Th-rich minerals with low Ba concentrations (Guo et al., 2015). Another difference between these two types of metamorphic fluids is that the estimated $\Delta^{138/134}\mathrm{Ba}_{\mathrm{Fluid\text{-}eclogite}}$ is about 0.40‰ in the case of phengite breakdown (Fig. 10), while it is about 0.20‰ in the case of lawsonite breakdown (Gu et al., 2021). Therefore, metasomatism by fluids derived from different dehydration reactions of the subducted slab may lead to the Ba/Th and Ba isotopic heterogeneity in the mantle wedge, and thus Ba isotopes could be used to trace the origin of metasomatic fluid. Collectively, the behavior of Ba isotope fractionation during phengite breakdown revealed in this study is of fundamental importance for understanding the Ba isotopic cycling in subduction zones and the Ba isotopic budget of the mantle wedge.

6. Conclusions

This study reports the major-trace element and Sr-Nd-Ba isotopic compositions of UHP eclogites and hosted HP quartz veins at the Bixiling area from the Dabie UHP metamorphic belt. The following conclusions can be drawn:

(1) The metamorphic quartz veins and their host eclogites at Bixiling have similar Sr-Nd isotopic compositions, indicating that the vein-forming fluid was internally derived from the host eclogites.

(2) The quartz vein whole-rock samples (average $\delta^{138/134}$Ba = 0.39 ± 0.11‰, *n* = 6), the vein-hosted eclogites (average $\delta^{138/134}$Ba = 0.35 ± 0.04‰, *n* = 4), and the quartz separates from the veins (average $\delta^{138/134}$Ba = 0.31 ± 0.04‰, *n* = 5) have relatively consistent Ba isotopic compositions. The $\delta^{138/134}$Ba of the vein-forming fluid is estimated to be 0.33 ± 0.03‰ (2SE, *n* = 9), which is significantly higher than that of the host eclogites (−0.09 ± 0.01‰, 2SE, *n* = 9). This result indicates large Ba isotope fractionation between the vein-forming fluid and the host eclogites, with the fluid preferentially enriched in heavy Ba isotopes.

(3) The petrological observation of symplectitic coronas of biotite + plagioclase around phengite and the higher $\delta^{138/134}$Ba of phengite (from −0.16 to −0.05‰) than that of biotite (from −0.34 to −0.22‰) in the host eclogites suggest that the heavy Ba isotopic composition of the vein-forming fluid may originate from the retrograde breakdown of phengite to biotite in the host eclogites.

(4) As phengite is the dominant host mineral of Ba in HP-UHP continental crust rocks and its breakdown during slab exhumation commonly occurs, the resulting fluids with high Ba concentrations and heavy Ba isotopes would exert important effects on the cycle of Ba and its isotopes in subduction zones.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is financially supported by grants from the National Natural Science Foundation of China (41873005, 42273002, 41873009, 41503002), the Anhui Provincial Natural Science Foundation (2208085 J33), the Fundamental Research Funds for the Central Universities (WK2080000056), and the West Light Foundation of the Chinese Academy of Sciences (xbzg-zdsys-202108). We thank Ping Xiao for her help with the measurements of trace elements and Sr-Nd isotopes. We also thank Professor Yi-Can Liu and Dr. Shun Guo for their suggestions on the earlier version of this manuscript. The constructive comments from Dr. Yunchao Shu and two anonymous reviewers and efficient handling from Dr. Julie Prytulak and Dr. Jeffrey Catalano are greatly appreciated.

Appendix A. Supplementary material

Research data is provided within the Supplementary Material.

Supplementary material to this article can be found online at https://doi.org/10.1016/j.gca.2022.11.030.

References

Ames, L., Tilton, G.R., Zhou, G.Z., 1993. Timing of collision of the Sino-Korean and Yangtse cratons: U-Pb zircon dating of coesite-bearing eclogites. Geology 21, 339–342.

An, Y.J., Li, X., Zhang, Z.F., 2019. Barium isotopic compositions in thirty-four geological reference materials analysed by MC-ICP-MS. Geostand. Geoanal. Res. 44, 183–199.

Bai, R., Jackson, M.G., Huang, F., Moynier, F., Devos, G., Halldórsson, S.A., Lisiecki, L., Yin, H., Peng, Y., Nan, X., 2022. Barium isotopes in ocean island basalts as tracers of mantle processes. Geochim. Cosmochim. Acta 336, 436–447.

Bebout, G.E., 2007. Metamorphic chemical geodynamics of subduction zones. Earth Planet. Sci. Lett. 260, 373–393.

Bebout, G.E., 2014. Chemical and isotopic cycling in subduction zones. In: Turekian, K.K. (Ed.), Treatise Geochem. Elsevier, Oxford, pp. 703–747.

Becker, H., Jochum, K.P., Carlson, R.W., 1999. Constraints from high-pressure veins in eclogites on the composition of hydrous fluids in subduction zones. Chem. Geol. 160, 291–308.

Bridgestock, L., Hsieh, Y.-T., Porcelli, D., Homoky, W.B., Bryan, A., Henderson, G.M., 2018. Controls on the barium isotope compositions of marine sediments. Earth Planet. Sci. Lett. 481, 101–110.

Chavagnac, V., Jahn, B., 1996. Coesite-bearing eclogites from the Bixiling complex, Dabie mountains, China: Sm-Nd ages, geochemical characteristics and tectonic implications. Chem. Geol. 133, 29–51.

Chavagnac, V., Jahn, B.M., Villa, I.M., Whitehouse, M.J., Liu, D.Y., 2001. Multichronometric evidence for an in situ origin of the ultrahigh-pressure metamorphic terrane of Dabieshan, China. J. Geol. 109, 633–646.

Chen, T.N., Chen, R.X., Zheng, Y.F., Zhou, K., Yin, Z.Z., Wang, Z.-M., Gong, B., Zha, X.-P., 2022. The effect of supercritical fluids on Nb-Ta fractionation in subduction zones: Geochemical insights from a coesite-bearing eclogite-vein system. Geochim. Cosmochim. Acta 335, 23–55.

Chen, F., Satir, M., Ji, J., Zhong, D., 2002. Nd-Sr-Pb isotopes of Tengchong Cenozoic volcanic rocks from western Yunnan, China: evidence for an enriched-mantle source. J. Asian Earth Sci. 21, 39–45.

Chen, R.X., Zheng, Y.F., Gong, B., Zhao, Z.F., Gao, T.S., Chen, B., Wu, Y.B., 2007. Origin of retrograde fluid in ultrahigh-pressure metamorphic rocks: Constraints from mineral hydrogen isotope and water content changes in eclogite–gneiss transitions in the Sulu orogen. Geochim. Cosmochim. Acta 71, 2299–2325.

Chen, R.X., Zheng, Y.F., Hu, Z.C., 2012. Episodic fluid action during exhumation of deeply subducted continental crust: Geochemical constraints from zoisite–quartz vein and host metabasite in the Dabie orogen. Lithos 155, 146–166.

Chen, Y.X., Zhou, K., Zheng, Y.F., Chen, R.X., Hu, Z.C., 2015. Garnet geochemistry records the action of metamorphic fluids in ultrahigh-pressure dioritic gneiss from the Sulu orogen. Chem. Geol. 398, 46–60.

Dahl, P.S., 1996. The crystal-chemical basis for Ar retention in micas: Inferences from interlayer partitioning and implications for geochronology. Contrib. Mineral. Petrol. 123, 22–39.

Deng, G.X., Kang, J.T., Nan, X.Y., Li, Y.L., Guo, J.H., Ding, X., Huang, F., 2021. Barium isotope evidence for crystal-melt separation in granitic magma reservoirs. Geochim. Cosmochim. Acta 292, 115–129.

El Korh, A., Schmidt, S.T., Vennemann, T., Ulianov, A., 2011. Trace element and O-isotope composition of polyphase metamorphic veins of the Ile de Groix (Armorican Massif, France). In: Dobrzhinetskaya, L.F., Faryad, S.W., Wallis, S., Cuthbert, S. (Eds.), Ultrahigh-Pressure Metamorphism. Elsevier, London, pp. 243–291.

Enami, M., Banno, Y., 2001. Partitioning of Sr between coexisting minerals of the hollandite- and piemontite-groups in a quartz-rich schist from the Sanbagawa metamorphic belt, Japan. *Am. Mineral.* 86, 205–214.

Franz, G., Liebscher, A., 2004. Physical and chemical properties of the epidote minerals – An introduction. Rev. Minerl. Geochem. 56, 1–82.

Franz, G., Thomas, S., Smith, D.C., 1986. High-pressure phengite decomposition in the Weissenstein eclogite, Munchberger Gneiss Massif, Germany. *Contrib. Mineral. Petrol.* 92, 71–85.

Frei, D., Liebscher, A., Franz, G., Dulski, P., 2004. Trace element geochemistry of epidote minerals. Rev. Minerl. Geochem. 56, 553–605.

Götze, J., Pan, Y.M., Müller, A., 2021. Mineralogy and mineral chemistry of quartz: A review. Mineral. Mag. 85, 639–664.

Green, T.H., Adam, J., 2003. Experimentally-determined trace element characteristics of aqueous fluid from partially dehydrated mafic oceanic crust at 3.0 GPa, 650–700 °C. Eur. J. Mineral. 15, 815–830.

Gu, L.X., Du, J.G., Zhai, J.P., Zhao, C.H., Fan, J.G., Zhang, W.L., 2002. Eclogites of the Dabie region: Retrograde metamorphism and fluid evolution. Acta. Geol. Sin. Engl. 76, 166–182.

Gu, X.F., Guo, S., Yu, H.M., Xu, J., Huang, F., 2021. Behavior of barium isotopes during high-pressure metamorphism and fluid evolution. Earth Planet. Sci. Lett. 575, 117176.

Guo, S., Ye, K., Chen, Y., Liu, J.B., Mao, Q., Ma, Y.G., 2012. Fluid-rock interaction and element mobilization in UHP metabasalt: Constraints from an omphacite-epidote vein and host eclogites in the Dabie orogen. Lithos 136–139, 145–167.

Guo, S., Chen, Y., Ye, K., Su, B., Yang, Y.H., Zhang, L.M., Liu, J.B., Mao, Q., 2015. Formation of multiple high-pressure veins in ultrahigh-pressure eclogite (Hualiangting, Dabie terrane, China): Fluid source, element transfer, and closed-system metamorphic veining. Chem. Geol. 417, 238–260.

Guo, S., Tang, P., Su, B., Chen, Y., Ye, K., Zhang, L.M., Gao, Y.J., Liu, J.B., Yang, Y.H., 2017. Unusual replacement of Fe-Ti oxides by rutile during retrogression in amphibolite-hosted veins (Dabie UHP terrane): A mineralogical record of fluid-induced oxidation processes in exhumed UHP slabs. Am. Mineral. 102, 2268–2283.

Guo, S., Zhao, K.D., John, T., Tang, P., Chen, Y., Su, B., 2019. Metasomatic flow of metacarbonate-derived fluids carrying isotopically heavy boron in continental subduction zones: Insights from tourmaline-bearing ultra-high pressure eclogites and veins (Dabie terrane, eastern China). Geochim. Cosmochim. Acta 253, 159–200.

Guo, S., Su, B., John, T., Zhao, K.D., Tang, P., Chen, Y., Li, Y.B., 2022. Boron release and transfer induced by phengite breakdown in subducted impure metacarbonates. Lithos 408–409, 106548.

Hao, L.L., Nan, X.Y., Kerr, A.C., Li, S.Q., Wu, Y.B., Wang, H., Huang, F., 2022. Mg-Ba-Sr-Nd isotopic evidence for a mélange origin of early Paleozoic arc magmatism. Earth Planet. Sci. Lett. 577, 117263.

Hart, S.R., Gerlach, D.C., White, W.M., 1986. A possible new Sr-Nd-Pb mantle array and consequences for mantle mixing. Geochim. Cosmochim. Acta 50, 1551–1557.

Heinrich, C.A., 1982. Kyanite-eclogite to amphibolite facies evolution of hydrous mafic and pelitic rocks, Adula-Nappe, Central Alps. Contrib. Mineral. Petrol. 81, 30–38.

Hermann, J., Spandler, C., Hack, A., Korsakov, A.V., 2006. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zones. Lithos 92, 399–417.

Hou, Z.H., Wang, C.X., 2007. Determination of 35 trace elements in geological samples by inductively coupled plasma mass spectrometry. J. Univ. Sci. Technol. China 37, 940–944. in Chinese with English abstract.

Huang, J., Xiao, Y., Gao, Y., Hou, Z., Wu, W., 2012. Nb-Ta fractionation induced by fluid-rock interaction in subduction-zones: constraints from UHP eclogite- and vein-hosted rutile from the Dabie orogen, Central-Eastern China. J. Metamorph. Geol. 30, 821–842.

Huang, J., Guo, S., Jin, Q.Z., Huang, F., 2020. Iron and magnesium isotopic compositions of subduction-zone fluids and implications for arc volcanism. Geochim. Cosmochim. Acta 278, 376–391.

Kessel, R., Schmidt, M.W., Ulmer, P., Pettke, T., 2005. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. Nature 437, 724–727.

Larsen, R.B., Polvê, M., Juve, G., 2000. Granite pegmatite quartz from Evje-Iveland: trace element chemistry and implications for the formation of high-purity quartz. Norges Geologiske Undersøkelse 436, 57–66.

Larsen, R.B., Henderson, I., Ihlen, P.M., Jacamon, F., 2004. Distribution and petrogenetic behaviour of trace elements in granitic pegmatite quartz from South Norway. Contrib. Mineral. Petrol. 147, 615–628.

Li, S.G., Jagoutz, E., Chen, Y.Z., Li, Q.L., 2000. Sm-Nd and Rb-Sr isotopic chronology and cooling history of ultrahigh pressure metamorphic rocks and their country rocks at Shuanghe in the Dabie Mountains, Central China. *Geochim. Cosmochim. Acta* 64, 1077–1093.

Li, W.Y., Teng, F.Z., Xiao, Y.L., Huang, J., 2011. High-temperature inter-mineral magnesium isotope fractionation in eclogite from the Dabie orogeny, China. *Earth Planet. Sci. Lett.* 304, 224–230.

Li, S.G., Xiao, Y.L., Liou, D.L., Chen, Y.Z., Ge, N.J., Zhang, Z.Q., Sun, S.S., Cong, B.L., Zhang, R.Y., Hart, S.R., Wang, S.S., 1993. Collision of the North China and Yangtse Blocks and formation of coesite-bearing eclogites: Timing and processes. Chem. Geol. 109, 89–111.

Li, Y.H., Yu, H.M., Gu, X.F., Guo, S., Huang, F., 2020. Silicon isotopic fractionation during metamorphic fluid activities: constraints from eclogites and ultrahigh-pressure veins in the Dabie orogeny, China. *Chem. Geol.* 540, 119550.

Li, X.P., Zheng, Y.F., Wu, Y.B., Chen, F.K., Gong, B., Li, Y.L., 2004. Low-T eclogite in the Dabie terrane of China: petrological and isotopic constraints on fluid activity and radiometric dating. Contrib. Mineral. Petrol. 148, 443–470.

Liu, Y.C., Gu, X.F., Li, S.G., Hou, Z.H., Song, B., 2011. Multistage metamorphic events in granulitized eclogites from the North Dabie complex zone, central China: Evidence from zircon U-Pb age, trace element and mineral inclusion. Lithos 122, 107–121.

Liu, D.Y., Jian, P., Kröner, A., Xu, S.T., 2006. Dating of prograde metamorphic events deciphered from episodic zircon growth in rocks of the Dabie-Sulu UHP complex, China. *Earth Planet. Sci. Lett.* 250, 650–666.

Liu, F.L., Liou, J.G., 2011. Zircon as the best mineral for P-T-time history of UHP metamorphism: A review on mineral inclusions and U-Pb SHRIMP ages of zircons from the Dabie-Sulu UHP rocks. J. Asian Earth Sci. 40, 1–39.

McDonald, C.S., Regis, D., Warren, C.J., Kelley, S.P., Sherlock, S.C., 2018. Recycling argon through metamorphic reactions: The record in symplectites. Lithos 300, 200–211.

Mcdonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chem. Geol. 120, 223–253.

Nan, X.Y., Wu, F., Zhang, Z.F., Hou, Z.H., Huang, F., Yu, H.M., 2015. High-precision barium isotope measurements by MC-ICP-MS. J. Anal. At. Spectrom. 30, 2307–2315.

Nan, X.Y., Yu, H.M., Rudnick, R.L., Gaschnig, R.M., Xu, J., Li, W.Y., Zhang, Q., Jin, Z.D., Li, X.H., Huang, F., 2018. Barium isotopic composition of the upper continental crust. Geochim. Cosmochim. Acta 233, 33–49.

Nan, X.Y., Yu, H.M., Kang, J.T., Huang, F., 2022. Re-visiting barium isotope compositions of mid-ocean ridge basalts and the implications. J. Univ Sci. Technol. China 52. 1 (7 pp).

Nielsen, S.G., Horner, T.J., Pryer, H.V., Blusztajn, J., Shu, Y., Kurz, M.D., Le Roux, V., 2018. Barium isotope evidence for pervasive sediment recycling in the upper mantle. Sci. Adv. 4, eaas8675.

Nielsen, S.G., Shu, Y.C., Auro, M., Yogodzinski, G., Shinjo, R., Plank, T., Kay, S.M., Horner, T.J., 2020. Barium isotope systematics of subduction zones. Geochim. Cosmochim. Acta 275, 1–18.

Okay, A.I., 1993. Petrology of a diamond and coesite-bearing metamorphic terrain: Dabie Shan, China. *Eur. J. Mineral.* 5, 659–675.

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.

Schmidt, M.W., Poli, S., 1998. Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth Planet. Sci. Lett. 163, 361–379.

Schmidt, M.W., Vielzeuf, D., Auzanneau, E., 2004. Melting and dissolution of subducting crust at high pressures: the key role of white mica. Earth Planet. Sci. Lett. 228, 65–84.

Sheng, Y.M., Xia, Q.K., Dallai, L., Yang, X.Z., Hao, Y.T., 2007. H_2O contents and D/H ratios of nominally anhydrous minerals from ultrahigh-pressure eclogites of the Dabie orogen, eastern China. Geochim. Cosmochim. Acta 71, 2079–2103.

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., 2006. High-pressure veins in eclogite from New Caledonia and their significance for fluid migration in subduction zones. Lithos 89, 135–153.

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. Mineral. 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. Spec. Publ. 42, 313–345.

van Zuilen, K., Nägler, T.F., Bullen, T.D., 2016. Barium isotopic compositions of geological reference materials. Geostand. Geoanal. Res. 40, 543–558.

Wang, X.M., Liou, J.G., Mao, H.K., 1989. Coesite-bearing eclogite from the Dabie mountains in central China. Geology 17, 1085–1088.

Wei, C.J., Qian, J.H., Tian, Z.L., 2013. Metamorphic evolution of medium-temperature ultra-high pressure (MT-UHP) eclogites from the South Dabie orogen, Central China: an insight from phase equilibria modelling. J. Metamorph. Geol. 31, 755–774.

Wu, F., Turner, S., Schaefer, B.F., 2020. Mélange versus fluid and melt enrichment of subarc mantle: A novel test using barium isotopes in the Tonga-Kermadec arc. Geology 48, 1053–1057.

Xiao, Y.L., Hoefs, J., van den Kerkhof, A.M., Fiebig, J., Zheng, Y.F., 2000. Fluid history of UHP metamorphism in Dabie Shan, China: a fluid inclusion and oxygen isotope study on the coesite-bearing eclogite from Bixiling. Contrib. Mineral. Petrol. 139, 1–16.

Xiao, Y.L., Hoefs, J., van den Kerkhof, A.M., Simon, K., Fiebig, J., Zheng, Y.F., 2002. Fluid evolution during HP and UHP metamorphism in Dabie Shan, China: Constraints from mineral chemistry, fluid inclusions and stable isotopes. J. Petrol. 43, 1505–1527.

Xu, S.T., Okay, A.I., Ji, S.Y., Sengor, A.M.C., Wen, S., Liu, Y.C., Jiang, L.L., 1992. Diamond from the Dabie shan metamorphic rocks and its implication for tectonic setting. Science 256, 80–82.

Xu, Z., Zheng, Y.F., Zhao, Z.F., 2022. Barium isotope fractionation during dehydration melting of the subducting oceanic crust: Geochemical evidence from OIB-like continental basalts. Chem. Geol. 594, 120751.

You, Z.D., Suo, S.T., Zhong, Z.Q., 2000. Retrogressive microstructures in high-pressure and ultrahigh-pressure metamorphic rocks in the Dabie Mountains: Enlightenment to the exhumation process. Acta Geol. Sin. 74, 224–233. in Chinese with English abstract.

Yu, H.M., Nan, X.Y., Wu, F., Widom, E., Li, W.Y., Kuentz, D., Huang, F., 2022. Barium isotope evidence of a fluid-metasomatized mantle component in the source of Azores OIB. Chem. Geol. 610, 121097.

Zack, T., John, T., 2007. An evaluation of reactive fluid flow and trace element mobility in subducting slabs. Chem. Geol. 239, 199–216.

Zack, T., Rivers, T., Foley, S.F., 2001. Cs-Rb-Ba systematics in phengite and amphibole: an assessment of fluid mobility at 2.0 GPa in eclogites from Trescolmen, Central Alps. *Contrib. Mineral. Petrol.* 140, 651–669.

Zhang, R.Y., Liou, J.G., Cong, B.L., 1995. Talc-, magnesite- and Ti-clinohumite-bearing ultrahigh-pressure meta-mafic and ultramafic complex in the Dabie mountains, China. *J. Petrol.* 36, 1011–1037.

Zhang, Z.M., Shen, K., Liou, J.G., Dong, X., Wang, W., Yu, F., Liu, F., 2011. Fluid-rock interactions during UHP metamorphism: A review of the Dabie-Sulu orogen, east-central China. J. Asian Earth Sci. 42, 316–329.

Zhao, Y.P., Tang, Y.J., Xu, J., Zeng, Z., Ying, J.F., Tian, H.C., Huang, F., 2021. Barium isotope evidence for recycled crustal materials in the mantle source of continental basalts. Lithos 390–391, 106111.

Zheng, Y.F., 2008. A perspective view on ultrahigh-pressure metamorphism and continental collision in the Dabie-Sulu orogenic belt. Chin. Sci. Bull. 53, 3081–3104.

Zheng, Y.F., 2009. Fluid regime in continental subduction zones: petrological insights from ultrahigh-pressure metamorphic rocks. J. Geol. Soc. Lond. 166, 763–782.

Zheng, Y.F., Fu, B., Xiao, Y.L., Li, Y.L., Gong, B., 1999. Hydrogen and oxygen isotope evidence for fluid-rock interactions in the stages of pre- and post-UHP metamorphism in the Dabie Mountains. Lithos 46, 677–693.

Zheng, Y.F., Fu, B., Gong, B., Li, L., 2003. Stable isotope geochemistry of ultrahigh pressure metamorphic rocks from the Dabie-Sulu orogen in China: implications for geodynamics and fluid regime. Earth-Sci. Rev. 62, 105–161.

Zheng, Y.F., Gao, T.S., Wu, Y.B., Gong, B., Liu, X.M., 2007. Fluid flow during exhumation of deeply subducted continental crust: zircon U-Pb age and O-isotope studies of a quartz vein within ultrahigh-pressure eclogite. J. Metamorph. Geol. 25, 267–283.

Zheng, Y.F., Hermann, J., 2014. Geochemistry of continental subduction-zone fluids. Earth Planets Space 66, 1–16.

Zheng, Y.F., Xia, Q.X., Chen, R.X., Gao, X.Y., 2011. Partial melting, fluid supercriticality and element mobility in ultrahigh-pressure metamorphic rocks during continental collision. Earth-Sci. Rev. 107, 342–374.