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Key Points:

- Garnet, phengite, and apatite record HP fluid-aided alteration in an eclogite-vein system from the Dabie UHP terrane
- The active HP fluid is a Si-Al-Na-Ba-rich aqueous fluid formed closed to the wet solidus
- A high fluid flux caused considerable element mobility during the vein formation

Supporting Information:

- Supporting Information S1
- Table S1
- Table S2
- Table S3
- Table S4

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High-Pressure Fluid-Rock Interaction and Mass Transfer During Exhumation of Deeply Subducted Rocks: Insights From an Eclogite-Vein System in the Ultrahigh-Pressure Terrane of the Dabie Shan, China

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Abstract A petrological study was performed on an eclogite-vein system from the Dabie ultrahigh-pressure terrane by focusing on high-pressure (HP) fluid-rock interaction and mass transfer during exhumation. The veins comprise mainly garnet and quartz and resulted from a HP leaching process along fractures in the eclogite during exhumation. Relict peak garnet, phengite, and apatite in this rock system were altered by HP fluids forming characteristic compositional zonings. Zoned garnet in the eclogite records an isothermal exhumation from 3.3 GPa and 665–680 °C. Partial dissolution of garnet and a back incorporation of Mn-heavy rare earth element (REE)-Y increased the content of these elements in the altered garnet zone in the veins. Altered phengite is characterized by a Ba-rich rim. Fluid-aided alteration reduced the light REE (LREE) contents and produced oriented monazite, calcite, and pyrrhotite inclusions within apatite, reflecting mobilization and redistribution of LREEs, CO₃²⁻, Fe, and S between these minerals. The active HP fluid is proposed to have been a Si-Al-Na-Ba-rich aqueous fluid, as indicated by sodic plagioclase rims around various eclogitic minerals and by the altered phengite composition. Mass balance calculations reveal that LREEs, middle REEs, and Zr-Hf-Th-U were added to and Li, large ion lithophile elements, and Ti-Nb were removed from the quartz-garnet veins, requiring a high fluid flux. These findings shed new light on the nature and behavior of HP fluids and highlight their key role in resetting mineral chemistry and mass transfer in subduction zone metamorphic environments.

1. Introduction

The migration of fluids governs mass and sometimes heat transfer between the different geological realms of oceanic crust and mantle in subduction zones. Slab-derived fluids associated with subduction zone high-pressure (HP) and ultrahigh-pressure (UHP) metamorphism are responsible for mantle wedge metasomatism, the production of arc magmas (e.g., McCulloch & Gamble, 1991; Schmidt & Poli, 1998), and the formation of large ore deposits (e.g., Rosenbaum et al., 2005; Sun et al., 2004). Furthermore, they can promote metamorphic reequilibration (e.g., Austrheim, 1987; Konrad-Schmolke et al., 2011) and trigger earthquakes (e.g., Davies, 1999; Viete et al., 2018). Therefore, decoding the nature and behavior of HP-UHP fluids in subducted slabs is crucial for constraining geophysical and geochemical processes in subduction zones.

The direct action of HP-UHP fluids in subduction zones is inaccessible. Petrological modeling provides a theoretical basis for understanding the fluid nature at elevated pressure-temperature (P-T) conditions. As reviewed in Hermann et al. (2006), slab-derived fluids are commonly dilute aqueous fluids (i.e., a H₂O-dominated solution dissolving variable components such as silicate and carbonate) at subsolidus conditions if the pressure is below the second critical point of an H₂O-saturated rock system. The solute content in aqueous fluids increases with pressure and/or temperature. If the pressure exceeds the second critical point, the solute contents in aqueous fluids can increase considerably with temperature within a certain temperature range. More recent experimental studies have shown that HP aqueous fluids could dissolve up to 10 wt.% Na-Al-Si components during pre-melting polymerization and become less dilute if the temperature is close to the wet solidus of the albite/jadeite + paragonite + quartz system (Manning et al., 2010; Wohlers et al., 2011). Such solute-rich aqueous fluids in natural metamorphic rocks have rarely been discussed in the literature.

Various types of HP veins have been documented in HP-UHP metamorphic rocks (Ague, 2014; Bebout & Penniston-Dorland, 2016). Guo et al. (2012) even found coesite-bearing veins in UHP eclogites from the Dabie orogen. HP-UHP veins usually resulted from channelized advection of reactive fluids along fractures in the host lithologies (e.g., Beinlich et al., 2010; Guo et al., 2012; John et al., 2008; Li et al., 2013; Lü et al., 2012; Spandler & Hermann, 2006; Taetz et al., 2016), whereas fluid-aided segregation in locally closed rock systems could also lead to their formation (Widmer & Thompson, 2001). Such veins could be formed during both prograde (e.g., Beinlich et al., 2010; John et al., 2008; Li et al., 2013; Spandler & Hermann, 2006) and retrograde (e.g., Chen et al., 2012; Guo et al., 2012; Lü et al., 2012) stages. Either external or internal fluids could be responsible for the formation of HP-UHP veins. In the former case, the veins are usually lined by altered selvages of the host rock, whereas in the latter case such altered selvages are often not present (cf. Taetz et al., 2016). Through mass balance calculations, quantitative constraints can be placed on the element mobility accompanying vein formation (e.g., Beinlich et al., 2010; Guo et al., 2012; John et al., 2008; Li et al., 2013; Spandler & Hermann, 2006; Taetz et al., 2016). Thus, HP-UHP veins, together with their host rocks, provide a good opportunity to trace fluid activity and to investigate fluid-rock interaction and mass transfer in deep subduction zones.

The common occurrence of veins in HP-UHP rocks could be due to fluid advection through major fluid conduits in deep subduction zones. Nevertheless, pervasive fluid advection at eclogite-facies conditions has also been suggested (e.g., Giuntoli, Lanari, Burn, et al., 2018; Giuntoli, Lanari, & Engi, 2018; Halama et al., 2014; Konrad-Schmolke et al., 2011; Liu, Massonne, Wu, et al., 2017). Focused fluid advection could lead to both macroscopic and microscopic alteration of the fluid-altered rocks. In contrast, pervasive fluid advection often causes microscopic alteration along mineral grain boundaries, which can result in metasomatic zoning in minerals (Giuntoli, Lanari, & Engi, 2018; Halama et al., 2014; Konrad-Schmolke et al., 2011; Liu, Massonne, Wu, et al., 2017). In some cases, the metasomatic fluid composition could be quantitatively constrained based on the altered mineral composition (Liu, Massonne, Wu, et al., 2017). New minerals can also be produced. Apatite is a common accessory phase in HP-UHP rocks, which is sensitive to fluid alteration (Harlov, 2015). Apatite altered by fluids usually contains oriented mineral (e.g., monazite, dolomite, pyrrhotite) inclusions (e.g., Broska et al., 2014; Hansen & Harlov, 2007; Harlov & Förster, 2002; Janots et al., 2018; Liu, Massonne, Wu, et al., 2017; Zhu & Massonne, 2005). Either case is helpful in tracing the fluid activity and decoding the nature and behavior of fluids in deep subduction zones.

In this study, we investigate an eclogite-vein system from the Dabie UHP terrane that records fluid-rock interaction under HP recrystallization conditions during exhumation. Both focused and pervasive fluid advectations are documented. We characterize the compositional zonings of relict peak minerals (garnet, phengite, and apatite) and oriented mineral inclusions in apatite, which are related to fluid-aided alteration, and discuss their formation mechanism. The nature of the active HP fluid is constrained in detail. Finally, the element mobility and mass transfer leading to the vein formation are quantitatively estimated through mass balance calculations.

2. Geological Setting and Sampling

The Dabie-Sulu orogenic belt in east-central China is considered to be one of the largest UHP terranes on Earth. This belt resulted from the Triassic continental collision between the North China and South China blocks (Ernst et al., 2007; Li et al., 1993; Zhang et al., 2009). It is separated into the eastern Sulu terrane and the western Dabie terrane by the sinistral Tanlu strike-slip fault. The western part of the Dabie terrane is further truncated by the Shangma fault and known as the Hongan terrane (Figure 1a).

Several large-scale EW trending faults divide the Dabie terrane into five major lithotectonic units with different metamorphic histories (Hacker et al., 2000; Zheng et al., 2005). From north to south, these units are (1) the Beihuaiyang greenschist-facies unit made up of low-grade metasedimentary and metaigneous rocks that are overlain by Jurassic-Cretaceous sedimentary and volcanic rocks; (2) the North Dabie high-T granulite-facies unit composed of typical amphibolite- to granulite-facies rocks, migmatitic gneisses, and minor mafic to ultramafic rocks; (3) the Central Dabie medium-T/UHP eclogite-facies unit including abundant orthogneisses and paragneisses that enclose subordinate bodies of coesite-bearing eclogite, pure to impure marble, calc-silicate rock, jadeite quartzite, and ultramafic rock; (4) the South Dabie low-T eclogite-facies unit characterized by low-T eclogites; and (5) the Susong blueschist-facies unit (Figure 1a).

Figure 1. (a) Geological sketch map of the Qinling-Dabie-Sulu orogen, following Zheng et al. (2005). Note that extensive amphibolite-facies rocks with granulite-facies and UHP relics are also present in Qinling to the northwest of the Dawu fault (Wu & Zheng, 2013). (b) Regional geographic context, following Schmid et al. (2000). The village of Ganjialing, from where the eclogite-vein system (GJL12-4) was collected, is indicated by a red triangle.

The whole Dabie terrane was intruded by extensive Early Cretaceous granitoid (e.g., Chen et al., 2002; Zhang et al., 2002).

Coesite has been reported in various rocks from the Central Dabie medium-T/UHP eclogite-facies unit. The discovery of coesite in zircon from amphibolite-facies gneisses led Liu et al. (2001) to suggest that the whole rock sequence in this unit experienced an in situ UHP metamorphism. In addition to coesite, some other UHP indicators have also been reported, such as diamond (Xu et al., 1992; Xu et al., 2005), magnetite lamellae in olivine (Zhang et al., 1999), α - PbO_2 -type TiO_2 lamellae in rutile (Wu et al., 2005), and clinoenstatite exsolution in clinopyroxene (Liu et al., 2007). Peak P-T conditions for the Dabie UHP rocks are normally constrained to 3.0–4.5 GPa and 650–750 °C (e.g., Carswell et al., 1997; Guo et al., 2012; Liu et al., 2015; Okay, 1993; Schmid et al., 2000; Wei et al., 2013). A nearly isothermal decompression is commonly envisaged after the peak UHP metamorphism, which was followed by an amphibolite- to epidote-amphibolite-facies overprint. Zircon dating reveals protracted UHP metamorphism from 240 to 225 Ma and 215–205 Ma for the amphibolite-facies retrogression, indicating an exhumation rate on the order of approximately 3–10 mm per year during the early stage (Liu & Liou, 2011; Zheng et al., 2009).

The Dabie UHP rocks commonly have a protolith that formed in a continental rift setting to the north margin of the South China block in the middle Neoproterozoic. The protolith experienced extensive meteoric-hydrothermal alteration and obtained extremely negative $\delta^{18}\text{O}$ values before deep subduction (Zheng et al., 2003). The preservation of such an oxygen isotope signature in these rocks after deep subduction suggests limited fluid activities during UHP metamorphism (Rumble et al., 2000; Zhang et al., 2009; Zheng et al., 2003). During exhumation, the fluid activities became stronger, as recorded by the formation of amphibole

Figure 2. Image of a polished cross section of the eclogite-vein system. The coin is 19.05 mm in diameter. Note that some scratches from the cutting saw are still left on the polished surface.

and zoisite porphyroblasts (Massonne, 2012) and the wide occurrence of various eclogite-facies veins in UHP rocks (e.g., Chen et al., 2012; Guo et al., 2012; Liu et al., 2015; Zhang et al., 2008; Zheng et al., 2007). These veins generally consist of various combinations of quartz, kyanite, epidote-group minerals, garnet, omphacite, phengite, paragonite, rutile, and apatite, most of which were directly precipitated from the circulating aqueous fluids. In some cases, coesite can be observed in the vein minerals (Guo et al., 2012). Such observations suggest that these veins mainly formed during the transition from the UHP to the HP recrystallization stages being consistent with zircon dating results (Chen et al., 2012; Zheng et al., 2007).

Sample GJL12-4, investigated here, was collected at a small blasted outcrop (GPS coordinates: N30°38.666', E116°19.619') in the Ganjialing area in the central Dabie medium-T/UHP eclogite-facies unit (Figure 1b). Villagers blasted this outcrop to make space for a house and many fresh loose boulders were thus extracted. Impure dolomite marble and calc-silicate rock constitute the main rock types at this outcrop and enclose eclogite blocks/boudins with various sizes (Liu et al., 2015). GJL12-4 is a small loose boulder of eclogite hosting centimeter-sized quartz-garnet veins (Figure 2). It is believed to have been enclosed by the marbles as dolomite is a rock-forming mineral in the sample, which is a common feature for those in situ eclogites in the marble. Earlier studies of the impure marbles have led to the discovery of coesite inclusions in dolomite and the derivation of peak P-T conditions of 4.2 ± 0.32 GPa and 745 ± 65 °C (Liu et al., 2015). In addition, intergranular coesite has been found in a dolomite-rich metasedimentary rock from this outcrop (Liu, Massonne, Zhang, et al., 2017).

3. Analytical Methods

The petrography of our samples was carefully examined on thin sections by a polarizing microscope and a FEI Quanta 450 FEG scanning electron microscope with an Oxford INCA X-Max 50 energy dispersive spectrometer, used for semiquantitative analysis, at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (CUG), Wuhan. A CL8200 MK5 microscope was additionally applied for petrographic observations at the State Key Laboratory of Biogeology and Environmental Geology, CUG, Wuhan. The working voltage and beam current were 12.1 kV and 198 μ A, respectively.

Raman spectra of apatite were acquired using a Renishaw RM-1000 Raman spectrometer (532 nm line of an Ar⁺ laser, an output power of 22 mW, gratings 1,800 lines per millimeter, and confocal mode) equipped with a Leica microscope at the GPMR. The 521 cm^{-1} signal produced by a synthetic monocrystalline Si standard was used for calibrating the spectrometer.

Bulk-rock compositions were determined at the GPMR. The major element compositions were measured by X-ray fluorescence (XRF) on fused glass disks, using a Shimadzu XRF-1800 sequential XRF spectrometer. Prior to analysis, the loss on ignition was determined by heating the dried rock powders to 1000 °C for 90 min. The trace element compositions were analyzed by an Agilent 7500a inductively coupled mass spectrometry (ICP-MS) after digestion of about 20 mg samples by HF + HNO₃ in Teflon bombs. More details on the analytical procedures, precision, and accuracy of the bulk-rock compositions have been described in Ma et al. (2012) and Liu, Zong, et al. (2008), respectively.

Major element compositions of all minerals were measured using two JEOL JXA-8100 electron microprobes (EMPs) with four wavelength dispersive X-ray spectrometers at the GPMR and the Key Laboratory of Submarine Geosciences, State Oceanic Administration, Hangzhou. The analyses were performed with 1–5 μ m beam diameter, 15 kV accelerating voltage, 20 nA beam current, and 10–30 s counting time on peak and background each per specific K α and Ba L α radiation. Natural and synthetic minerals and oxides were used as standards. The ZAF method was applied for matrix correction. Reproducibility and accuracy are better than 2% and 5% (1 σ) if the oxide contents are >1% and <1%, respectively.

Major element analyses of garnet, mica, amphibole, epidote, plagioclase, and apatite were also conducted with a CAMECA SX100 EMP at the Institut für Mineralogie und Kristallchemie, Universität Stuttgart. The working conditions were 15 kV accelerating voltage, 20 nA beam current, and 10–30 s counting time on peak and background each (except 60 s for S in apatite). Either a focused beam or a scan mode was used depending on the variation and size of the analyzed minerals. Natural and synthetic minerals and oxides were used as standards. The PaP correction procedure provided by CAMECA was applied for matrix correction. Analytical errors have been reported by Massonne (2012). X-ray maps of selected elements in minerals were obtained using the CAMECA EMP with an accelerating voltage of 15 kV, a beam current of 50 nA, a pixel size of 2–4 μm , and dwell time of 100 ms per pixel.

Trace element compositions of minerals were determined in situ on thin sections using laser ablation (LA)-ICP-MS at the GPMR. Laser sampling was performed by a GeoLas 2005 system equipped with a 193 nm ArF-excimer laser. The laser beam size, frequency, and energy were 32 or 44 μm , 6 Hz, and 70 mJ, respectively. An Agilent 7500a ICP-MS was used to determine ion-signal intensities. Helium was the carrier gas and mixed with Ar through a T-connector before entering the ICP. Nitrogen was introduced into the central gas flow (Ar + He) of the Ar plasma to improve the detection limit and precision (Hu et al., 2008). For each analysis, the Agilent Chemstation was used to determine the background intensity for 20 s followed by 50 s for the sample analysis. The off-line selection and integration of background and sample signals, time drift correction, and quantitative calibration were processed using the program ICPMSDataCal (Liu, Hu, et al., 2008). The element concentrations were calibrated against multiple USGS reference glasses of BIR-1G, BCR-2G, and BHVO-2G without using an internal standard (Liu, Hu, et al., 2008). Reproducibility and accuracy were assessed to be better than $\pm 10\%$ (1σ) for most trace elements based on repeated analyses of the reference materials.

4. Petrography

Petrographic features of the eclogite-vein system (GJL12-4) have been briefly presented in Liu et al. (2018), which focused on the formation of composite mineral inclusions in garnet, and here are given in more detail. Six thin sections were prepared for different parts of the host eclogite, which reveal very similar petrographic features. The eclogite displays a fine- to medium-grained texture and partially preserved the peak mineral assemblage of garnet, omphacite, phengite, coesite, dolomite, magnesite, rutile, apatite, zircon, and pyrite. Garnet appears as granoblastic and atoll-shaped grains with a size of 0.1–1.5 mm (Figures 3a and 3b). It often forms aggregates and contains inclusions of omphacite (Figure 3c), coesite (Figure 5b), quartz, rutile, apatite, and zircon. Omphacite has been completely replaced by a symplectite of amphibole + plagioclase in the matrix and is only preserved as inclusions in garnet (Figure 3c). Phengite occurs as subhedral flakes (0.5–2 mm; Figures 3d–3f) that are locally surrounded by a corona of epidote. Dolomite has a grain size of 0.2–0.8 mm and contains coesite inclusions (Figure 3g). Magnesite, rutile, apatite, zircon, and pyrite are accessory phases, with magnesite only found as inclusions in dolomite (Figure 3g). Albite rims occur along the grain boundaries of garnet, apatite, dolomite, rutile, and quartz displaying a corroded texture (Figures 3h and 3i). Calcite appears in some albite rims around apatite (Figures 3i and 5b). Plagioclase + quartz associations, characterized by irregular quartz grains that are corroded and surrounded by plagioclase, are present in the eclogite. Plagioclase in the associations usually partially replaced phengite, within which small biotite blebs (often forming clusters) are embedded (Figures 3d–3f). The eclogite is heavily retrogressed, mainly characterized by relatively early formed xenoblasts and coronae of epidote and amphibole and by the later amphibole + plagioclase symplectites (Figures 3a, 3b, and 3f–3h). The xenoblasts and coronae display signs of corrosion if they are in contact to the albite rim or the plagioclase + quartz association (Figures 3b, 3f, and 3h). Epidote xenoblasts may enclose an allanite core and garnet relicts (Figures 3d and 3f).

The quartz-garnet vein, in sharp contact to the host eclogite, has a width from less than one to three centimeters (Figures 2 and 3a). Five thin sections prepared reveal an identical mineral assemblage and homogeneous microstructures. The veins consist of garnet (40–45 vol.%), quartz (40–45 vol.%), plagioclase (5–7 vol.%), amphibole (2–3 vol.%), apatite (1–2 vol.%), and epidote-allanite (1 vol.%) (Figure 4). Accessory minerals are phengite, K-feldspar, chlorite, rutile, ilmenite, titanite, calcite, pyrite, and zircon. Garnet (0.1–1.8 mm) is typically xenoblastic (Figure 4a) and locally partially replaced by epidote or amphibole. Inclusions of quartz, rutile, apatite, and zircon, but not relict coesite were observed in garnet. Composite mineral inclusions

Figure 3. Petrography of the eclogite. (a) Sharp contact between the eclogite and quartz-garnet vein, plane polarized light (PPL). (b) Representative mineral assemblage in the eclogite, PPL. (c) Composite inclusion of omphacite + K-feldspar + chlorite in garnet, backscattered electron (BSE) image. (d–f) Zoned phengite and epidote: phengite is characterized by a Ba-rich rim; epidote contains an allanite core and relict garnet. Note that both the phengite and the epidote are corroded by the plagioclase (BSE-brighter) + quartz (BSE-darker) association. (d) Crossed polarized light (CPL) and (e, f) BSE images. (g) Coesite and magnesite inclusions in dolomite, PPL. The dolomite grain is only partly shown to highlight the coesite inclusion, which is partly replaced by quartz along its rim. (h) Albite rim along the quartz-garnet-rutile grain boundary, CPL. Note that the albite rim corrodes the quartz but not the garnet. (i) Albite rim along the apatite-garnet grain boundary, CPL. Minor calcite occurs in the albite rim, also see Figure 5b. The larger apatite grain contains dense oriented monazite inclusions. Abbreviations used in this paper: Ab = albite; Ae = aegirine; Alm = almandine; Aln = allanite; Amp = amphibole; Ap = apatite; Bt = biotite; Cal = calcite; Chl = chlorite; Coe = coesite; Dia = diamond; Dol = dolomite; Ep = epidote; Gra = graphite; Gro = grossular; Grt = garnet; Ilm = ilmenite; Jd = jadeite; Kfs = K = feldspar; Law = lawsonite; Mgs = magnesite; Mz = monazite; Olg = oligoclase; Omp = omphacite; Pa = paragonite; Phn = phengite; Pl = plagioclase; Po = pyrrhotite; Prp = pyrope; Py = pyrite; Q = quartz; Ru = rutile; Sp = spessartine; Sym = symplectite; Tlc = talc; Ttn = titanite; Zr = zircon.

resulting from reactions between infiltrating fluids and precursor mineral inclusions are common (see Liu et al., 2018). Quartz (0.1–1.0 mm) is granoblastic and may contain numerous fluid inclusions. Plagioclase occurs as thin rims along the grain boundaries of garnet, quartz, apatite, rutile, and ilmenite, which may grade into wide bands or irregular pools (Figures 4b–4e). In addition to tiny oval cavities (broken fluid inclusions?), elongated crystals and/or irregular patches of K-feldspar are embedded in some of the plagioclase rims (Figure 4b). Amphibole occurs either as coronae or as aggregates texturally related to garnet and calcite. Epidote-allanite displays variable and irregular shapes, and usually fringes apatite and garnet (Figures 4c, 4d, and 5d–5f). Garnet (Figures 4b and 5f), quartz (Figures 4b–4e), and epidote-allanite (Figures 4c and 4d) are generally partially corroded if in contact with plagioclase. Phengite (0.6–1.4 mm) is always partially replaced by a symplectite of plagioclase + K-feldspar + biotite ± chlorite (Figure 4c). Rutile (up to 0.4 mm) is partially or totally replaced by titanite and/or ilmenite occasionally containing

Figure 4. Petrography of the quartz-garnet vein. (a) Representative mineral assemblage in the quartz-garnet vein, scanned image of a thin section. The dark minerals are epidote and amphibole. (b) Plagioclase rim along the garnet-rutile-ilmenite grain boundaries, BSE image. Minor K-feldspar is embedded within the plagioclase rim. The ilmenite after rutile contains a composite mineral inclusion of plagioclase + K-feldspar. Inset shows another plagioclase rim, which embeds skeletal crystals and patches of K-feldspar, BSE image. Note the tiny oval voids (broken fluid inclusions?) within the plagioclase rim. (c) Zoned phengite and epidote-allanite, BSE image: the phengite is partly replaced by a symplectite of biotite + plagioclase + K-feldspar + chlorite and the epidote-allanite is corroded by a plagioclase band. Inset is the Si map of the same area. (d) Irregularly zoned epidote-allanite, which encloses plagioclase, BSE image. (e, f) Irregular pyrite patches, which may form an intergrowth texture with epidote, BSE images. The tiny black inclusions in pyrite are plagioclase.

composite inclusions of plagioclase + K-feldspar (Figure 4b). Pyrite appears as irregular patches, which can enclose numerous tiny plagioclase inclusions and sometimes form an intergrowth texture with epidote (Figures 4e and 4f).

5. Apatite With Oriented Mineral Inclusions

Apatite in the eclogite occurs as subhedral to anhedral grains with sizes ranging from 0.1 to 0.8 mm (Figures 5a–5c). It is evenly distributed in the matrix and can be also included by garnet. Apatite in the matrix is locally fringed by epidote-allanite rims (Figure 5a). Nearly all the apatite grains contain numerous oriented monazite and calcite inclusions in an apparent topotaxial relationship, the long dimensions of which are parallel to the *c* axis of the host apatite (Figures 3i, 5a, and 5c). The monazite inclusions occur as acicular rods with diameters $\leq 2 \mu\text{m}$, whereas the calcite inclusions show variable shapes with grain sizes $\leq 20 \mu\text{m}$. In addition, the calcite can occur along the grain boundaries (Figure 5a) and seal the fractures in apatite. In colored CL images, apatite in the eclogite is commonly core to rim zoned. The core is grayish violet, whereas the rim is greenish yellow (Figures 5b and 5c). Oriented mineral inclusions are usually concentrated within the grayish violet core and absent within the greenish yellow rim.

Apatite in the quartz-garnet vein is typically anhedral, and has a grain size that can reach up to 1.5 mm (Figures 5d–5i). Grains of this mineral in the matrix tend to group together (Figure 5g) and commonly are rimmed by epidote-allanite coronae (Figures 5d–5f). In addition to monazite and calcite inclusions (Figures 5d and 5i), oriented pyrrhotite inclusions can be occasionally found in the apatite of the quartz-garnet vein (Figure 5e). In the quartz-garnet vein apatite containing dense oriented mineral inclusions is usually totally or partially enclosed by garnet (Figure 5i). Apatite grains not associated with garnet may also contain these inclusions, but with a much lower density (Figure 5h). In colored CL images, the quartz-garnet vein apatite is often weakly zoned and displays a greenish yellow color (Figures 5g and 5h). Strongly zoned

Figure 5. Apatite in the eclogite (a–c) and quartz-garnet vein (d–i). (a) Apatite containing oriented monazite and calcite inclusions and fringed by a thin allanite rim, BSE image. (b, c) Core-to-rim zoned apatite, CL images. (d–f) Apatite fringed by epidote-allanite, BSE images. Apatite in (d) and (e) contains oriented monazite and pyrrhotite inclusions, respectively. The white dashed lines in (e) and (f) outline the phase boundaries between quartz and plagioclase. (g) Amalgamated apatite with weak zoning, CL image. Monazite inclusions are nearly absent in these apatite grains. (h) Apatite with weak zoning but still containing oriented monazite inclusions, CL image. (i) Core-to-rim zoned apatite, which is partly enclosed by garnet, CL image. Note that (d) and (i) display the same apatite grain.

apatite grains (grayish violet core and greenish yellow rim) are generally totally or partially enclosed by garnet (Figure 5i). The oriented mineral inclusions are distributed within the zoned apatite in a similar pattern as that seen in apatite from the eclogite.

Raman microspectroscopy on apatite in the eclogite-vein system revealed P-O vibration modes at 430–446, 580–605, 963, and 1032–1080 cm^{-1} (Figure S1 in the supporting information). Signals corresponding to S-O (640, 1112, and 1186 cm^{-1}) and Si-O vibrations (813–836 cm^{-1}) were also detected but no signals of C-O vibrations (Figure S1).

6. Bulk-Rock Chemistry

The analyzed eclogite has 49.36 wt.% SiO_2 , 2.62 wt.% TiO_2 , and 0.31 wt.% P_2O_5 (Table 1). After normalization to chondrite (Sun & McDonough, 1989; noted by subscript “N”), the eclogite shows a concave rare earth element (REE) distribution pattern with a negative Eu anomaly ($\delta\text{Eu} = 2\text{Eu}_\text{N}/(\text{Sm}_\text{N} + \text{Gd}_\text{N}) = 0.74$; Figure 6a). The normalized values decrease from La_N to Eu_N and then increase from Eu_N to Ho_N ($\text{La}_\text{N}/\text{Sm}_\text{N} = 2.3$; $\text{Sm}_\text{N}/$

Table 1
Measured Bulk-Rock Compositions of Eclogite and Quartz-Garnet Vein and Mass Balance Calculation Result

Major element	Measured		Mass balance calculation	
	Eclogite (12-4-1) (wt.%)	Vein (12-4Q) (wt.%)	Vein/Eclogite ratio	Mass change (%)
SiO ₂	49.36	69.48	1.41	18
TiO ₂	2.62	0.85	0.32	−73
Al ₂ O ₃	12.94	8.55	0.66	−44
Fe ₂ O ₃ ^T	12.84	8.98	0.70	−41
MnO	0.23	0.19	0.83	−31
MgO	4.68	1.52	0.32	−73
CaO	10.58	7.05	0.67	−44
Na ₂ O	2.46	0.50	0.20	−83
K ₂ O	0.13	0.06	0.46	−61
P ₂ O ₅	0.31	1.40	4.52	280
LOI	3.02	0.52		
Total	99.17	99.10		−16
Trace element	(ppm)	(ppm)	ratio	(%)
Li	2.50	1.64	0.65	−45
Be	0.40	0.044	0.11	−91
Sc	42.8	26.5	0.62	−48
V	271	58.5	0.22	−82
Cr	47.8	15.4	0.32	−73
Ni	22.8	6.89	0.30	−75
Cu	32.9	37.3	1.13	−5
Zn	82.6	41.8	0.51	−58
Ga	15.8	5.92	0.37	−69
Rb	2.86	1.60	0.56	−53
Sr	84.4	60.7	0.72	−40
Y	62.3	74.1	1.19	0
Zr	184	468	2.54	114
Nb	21.2	8.98	0.42	−64
Sn	2.97	1.14	0.38	−68
Cs	0.12	0.059	0.50	−58
Ba	267	96.7	0.36	−70
La	14.0	23.9	1.70	43
Ce	29.0	57.2	1.97	66
Pr	3.36	7.38	2.19	84
Nd	14.2	34.9	2.46	107
Sm	3.94	10.1	2.56	115
Eu	1.16	2.51	2.18	83
Gd	5.83	10.8	1.85	56
Tb	1.32	1.87	1.42	19
Dy	9.81	12.1	1.23	3
Ho	2.15	2.57	1.20	1
Er	6.81	7.87	1.16	−3
Tm	1.03	1.14	1.11	−7
Yb	6.49	7.60	1.17	−2
Lu	0.97	1.15	1.18	−1
Hf	4.34	11.4	2.63	121
Pb	2.65	1.99	0.75	−37
Th	3.47	5.29	1.53	28
U	1.14	1.61	1.41	19
δEu	0.74	0.73		
(La/Sm) _N	2.30	1.53		
(Sm/Ho) _N	0.68	1.45		
(Ho/Lu) _N	0.99	1.00		

Note. Fe₂O₃^T = total iron; LOI = loss on ignition; δEu = 2Eu_N/(Sm_N + Gd_N); subscript N represents chondrite normalization; Y was chosen as the immobile element in the mass balance calculation; see text for explanation.

Figure 6. Chondrite-normalized REE distribution patterns (a) and primitive mantle-normalized trace element spider diagrams (b) of the eclogite and quartz-garnet vein. The values of chondrite and primitive mantle used through this paper are taken from Sun and McDonough (1989) and McDonough and Sun (1995), respectively.

$\text{Ho}_N = 0.68$); they remain nearly unchanged from Ho_N to Lu_N ($\text{Ho}_N/\text{Lu}_N = 0.99$). In the primitive mantle-normalized spider diagram (using values after McDonough & Sun, 1995), Li and the large ion lithophile elements (LILEs) Cs, Rb, K, and Sr are relatively depleted, whereas Ba and the high field strength elements (HFSEs) Th, U, Nb, Ti, Zr, and Hf are enriched (Figure 6b). In comparison, the analyzed quartz-garnet vein contains higher contents of SiO_2 (69.48 wt.%), P_2O_5 (1.40 wt.%), REEs, Th, U, Zr, and Hf and lower contents of most other analyzed elements (e.g., $\text{TiO}_2 = 0.85$ wt.%; Figure 6). Its REE distribution pattern is characterized by a decrease from La_N to Ho_N ($\text{La}_N/\text{Sm}_N = 1.53$; $\text{Sm}_N/\text{Ho}_N = 1.45$) and a flat pattern from Ho_N to Lu_N ($\text{Ho}_N/\text{Lu}_N = 1.0$; Figure 6a). In addition, the quartz-garnet vein displays a negative Eu anomaly ($\delta\text{Eu} = 0.73$) and shows a spider diagram with features similar to that of the eclogite, but with obvious positive P and negative Nb-Ti anomalies (Figure 6b).

7. Mineral Chemistry

7.1. Garnet

Most garnet grains in the eclogite are irregularly zoned with three identifiable zones (A, B, and C) based on backscattered electron (BSE) images, X-ray maps, and compositional analyses (Figures 7a–7e and S2). Zone A represents the earliest garnet generation. Zones B and C represent replacement areas of Zone A, giving rise to a patchy microstructure within the garnet. There is a transition zone between Zones B and A, whereas such a feature is not prominent between Zones C and A (Figures 7b–7d, S1b–S1d, and S1g–S1i). The textural relationships indicate that Zone B formed earlier than Zone C (Figures S1f–S1h). Among these three zones, Zone A is characterized by the lowest Fe and the highest Ca contents ($\text{Alm}_{45-51}\text{Gro}_{30-40}\text{Prp}_{14-18}\text{Sp}_1$); Zone B is characterized by the highest Mg and Fe and the lowest Ca contents ($\text{Alm}_{57-64}\text{Gro}_{18-21}\text{Prp}_{16-22}\text{Sp}_{1-2}$; the transition zone between Zones B and A displays compositions of $\text{Alm}_{52-58}\text{Gro}_{23-28}\text{Prp}_{16-20}\text{Sp}_{1-2}$); Zone C ($\text{Alm}_{49-59}\text{Gro}_{26-36}\text{Prp}_{11-14}\text{Sp}_{1-2}$) is characterized by the lowest Mg content and a Ca content similar to Zone A (Table S1 and Figures 7b–7e, 8a–8c, S1b–S1e, and S1g–S1j). It is noteworthy that Zones B and C contain nearly the same content of Mn as does Zone A. Garnet is the major host for the heavy REEs (HREEs) and Y in the eclogite, and also accommodates high amounts of Na, P, Ti, Sc, V, Cr, Co, Zn, and the middle REEs (MREEs; Table S2). The different garnet zones share a similar trace element composition and their REE distribution pattern is characterized by depletion in the light REEs (LREEs) and enrichment in the MREEs–HREEs (Table S2 and Figure 9a). The change from Gd_N to Lu_N is weak, corresponding to a flat HREE distribution pattern (Figure 9a).

Garnet in the quartz-garnet vein is often characterized by zoning with an abrupt compositional change from Zone A to B with B replacing A (Figures 7f–7j). The compositional range of Zone A ($\text{Alm}_{44-52}\text{Gro}_{31-42}\text{Prp}_{13-17}\text{Sp}_1$; Table S1 and Figures 8d–8f) in the quartz-garnet vein is comparable to that of Zone A of garnet in the eclogite. Zone B ($\text{Alm}_{51-59}\text{Gro}_{27-36}\text{Prp}_{7-12}\text{Sp}_{2-6}$) in the quartz-garnet vein contains lower Ca and Mg and higher Fe and Mn contents than Zone A (Table S1 and Figures 7f–7j and 8d–8f). The trace element signature of Zone A in the quartz-garnet vein is indistinguishable from garnet in the eclogite (Table S2 and Figure 9). However, Zone B in the quartz-garnet vein contains higher contents of REE from Gd to Lu and lower contents of REE from Gd to La, which results in a stronger differentiation among the REEs although the distribution pattern is still similar to that of Zone A (Table S2 and Figures 9b–9d). Furthermore, the Y content of Zone B is about three times higher and the contents of P, Zr, and the transition metal elements (TMEs) Zn, Co, and Ni are lower than those of Zone A (Table S2).

7.2. Apatite

Apatite in the sample is rich in F and OH and poor in Cl. Calculated on the basis of 12 oxygen and $\text{F} + \text{Cl} + \text{OH} = 1$, apatite in the eclogite contains 0.49–0.63 F per formula unit (pfu), 0.02–0.05 Cl pfu, and 0.34–0.48 OH pfu, whereas apatite in the quartz-garnet vein encompasses a wider compositional range and tends to

Figure 7. BSE images and element X-ray maps of garnet from the eclogite (a–e) and quartz-garnet vein (f–j). Garnet in the eclogite and quartz-garnet vein shows three (A–C) and two (A and B) distinct zones, respectively. Zones A–C in garnet from the eclogite are characterized by the lowest Fe, Ca, and Mg contents, respectively. Note that a transition zone is present between Zones A and B in the eclogite garnet, as indicated by the black arrow lines in (b).

Figure 8. Component (mol.%) diagrams of garnet from the eclogite (a–c) and quartz-garnet vein (d–f).

Figure 9. Chondrite-normalized REE distribution patterns of garnet in the eclogite-vein system. (a) shows all the analyses of garnet from the eclogite. (b–d) show three garnet grains from the quartz-garnet vein. Garnet Zone A from the eclogite is plotted in (b)–(d) as a reference.

Figure 10. Compositional diagrams (a–e) and chondrite-normalized REE distribution patterns (f) of apatite in the eclogite-vein system. The gray arrow lines in (a) and (d) indicate the compositional changing trends caused by coupled dissolution and reprecipitation. Numbers in (e) refer to two analyses with abnormal high Si contents, which fall outside of the diagram.

contain higher contents of F (0.50–0.73 pfu) and Cl (0.02–0.07 pfu) and, thus, a lower OH content (0.25–0.47 pfu; Table S3 and Figures 10a and 10b). The apatite also contains trace amounts of S, which are similar in apatite of both eclogite and quartz-garnet vein (60–440 vs. 88–320 ppm; Table S3 and Figure 10c). The volatile element contents vary considerably between apatite grains. In a CL-zoned apatite grain, the F content is slightly higher in the greenish yellow rim, whereas Cl and S show an ambiguous compositional variation between the core and the rim (Table S3).

Special attention was paid to avoid the possible effect of accidentally analyzing oriented mineral inclusions during LA-ICP-MS analysis. First of all, clear domains were preferentially analyzed. Second, the time-resolved counting curves of Th-U-LREEs (for monazite), Ca (for calcite), and Fe (for pyrrhotite) were monitored during processing the raw data in case of mineral inclusions were encountered and ablated. For all our analyses, the time-resolved counting curves of Ca and Fe are smooth and no effect of calcite or pyrrhotite was noted. Monazite inclusions may give rise to one or several Th-U-LREE spikes, which especially happened to the cores with grayish violet CL color. In such cases, smooth parts that avoided the spikes were selected to calculate the trace element contents. Moreover, time-resolved counting curves, which include the Th-U-LREE spikes, were used to recover the initial trace element contents in apatite before the formation of oriented mineral inclusions.

Apatite from the eclogite and the quartz-garnet vein show similar trace element compositions. This mineral is an important host for REEs, Y, Sr, Th, U, and Pb in the eclogite-vein system and also contains some Na, Si, Mn, Fe, and Ba (Table S4). Among these elements, the REE + Y and Na contents are positively correlated,

Figure 11. Compositional (a, b) and primitive mantle-normalized trace element spider diagrams (c) of phengite in the eclogite-vein system.

whereas no correlation occurs between REEs + Y and Si (Figures 10d and 10e). The REE contents and distribution patterns vary among the different CL-colored domains in apatite. The greenish yellow domains display a convex REE distribution pattern with $\text{Sm}_N/\text{La}_N = 2.25\text{--}21$ and $\text{Sm}_N/\text{Lu}_N = 1.56\text{--}24$ (Figure 10f). In the grayish violet domains, the contents of LREEs increase prominently and the REE distribution patterns become LREE-enriched and MREE-HREE-depleted ($\text{Sm}_N/\text{La}_N = 0.54\text{--}3.0$; $\text{Sm}_N/\text{Lu}_N = 6.41\text{--}147$; Table S4 and Figure 10f). The initial recovered composition of apatite shows an even higher LREE content and a REE distribution pattern depleted in HREEs ($\text{Sm}_N/\text{La}_N \leq 0.19\text{--}0.23$; $\text{Sm}_N/\text{Lu}_N \geq 39\text{--}321$; Table S4 and Figure 10f). It is noteworthy that apatite always shows a negative Eu anomaly ($\delta\text{Eu} = 0.44\text{--}0.73$; Table S4 and Figure 10f).

7.3. Mica

Phengite in both the eclogite and quartz-garnet vein is zoned. In the BSE images, the rim of the phengite is brighter than the interior zone (Figures 3e and 3f). In addition, oscillatory zoning was rarely found in phengite of the quartz-garnet vein (Figure 4c). The BSE-darker zones (Zone A) contain 3.38–3.56 Si pfu, 1.89–2.17 Al pfu, and 0.01–0.06 Ba pfu, whereas the BSE-brighter zones (Zone B) host lower Si (2.93–3.30 pfu) and higher Al (2.23–2.77 pfu) and Ba (0.10–0.24 pfu) contents (Table S1 and Figures 11a and 11b). The Si content of phengite is negatively correlated with the Al and Ba contents (Figures 11a and 11b), indicating that the phengite zoning is dominated by the exchange vectors of $[\text{Ba}][\text{IVAl}][\text{K}, \text{Na}]_{-1}[\text{Si}]_{-1}$ and $[\text{Fe}, \text{Mg}][\text{Si}][\text{VIAl}]_{-1}[\text{IVAl}]_{-1}$ (Harlow, 1995). In addition to Ba, phengite is relatively rich in Li (17–44 ppm), B (58–132 ppm), Cs (6.7–9.2 ppm), Rb (178–362 ppm), and Sr (15–156 ppm) (Table S2 and Figure 11c). As with Ba, Sr is poorer in Zone A than in Zone B (15–29 vs. 80–156 ppm; Table S2 and Figure 11c). Phengite contains 361–639 ppm V, 21–89 ppm Zn, and 38–94 ppm Cr (Table S2 and Figure 11c).

Biotite always occurs as replacement product of phengite and contains 10.0–12.7 wt.% MgO, 13.3–16.4 wt.% FeO, 3.8–9.2 wt.% BaO, and 0.8–3.6 wt.% TiO_2 (Table S1 and Figure 12) in the eclogite. For comparison, biotite in the quartz-garnet vein shows a lower BaO content (2.5–4.2 wt.%) and nearly the same MgO (10.0–11.8 wt.%), FeO (14.9–18.1 wt.%), and TiO_2 (0.5–3.1 wt.%) contents (Table S1 and Figure 12). For biotite each in the eclogite and quartz-garnet vein, the contents of MgO and FeO are negatively correlated whereas the contents of BaO and TiO_2 are positively correlated (Figure 12).

7.4. Amphibole

Amphibole xenoblasts and coronae (amphibole-I) in the eclogite contain 5.98–6.58 Si pfu and 1.83–2.97 Al pfu with $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios ranging from 0.56 to 0.81 (Table S1 and Figure 13). In the classification diagram of amphibole (Leake et al., 1997), the amphibole compositions mainly plot in the field of pargasite, tschermakite, and magnesiohastingsite (Figure 13a). Amphibole in the symplectite after omphacite (amphibole-II) in the eclogite contains higher Si (6.70–7.56 pfu) and lower Al (0.63–1.70 pfu) contents with $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios ranging from 0.66 to 0.77 (Table S1 and Figure 13). Amphibole-II is classified as magnesiohornblende and actinolite (Figure 13a). The Si (6.03–6.51 pfu) and Al (1.90–2.64 pfu) contents of amphibole in the quartz-garnet vein are nearly identical to those of amphibole-I in the eclogite but the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios (0.46–0.61; an exception at 0.72) are lower (Table S1 and Figure 13). Amphibole in the quartz-garnet vein is pargasite, tschermakite, magnesiohastingsite, ferropargasite, ferrotschermakite, and hastingsite (Figure 13a).

Figure 12. (a, b) Compositional diagrams of biotite in the eclogite-vein system.

Figure 13. (a, b) Compositional diagrams of amphibole from the eclogite-vein system. The amphibole classification in (a) is after Leake et al. (1997).

Amphibole-I in the eclogite and amphibole in the quartz-garnet vein were measured for their trace element compositions, which are nearly identical (Table S2 and Figures 14a and 14b). They are relatively enriched in HREEs and depleted in LREEs, with REE distribution patterns similar to those of garnet (Figure 14a). In addition, certain amounts of Li (3.5–12.8 ppm), LILEs (e.g., 157–416 ppm Ba; 11–21 ppm Sr), and TMEs (e.g., 240–644 ppm V; 206–231 ppm Zn; 85–152 ppm Sc) were detected in amphibole (Table S2 and Figure 14b).

7.5. Epidote-Group Minerals

Epidote-group minerals (16.2–23.3 wt.% CaO, 21.5–26.7 wt.% Al₂O₃, and 6.9–8.4 wt.% FeO calculated for total Fe) in the eclogite-vein system include epidote and allanite (Table S1). Because the epidote-allanite rims fringing apatite were often too thin to be analyzed, only one epidote xenoblast containing an allanite core in the eclogite and two zoned epidote-allanite xenoblasts in the quartz-garnet vein were analyzed for their trace element chemistry. The results revealed that epidote-group minerals, in addition to apatite, are important repositories of REEs, Y, Sr, Th, U, and Pb in the eclogite-vein system (Table S2 and Figures 14c and 14d). The contents of LREEs, Th, U, and Pb are positively correlated with each other, whereas the content of Sr varies independently between 2,020 and 4,620 ppm. All the analyzed epidote and allanite display a REE distribution pattern that declines for the HREEs and shows different Eu anomalies (epidote in the eclogite: La_N/Lu_N = 4.4–13, δEu = 1.9–3.8; allanite in the eclogite: La_N/Lu_N = 22700–24900, δEu = 0.54–0.59; epidote-allanite in the quartz-garnet vein: La_N/Lu_N = 100–18400, δEu = 0.78–1.02) (Table S2 and Figures 14c and 14d).

7.6. Feldspar

In the eclogite, the albite rims and plagioclase in the symplectite after omphacite have a similar composition of 96–97 mol.% albite and 3–4 mol.% anorthite, whereas plagioclase in the quartz + plagioclase associations contains 66–87 mol.% albite and 14–33 mol.% anorthite (Table S1). In the quartz-garnet vein, plagioclase is oligoclase with 83–89 mol.% albite and 11–17 mol.% anorthite. K-feldspar contains 65–93 mol.% orthoclase, 3–9 mol.% albite, and 4–28 mol.% celsian (Table S1).

Plagioclase in the eclogite-vein system contains 37–680 ppm Sr and 25–744 ppm Ba, with the contents of most other trace elements below the detection limits (Table S2). The contents of Sr and Ba are positively correlated with the CaO content.

7.7. Rutile-Ilmenite-Titanite

Rutile is the main host of Nb (460–1270 ppm) and Ta (20–138 ppm) in the eclogite-vein system, and contains high contents of Zr (73–144 ppm), Hf (3.4–5.5 ppm), V (755–1850 ppm), and Cr (32–210 ppm) (Table S4 and Figure 15). The ratios of Nb/Ta and Zr/Hf of rutile are 8–27 and 19–29, respectively. Ilmenite replacing rutile contains much lower contents of Nb (22–138 ppm) and Ta (4.8–14.4 ppm), Zr (4.9–13.2 ppm), and Hf (0.3–0.9 ppm) than rutile (Table S4 and Figure 15). The contents of V (400–1050 ppm) and Cr (60–102 ppm) and the Nb/Ta (4–17) and Zr/Hf (9–23) ratios of ilmenite are slightly lower than those of rutile (Table S4). Titanite was found as a replacement product of rutile only in the quartz-garnet vein and hosts 3.2–5.7 wt.% Al₂O₃ (Table S3).

Figure 14. Chondrite-normalized REE distribution patterns and primitive mantle-normalized trace element spider diagrams of amphibole (a, b) and epidote-allanite (c, d) in the eclogite-vein system.

7.8. Carbonate

Dolomite in the eclogite has a formula of $(\text{Ca}_{0.49-0.51}\text{Mg}_{0.37-0.42}\text{Fe}_{0.08-0.11})\text{CO}_3$ and 650–2250 ppm Mn, 455–785 ppm Sr, 12.8–53.0 ppm Ba, and 7.99–27.7 ppm Pb (Tables S3 and S4). Magnesite in the eclogite is characterized by a formula of $(\text{Ca}_{0.02}\text{Mg}_{0.69-0.72}\text{Fe}_{0.26-0.28})\text{CO}_3$ (Table S3). Calcite in various textural settings is nearly pure CaCO_3 , as revealed by energy dispersive spectrometer analyses.

7.9. Omphacite

Two measurements were performed on two omphacite inclusions in the eclogite, which yielded a jadeite content of 56 and 58 mol.% but no calculated acmite component (Table S1).

8. Metamorphic Evolution and P-T Path Construction

In order to constrain the P-T evolution of the eclogite(-vein) system, P-T pseudosections were calculated using the PERPLE_X program (Connolly, 2005; version 6.6.6) and the thermodynamic data set of Holland and Powell (1998, with updates) for the P-T range 1.0–4.5 GPa and 500–800 °C (for details see Text S1). The calculation results are displayed in Figures 16 and S3.

Figure 15. Primitive mantle-normalized trace element spider diagrams of rutile and ilmenite from the eclogite-vein system.

The presence of coesite in the eclogite (Figures 3g and 5b) suggests peak pressures higher than 2.7 GPa (see the quartz-coesite transition curve in the P-T pseudosection of Figure 16). In order to derive the absolute peak P-T conditions, the compositional range of garnet Zone A was used. According to the contoured P-T pseudosection (Figure 16), the Mg-poorest and Ca-richest composition ($\text{Prp}_{14-15}\text{Gro}_{36-40}$) of this Zone A might represent the most primary composition. As the isopleths for the here relevant garnet components are nearly parallel to each other in the UHP field, accurate P-T estimates cannot be obtained solely from the garnet composition. In this case, the Si isopleths for phengite can be additionally used to derive the peak P-T conditions. The primary Si content in phengite (Zone A) was estimated to be 3.53 pfu as average of six analyses with the highest

Figure 16. (a) P-T pseudosection modeled for the eclogite. The used bulk-rock composition is listed above the figure. (b) Isopleths of the garnet volume content, grossular and pyrope contents (mol.%) in garnet, and Si content (pfu) in phengite calculated for the eclogite. The red ellipse A represents the (possibly minimum) peak P-T conditions constrained by using the compositions of Zone A of garnet and phengite in the eclogite. The dashed red and yellow arrow lines are two possible exhumation P-T paths experienced by the eclogite, as discussed in the text. The formation stages of garnet Zones B and C in the eclogite are schematically indicated by letters B and C on these two P-T paths.

Figure 17. P-T paths (thick arrow lines) constructed for the Dabie UHP eclogites and the wet basalt solidus (Lambert & Wyllie, 1972). The dark blue area represents the retrograde P-T conditions constrained for the eclogite by using the quartz-bearing amphibole-plagioclase thermometer of Holland and Blundy (1994). The blue solid circle represents the second critical point of the basalt (Mibe et al., 2011). Decreasing H_2O activity in aqueous fluids could shift the wet basalt solidus to higher temperatures. Isopleths of 73 and 144 ppm Zr in rutile (black thin lines) were plotted using the Zr-in-rutile geothermometer calibrated by Tomkins et al. (2007). Phase-transition curves of diamond = graphite, coesite = quartz, and albite = jadeite + quartz are after Bundy (1980), Bohlen and Boettcher (1982), and Li et al. (2004), respectively.

eclogite-vein system yielded temperatures of 548–594, 587–635, and 630–681 °C at 1.0, 2.0, and 3.5 GPa, respectively (Figure 17). The isopleths of Zr contents in measured rutile fall to the left of the isothermal decompression P-T path established above (Figure 17), indicating either reequilibration of rutile during retrogression, slight temperature overestimation by the applied garnet isopleths and/or slight temperature underestimation by Zr-in-rutile geothermometry.

According to the mineral textures and compositions as well as phase equilibria modeling results presented above, metamorphic evolution (including the alteration and dissolution sequence of relict peak minerals; see following discussion) of the eclogite-vein system is summarized in Table 2. It should be further noted that $X(CO_2)$ in the modeled fluids was very low (0.02–0.03) under peak conditions, gradually increased to 0.24 during early exhumation, and decreased again during late retrogression (Figure S3).

9. Mass Balance Calculations

As already discussed in Liu et al. (2018), the quartz-garnet vein, studied here, formed by a leaching process that progressed along fractures that were developed in the host eclogite during exhumation and before the amphibolite-facies overprint. Infiltration of external fluids should have initiated the fluid-rock interaction. In the quartz-garnet vein, the original rock-forming minerals except garnet were completely or largely dissolved and, thus, removed, whereas net quartz and new plagioclase and epidote-allanite were formed. In addition, net apatite grew in the quartz-garnet vein, as indicated by a higher apatite content in the quartz-garnet vein than in the eclogite (1–2 vs < 0.5 vol.%). Mass balance calculations were conducted to constrain the net change of total mass of the altered rock (i.e. the quartz-garnet vein in this study) and contents of

Si contents (Figures 11a and 11b). The corresponding isopleth intersects with the Prp_{14-15} isopleths at approximately 3.3 GPa and 665–680 °C (Figure 16), which, however, could represent a minimum estimate for the peak P-T conditions. These conditions are compatible with the observed peak mineral assemblage garnet, omphacite, phengite, coesite, dolomite, magnesite, and rutile (Figure 16).

The eclogite was overprinted by amphibolite-facies metamorphism during late retrogression resulting in an amphibole + plagioclase symplectite after omphacite (Figures 3a and 3b). P-T conditions of c. 490–560 °C at assumed 0.5–1.0 GPa (Figure 17) were constrained for the formation of this symplectite by using the quartz-bearing amphibole-plagioclase thermometer of Holland and Blundy (1994). The P-T evolution from the peak UHP to the amphibolite-facies stage was derived from the replacement products (garnet Zones B and C) of garnet Zone A. However, quantitative P-T estimates with the corresponding compositions are insecure because the effective bulk-rock compositions related to the formation of these garnet zones are difficult to estimate. Thus far, a nearly isothermal decompression P-T path has been often envisaged for the Dabie UHP rocks although direct quantitative P-T constraints are rare (e.g., Massonne, 2012; Okay, 1993; Rolfo et al., 2004; Wei et al., 2013; Zhang et al., 2003). As illustrated in Figure 16, if peak garnet in the eclogite experienced compositional adjustment along a nearly isothermal decompression P-T path, the grossular content should first decrease and then increase whereas the pyrope content should change in an inverse way. This can explain the compositional variation trend in garnet from Zone A to B and then to C (Figures 8a–8c). Moderate cooling during decompression could result in this compositional variation trend in garnet as well, but should also have led to the formation of paragonite in the eclogite (Figure 16), which was not observed.

Metamorphic temperatures were also constrained with Zr-in-rutile geothermometry. Application of this geothermometer, calibrated by Tomkins et al. (2007), on rutile (73–144 ppm Zr; Table S4) in the

Table 2*Metamorphic Evolution of the Eclogite-Vein System Deduced From Mineral Textures and Compositions as Well as Phase Equilibria Modeling Results*

Rock	Eclogite			Q-Grt vein		
Stage	UHP	HP	AM-facies	UHP	HP	AM-facies
Grt	Zone A	Zone B → Zone C		Zone A	Zone B + Partial dissolution	
Omp					Total dissolution	
Phn	Zone A	Zone B + Partial dissolution		Zone A	Zone B + Most dissolution	
Coe						
Mgs						
Dol					Total dissolution	
Ap		Oriented inclusion formation			Oriented inclusion formation	
Ru					Partial dissolution	
Py					Partial dissolution	
Q						
Aln-Ep						
Amp-I						
Ab ± Cal Rim						
Pl + Q + Bt						
Olg ± Kfs Rim						
Pl + Kfs + Bt ± Chl						
Ilm		?	?		?	?
Ttn						
Amp + Pl Sym						

Note. AM-facies: amphibolite-facies. Pl + Q + Bt refers to the plagioclase + quartz association which embeds biotite. The shading cells indicate that the mineral or mineral assemblage was stable at corresponding metamorphic stages. The sequence of alteration and dissolution of peak minerals and formation of retrograde minerals is only indicated schematically. The formation stage of ilmenite is ambiguous because it was controlled by local equilibrium.

single elements in the altered rock during the quartz-garnet vein formation. The calculation method is presented in Text S2. The calculation results are listed in Table 1 and displayed in Figure 18.

The altered eclogite lost 16% of its total mass during the quartz-garnet vein formation (Table 1). Specific to single elements, the quartz-garnet vein gained 18% SiO₂, 280% P₂O₅, 1–115% LREEs-MREEs, 114% Zr, 121%

Figure 18. Concentration ratio (left axis) and mass change (right axis) diagram for the studied major and trace elements. C^o and C^a represent element concentrations in the eclogite and quartz-garnet vein, respectively. Yttrium was chosen as the reference immobile element in the mass balance calculation.

Hf, 28% Th, and 19% U and lost 83% Na₂O, 61% K₂O, 44% Al₂O₃, 73% MgO, 44% CaO, 41% Fe₂O₃ (total iron), 31% MnO, 73% TiO₂, 45% Li, 58% Cs, 53% Rb, 70% Ba, 40% Sr, 37% Pb, 64% Nb, 48% Sc, 82% V, 73% Cr, 75% Ni, and 58% Zn of the original eclogite mass (Table 1 and Figure 18). The volatile contents were not measured for the eclogite-vein system. In spite of this, most CO₂ should have been removed from the quartz-garnet vein considering that dolomite is a rock-forming mineral in the eclogite and that carbonates are nearly absent in the vein.

10. Discussion

10.1. Fluid-Aided Alteration of Peak Minerals

The HP fluid-rock interaction resulted in not only the macroscopic alteration of the eclogite (i.e., formation of the quartz-garnet vein) but also microscopic alteration of relict peak phases (garnet, phengite, and apatite) in the eclogite-vein system (Table 2).

10.1.1. Garnet

During exhumation, peak garnet (i.e., Zone A) in the eclogite was partially replaced by garnet Zones B and C successively (Figures 7a–7d and 8a–8c). While the major element chemistry in these two new zones was adjusted considerably in response to the changing P-T conditions (Figure 16), their Mn contents and trace element chemistry, such as the HREE and Y contents, display little change (Table S2 and Figures 7e, 8c, and 9a). The contoured P-T pseudosection suggests that garnet Zone B formed before amphibole became a stable mineral in the eclogite (Figure 16). During this period, the modal content of garnet stayed nearly the same (Figure 16). Garnet is the main carrier of Mn, HREEs, and Y in the eclogite. Without its breakdown or growth, effective concentrations of these elements in the rock matrix could hardly change so that Zone B should largely retain the original contents of these elements in Zone A. The formation of garnet Zone C at the expense of Zones A and B was accompanied by the breakdown of garnet and the production of amphibole-I (Figure 16). Nevertheless, the breakdown degree of garnet might be low at this stage and the amphibole could accommodate most of the released HREEs, Y, and Mn (Table S2 and Figure 14a). This could partly explain why the concentrations of these elements in garnet Zone C are similar to those in Zones A and B.

Zone A in garnet from both the quartz-garnet vein and the eclogite shares a similar major and trace element composition (Figures 8 and 9), indicating that garnet in the quartz-garnet vein is a relict phase from the original eclogite. The chemical change by partial replacement of the relict peak garnet (i.e., Zone A) in the quartz-garnet vein by garnet Zone B (higher almandine and lower grossular and pyrope contents in B; Figures 7f–7i and 8d–8f) is interpreted as a response to both changing P-T conditions and bulk-rock composition during the vein formation. Garnet Zone B contains significantly higher Mn, HREE, and Y contents than garnet Zone A (Table S2 and Figures 7j, 8f, and 9b–9d), compatible with the partial dissolution of garnet in the quartz-garnet vein during the fluid-rock interaction (Figures 4b, 5f, and 7f) and implying a back incorporation for these elements.

Three possible mechanisms could have been responsible for the fluid-aided alteration of garnet: (1) volume diffusion, (2) partial resorption and subsequent regrowth, and (3) coupled dissolution and reprecipitation (e.g., Krause et al., 2013). The altered zones occur as irregular patches or as vein-like domains and networks in the garnet (Figures 7a and 7f, S1a, and S1f), which are incompatible with diffusional processes. Moreover, volume diffusion should have produced a smooth chemical gradient between the different zones. However, the altered and the unaltered zones in the studied garnet are usually in sharp contact (Figures 7 and S2). The smooth transition zone between Zones A and B in the eclogite garnet (Figures 7b, and S1b and S1g) might reflect a modification by later diffusion across what was originally a sharp compositional boundary. Partial resorption and subsequent regrowth can be ruled out because this process is not supported by the contoured P-T pseudosection and the constructed P-T path (Figure 16). Coupled dissolution and reprecipitation represents a fluid-aided chemical reaction driven by a minimization of the Gibbs free energy of the reaction system (Putnis, 2009; Putnis & Austrheim, 2010). The progress of such a reaction is realized by forming submicroscopic fluid channels between the reactant and the product to allow simultaneous dissolution of the original mineral phase and precipitation of an altered or new mineral phase. Once initiated, this reaction can be self-perpetuating as the dissolution of the reactant and the precipitation of the product can be mutually promoted by maintaining the chemical gradients in the channelized fluids (Andersen et al.,

1998a, 1998b). Coupled dissolution and reprecipitation can preserve the original shape and size of the altered mineral and give rise to a sharp compositional boundary between the unaltered and altered zones. Furthermore, such a reaction may create a pervasive, interconnected nanoporosity and/or microporosity in the altered zones due to the migration of a reaction front toward the unaltered zones, leaving behind submicroscopic fluid channels (Harlov et al., 2005; Hövelmann et al., 2010; Krause et al., 2013; Norberg et al., 2011). The molar volume change and the relative solubility of the original and reprecipitated mineral phases determine the porosity development (Putnis, 2009; Putnis & Austrheim, 2010). However, such kind of porosity was not observed in this study maybe because it is too small to be recognized by our analytical methods or it has been eliminated via an Ostwald ripening process of the porous volume during later textural recrystallization (Putnis, 2009; Putnis & Austrheim, 2010). It should be noted that the vein-like domains and networks have been described and interpreted as healed microfractures in Liu et al. (2018).

10.1.2. Phengite

Phengite in the eclogite-vein system records chemical alteration mainly along rims (Figures 3e, 3f, and 4c). The sharp compositional boundary between the altered and unaltered zones implies that this chemical alteration was also realized via a fluid-aided coupled dissolution and reprecipitation reaction. Retrograde overgrowth could not produce a Zone B according to the results of phase modeling shown in Figure S3. The altered phengite Zone B contains lower Si and higher Al and Ba contents than the unaltered Zone A (Figures 11a and 11b). The decrease of Si in Zone B is due to decreasing pressure during exhumation (Figure 16). A fluid rich in Ba must have contributed to the enrichment of this element in Zone B, which further led to the decrease of the Si content in this zone by the substitution $[\text{Ba}]^{IV}[\text{Al}] [\text{K}, \text{Na}]_{-1}[\text{Si}]_{-1}$. Barium in the fluid could be externally introduced and/or attributed to the dissolution of phengite (the major host of Ba before the quartz-garnet vein formation) in the rock. The latter process should be especially emphasized for the quartz-garnet vein, in which phengite was nearly completely dissolved. Phengite in the eclogite was only partially dissolved, as indicated by phengite flakes with the plagioclase + quartz association at their rims (Figures 3d–3f).

10.1.3. Apatite

Apatite in the studied rocks contains oriented monazite, calcite, and pyrrhotite inclusions (Figures 3i and 5). Calcite also occurs along the apatite grain boundaries (Figure 5a) and seals the fractures in apatite. Oriented monazite and pyrrhotite inclusions in apatite have been reported from a variety of rocks from several UHP localities, including the Dabie and Sulu UHP terranes in China (Liang et al., 2006; Liu, Massonne, Wu, et al., 2017; Sun et al., 2007; Zhang & Liou, 1999; Zhu & Massonne, 2005, 2007), the Pohorje Mountains in Slovenia (Krenn et al., 2009), the Rhodope UHP metamorphic province in Greece (Kostopoulos et al., 2010), and the Tromsø Nappe of the Scandinavian Caledonides in Norway (Broska et al., 2014). Dolomite inclusions oriented parallel to the c-axis of apatite have been found in UHP carbonate-rich rocks in the Tromsø Nappe of the Scandinavian Caledonides in Norway (Broska et al., 2014), but the oriented calcite inclusions found in apatite of this study, as far as we know, have never been documented for any UHP rock. It should be noted that oriented mineral inclusions like monazite and pyrrhotite have been also reported frequently for apatite formed at non-UHP and even low pressure conditions (e.g., Hansen & Harlov, 2007; Harlov et al., 2007; Harlov & Förster, 2002; Hurai et al., 2017; Janots et al., 2018; Pan, 1997; Pan et al., 1993; Rajesh et al., 2013; Xing & Wang, 2017). While these inclusions have been interpreted as products resulting from an “exsolution” process during decompression of UHP rocks (Liang et al., 2006; Sun et al., 2007; Zhang & Liou, 1999; Zhu & Massonne, 2005, 2007), they have been more commonly interpreted as products of metasomatic reactions (e.g., Broska et al., 2014; Harlov et al., 2002, 2005; Harlov & Förster, 2002; Harlov & Förster, 2003; Janots et al., 2018; Liu, Massonne, Wu, et al., 2017; Pan, 1997; Pan et al., 1993; Rajesh et al., 2013). It has been demonstrated by experimental fluid-aided alteration of apatite that fluid-aided coupled dissolution and reprecipitation plays a key role in the formation of oriented monazite ($\pm$ xenotime) inclusions in apatite (Antignano & Manning, 2008; Harlov et al., 2002, 2005; Harlov & Förster, 2003). We propose that oriented calcite and pyrrhotite inclusions in this study also resulted from a coupled dissolution and reprecipitation reaction (see Broska et al., 2014).

The flexible crystal structure of apatite can accommodate a wide range of elements ($\text{M}_{10}(\text{ZO}_4)_6\text{X}_2$; $\text{M} = \text{Ca}, \text{Fe}, \text{REEs} + \text{Y}, \text{Na}, \text{etc.}$; $\text{Z} = \text{P}, \text{Si}, \text{etc.}$; $\text{X} = \text{OH}, \text{F}, \text{Cl}, \text{etc.}$; Hughes & Rakovan, 2015; Pan & Fleet, 2002). REEs + Y can be incorporated in apatite through the following two principle coupled substitutions:

Reaction between a (REE + Y)-rich apatite and a fluid rich in H₂O can remove REEs + Y, Na, and Si from the apatite. The released REEs + Y can react with phosphorus from the apatite or a fluid to form oriented monazite and/or xenotime inclusions in the apatite (e.g., Harlov et al., 2002, 2005; Harlov & Förster, 2002; Harlov & Förster, 2003). In this study, only monazite and no xenotime inclusions were observed in the apatite implying that LREEs were released during the fluid-aided alteration of apatite due in part to their greater relative abundance compared to the HREEs. Regarding the altered apatite, a positive correlation between REEs + Y and Na and lack of such a correlation between the REEs + Y and Si contents (Figures 10d and 10e) indicate that the reverse of reaction (3) governed the formation of monazite. The LREEs released from the apatite in the eclogite-vein system reacted with other elements (Ca, Fe, Al, and Si) in the fluid to form LREE-rich epidote and allanite, which commonly fringe the apatite (Figures 5a and 5d–5f). Similar epidote and allanite rims and explanations on their formation have been also reported for the apatite-iron oxide ores from the Shevaroy massif, southern India (Hansen & Harlov, 2007), and the Grängesberg Mining District in the Bergslagen ore province, Sweden (Jonsson et al., 2016), and the polymetamorphic lower crustal rocks from the Bergen Arcs, Norway (Janots et al., 2018). Some epidote-allanite grains in the quartz-garnet vein are not texturally related to apatite (Figures 4c and 4d), but they are also inferred to have formed as suggested above. The oscillatory and irregular zonings of these grains indicate fast growth of epidote-allanite with a heterogeneous and/or pulsed supply of LREEs from local apatite.

Apatite in this study always displays a negative Eu anomaly (Figure 10f). Earlier studies on UHP rocks from the Dabie and Sulu terranes revealed that peak metamorphic apatite commonly shows no Eu anomaly and that a negative Eu anomaly in apatite generally represents a retrograde feature (e.g., Chen et al., 2009; Guo et al., 2012; Liu et al., 2013; Tang et al., 2007). According to these studies, we propose that the Eu anomaly observed in this study resulted from the HP fluid-apatite interaction accompanying the release of LREEs from apatite. Experiments have shown that Eu²⁺ is much less compatible than LREE³⁺ in apatite (Ayers & Watson, 1993; Watson & Green, 1981). This indicates that (1) in the absence of a negative Eu anomaly, Eu was present primarily as Eu³⁺ in the peak apatite, and (2) Eu²⁺, if present, should be preferentially expelled from the apatite structure during the LREE release and redistribution. This would imply that the HP fluid had the capability to reduce the original Eu³⁺ to Eu²⁺ in order to facilitate the formation of a negative Eu anomaly in the apatite. The released Eu²⁺ would most likely be sequestered by the simultaneously or slightly later formed plagioclase. Noteworthy is that epidote in the eclogite shows a positive Eu anomaly (Figure 14c) and is partially corroded by plagioclase (Figure 3f). This indicates that, before plagioclase formation, earlier formed epidote preferentially sequestered Eu²⁺ released from apatite.

Bicarbonate in metasomatic fluids was proposed to provide the carbon source for the formation of oriented dolomite rods in apatite of UHP carbonate-rich rocks from the Tromsø Nappe of the Scandinavian Caledonides (Broska et al., 2014). Alternatively, the host apatite itself could have provided the carbon for the formation of the oriented calcite inclusions in this study. It has been revealed that apatite in the Dabie UHP eclogites can contain up to several wt.% CO₃²⁻, which replaces PO₄³⁻ (Li & Zheng, 1999). The coupled substitution reactions CO₃²⁻ + SiO₄⁴⁻ = 2PO₄³⁻, CO₃²⁻ + Na⁺ = Ca²⁺ + PO₄³⁻, and 2CO₃²⁻ + vacancy = Ca²⁺ + 2PO₄³⁻ demonstrate how CO₃²⁻ could be incorporated in the apatite structure (Pan & Fleet, 2002). However, Raman microspectroscopy did not provide conclusive evidence for the presence of CO₃²⁻ in apatite from this study (Figure S1), which might have been mostly removed from the apatite structure.

Explanations regarding the formation of pyrrhotite inclusions in apatite are more complicated (Broska et al., 2014; Janots et al., 2018). Iron can substitute for Ca on the M site in apatite, whereas S mainly occupies the anion column site in apatite in the form of SO₄²⁻ (Pan & Fleet, 2002). Nonetheless, both Fe and S could also have been sourced from the metasomatic fluid. If this would be true, both elements might have been dissolved from pyrite in the rock (Figures 4e, 4f, and 5f). More likely, S was provided by SO₄²⁻ in the host apatite and reduced from S⁶⁺ to S²⁻.

The degree of alteration in apatite varies with respect to scale. Apatite in the eclogite is usually core-to-rim zoned, as revealed by CL images and compositional analyses (Figures 5b, 5c, and 10f). Monazite inclusions

are dense in the grayish violet core, and absent in the greenish yellow rim (Figures 5b and 5c). These differences suggest that more LREEs were leached from the apatite rim and that the apatite rim experienced a higher alteration degree. Core-to-rim-zoned apatite also occurs in the quartz-garnet vein, but such apatite grains are always protected as inclusions or half-inclusions in garnet (Figure 5i). Most apatite grains in the quartz-garnet vein are weakly zoned, display a greenish yellow CL color (Figures 5g and 5h), show LREE contents similar to those in the rim of the zoned apatite grains (Figure 10f), and contain less monazite inclusions than the core of the zoned apatite grains (Figures 5g–5i). All these features suggest that apatite in the quartz-garnet vein experienced a higher alteration degree compared to those in the eclogite. The vein apatite tends to contain higher contents of F and Cl than the eclogite apatite (Figures 10a and 10b) implying that the fluid-aided alteration increased the F and Cl contents in apatite.

10.2. Nature of Active HP Fluid

The sodic plagioclase (albite-oligoclase) rims (Figures 3h, 3i, 4b, and 4c) in the eclogite-vein system are similar to melt pseudomorphs found in rocks that have experienced partial melting (Holness & Sawyer, 2008; Sawyer, 1999; Vernon, 2011). This feature suggests that melt might have been present during isothermal decompression. Indeed, the nearly isothermal decompression P-T path, established in this study, slightly oversteps the wet solidus of a basaltic eclogite before the amphibolite-facies overprint (Figure 17). However, the presence of CO₂ and NaCl (see later discussion) in aqueous fluids could reduce the H₂O activity so that the melting temperature would increase (Manning, 2018). Thus, using the P-T path and solidus for a pure H₂O-basalt system cannot confirm whether or not partial melting in the eclogite-vein system occurred. If partial melting had indeed occurred during HP fluid-rock interaction, a felsic melt should have been produced (Lambert & Wyllie, 1972). This means that crystallization products like the rims of sodic plagioclase around eclogitic minerals should have also included quartz (e.g., Ferrero et al., 2012; Holness & Sawyer, 2008). However, instead of being overgrown, quartz in the eclogite-vein system is corroded by the lately formed sodic plagioclase rims (Figures 3h and 4e). The plagioclase + quartz association in the eclogite could be such a product (Figures 3d–3f), but the corroded feature of quartz grains in this association implies that they are relicts from one or several precursor quartz grains instead of a crystallization product. Altogether, quartz unambiguously forming from a crystallizing melt was not observed in the samples. Accordingly, a solute-rich aqueous fluid instead of a hydrous melt is proposed to have been responsible for the formation of the sodic plagioclase rim and the plagioclase + quartz association. Compared with hydrous melts, aqueous fluids have a much lower viscosity (Audétat & Keppler, 2004; Hack & Thompson, 2011), could, thus, more easily migrate along grain boundaries, and are more compatible with the pervasive distribution of sodic plagioclase as rims around eclogitic minerals in the rock matrix. Furthermore, K-feldspar embedded in the sodic plagioclase rims is rich in BaO (up to 13.8 wt.%; Table S1). The formation of Ba-rich K-feldspar is generally thought to occur by aqueous fluids (Harlov et al., 1998; Henry & Will, 2015; Moro et al., 2001; Shi et al., 2010).

Solubility experiments have revealed that aqueous fluids in the Na₂O-Al₂O₃-SiO₂-H₂O system can dissolve more than 10 wt.% solutes under HP metamorphic conditions close to the wet solidus (Manning, 2018; Manning et al., 2010; Wohlers et al., 2011). In addition to simple ions, ion pairs, monomers, and dimers, polymerized Na-Al-Si-O clusters can occur in such fluids. Changing P-T conditions can cause the fluids to directly precipitate sodic plagioclase ($\pm$ other aluminosilicate minerals) since the content of these clusters will be reduced in the aqueous fluids (Manning, 2018; Manning et al., 2010; Wohlers et al., 2011). By dissolution and reprecipitation, the fluids can also react with quartz and phengite + quartz to produce the observed sodic plagioclase rims and the plagioclase + quartz associations, respectively. For each of these cases, dissolution of a precursor Na-rich mineral has to be invoked to interpret the precipitation of sodic plagioclase in this study. Omphacite is the best candidate mineral as it could release a significant jadeite component into the fluid during decompression. Sodic plagioclases in different textural settings contain different albite contents (Table S1), and their formation likely represents a prolonged process. Both the chemical evolution of the active HP fluid and changing P-T conditions could have been responsible for such compositional differences.

The occurrence of sodic plagioclase rims in the eclogite-vein system implies that the active HP fluid is a Si-Al-Na-rich aqueous fluid. As calculated above, the mobilization of other major elements, like Ca, Mg, Fe, Mn, and C, indicates that they are additional important components in the fluid. For trace elements, it

has been pointed out that the active HP fluid is rich in Ba. On the basis of the Ba, Rb, and Cs contents in phengite Zone B and the partition coefficients of these elements between phengite and aqueous fluids empirically calibrated at 1.8–2.0 GPa and 650 °C by Zack et al. (2001), concentrations of 0.5–2.8 wt.% Ba, 23–48 ppm Rb, and 7.0–9.2 ppm Cs were estimated for the fluid. In addition, a Cl content of 0.4–1.8 wt.% was obtained for the fluid by using the Cl partitioning coefficient between apatite and aqueous fluids experimentally calibrated at 2.5 GPa and 660 °C (run no. C3314; Li & Hermann, 2015). Further quantitative estimates on the trace element chemistry of the HP fluid cannot be made as the partitioning coefficients for most other trace elements between altered or newly precipitated minerals and aqueous fluids are not available.

10.3. Mass Transfer and Element Mobilization During the Quartz-Garnet Vein Formation

10.3.1. Mobilization of Major Elements

The quartz-garnet vein gained 18% SiO₂ and 280% P₂O₅ (see above), which is consistent with the modal content increase of quartz and apatite in the quartz-garnet vein. The dissolution of omphacite (Na-Al-Mg-Ca-Fe), phengite (K-Al-Mg-Fe), dolomite (Mg-Ca-Fe-Mn), and rutile (Ti) led to the removal of Na, K, Al, Mg, Ca, Fe, Mn, Ti, and most CO₂ from the quartz-garnet vein.

10.3.2. Mobilization of Trace Elements

As already noticed in early studies, the mobility of different groups of trace elements during fluid-rock interaction depends on the reactivity and solubility of one or two key host minerals in the eclogite-facies rocks, for example, Cs-Rb-Ba by phengite; Sr-Pb-LREEs-Th-U by epidote-group minerals and apatite; MREEs by epidote-group minerals, apatite, and garnet; HREEs-Y by garnet; Nb-Ta by rutile and titanite; and Zr-Hf by zircon (e.g., Beinlich et al., 2010; Guo et al., 2012; John et al., 2008; Li et al., 2013; Rubatto & Hermann, 2003; Spandler & Hermann, 2006; Taetz et al., 2016).

In this study, Li (45%) and LILEs (Cs 58%, Rb 53%, Ba 70%, Sr 40%, and Pb 37%) were variably removed from the quartz-garnet vein. While this study did not measure the trace element composition of omphacite, early researches have revealed that this phase is the major host of Li in basaltic eclogites (Spandler & Pirard, 2013, and references therein). Therefore, the observed dissolution and removal of omphacite can well account for the loss of Li from the quartz-garnet vein. The loss of Cs, Rb, and Ba can be largely attributed to the dissolution of phengite. Phengite constitutes another important host of Li in the eclogite (Table S2) so that its dissolution also contributed partly to the loss of Li. Apatite is a major host of Sr and Pb in the peak eclogite (Table S4). As described above, the introduction of P₂O₅ led to net growth of apatite in the quartz-garnet vein during the fluid-rock interaction, in contrast to the loss of Sr and Pb. Together with the LREEs, these two elements could have been leached away from the apatite but they could have been accommodated by the newly precipitated epidote-allanite (Table S2). In addition to apatite, dolomite is another important host of Sr and Pb in the peak eclogite (Table S4), which is able to accommodate much higher amounts of these elements than apatite. Thus, the loss of Sr and Pb could be attributed to the total dissolution of dolomite in the quartz-garnet vein.

While HREEs and Y were immobile during the quartz-garnet vein formation (see Text S2), the abundances of LREEs and MREEs increased in the quartz-garnet vein. The gain degree increased gradually from La (43%) to Sm (115%) and then decreased to Ho (1%). This pattern is similar to the REE distribution pattern of the highly altered and newly grown apatite in the quartz-garnet vein (Figure 10f), which indicates that the LREE and MREE gains were mainly controlled by the net growth of apatite in the quartz-garnet vein.

With respect to HFSEs, the quartz-garnet vein gained Zr (114%), Hf (121%), Th (28%), and U (19%), whereas Nb (64%) was lost. Gains in Zr and Hf indicate net growth of zircon in the quartz-garnet vein, whereas gains in Th and U can be attributed to the net growth of apatite and new precipitation of epidote-allanite. Losses in Nb and Ti are coupled and reflect the dissolution of rutile. Aqueous fluids released from subducted slabs are generally believed to be strongly depleted in Ti-Nb-Ta and Zr-Hf, implying low solubility of these elements in subduction-zone aqueous fluids (Brenan et al., 1994, 1995; Frezzotti & Ferrando, 2015; Green & Adam, 2003; Kessel et al., 2005; Liu, Massonne, Wu, et al., 2017; Malaspina et al., 2006; Stalder et al., 1998). However, just like this study, other studies have also reported distinct (small-scale?) mobilization of Ti-Nb-Ta and Zr-Hf during fluid-rock interaction from several HP and UHP terranes (e.g., Beinlich et al., 2010; Gao et al., 2007; Guo et al., 2012; John et al., 2008; Li et al., 2013; Rubatto & Hermann, 2003; Taetz et al., 2016; Zhang et al., 2008). Rutile has a very low solubility in pure H₂O (Audétat & Keppler, 2005; Tropper & Manning, 2005), but the addition of F and Na-Al-Si components in aqueous fluids can significantly

Table 3
Calculated Fluid-Rock Ratios to Interpret the Formation of Quartz-Garnet Vein

	Eclogite (wt.%)	Mass change (%)	M_e (10^{-3} mol/cm ³)	Fluid ^a (wt.%)	ΔC_e (10^{-3} mol/cm ³)	$M_e/\Delta C_e$ (cm ³ /cm ³)
SiO ₂	49.36	18	5.11	8.246	1.72	2.97
Al ₂ O ₃	12.94	44	1.93	1.135	0.14	13.8
Na ₂ O	2.46	83	1.14	1.183	0.24	4.76

Note. The eclogite and fluid densities were assumed as 3.45 and 1.25 g/cm³, respectively.

^aOxide solubilities in aqueous fluid are from Wohlers et al. (2011), which were assumed as ΔC_e s. See text for calculation details.

enhance the solubility of rutile such that it facilitates the mobilization of Ti-Nb-Ta due to the formation of various complexes (Antignano & Manning, 2008; Chen et al., 2018; Hayden & Manning, 2011; Manning et al., 2008; Rapp et al., 2010; Tanis et al., 2016). As discussed above, the active HP fluid in the quartz-garnet vein was rich in Na-Al-Si components. In addition, certain amounts of F must have been in the fluid because the altered apatite is rich in F (1.9–2.8 wt.%), although F is strongly partitioned into apatite relative to aqueous fluids (Li & Hermann, 2015). Similarly, complexing with halogens and Na-Al-Si could explain the distinct mobilization of Zr-Hf in the aqueous fluids (Ayers et al., 2012; Bernini et al., 2013; Jahn et al., 2015; Mysen, 2015; Wilke et al., 2012).

The quartz-garnet vein also lost significant amounts of TMEs (Sc 48%, V 82%, Cr 73%, Ni 75%, and Zn 58%). This is explained by the dissolution of omphacite, phengite, dolomite, and pyrite (Tables S2 and S4; Li et al., 2013).

10.3.3. Fluid Advection and Flux

Fluid advection is a key mechanism for mass transfer and element mobilization during fluid-rock interaction and can be focused in a deformation-induced channel (e.g., a hydraulic fracture or a shear zone). Alternatively, this interaction can be related to pervasive infiltration along grain boundaries and other microstructures (Ague, 2014; Austrheim, 2013; Bebout & Penniston-Dorland, 2016; Bickle, 1992; Ferry, 1994). A fluid channel is characterized by a higher porosity and permeability than the surrounding metamorphic rocks so that focused fluid advection generally results in a much larger fluid flux and a more distinct alteration to the fluxed rocks than does pervasive fluid infiltration. For instance, focused fluid advection in a fracture often results in veins consisting of newly precipitated phases and macroscopic leached selvages on both sides of the fracture (e.g., Beinlich et al., 2010; Guo et al., 2012; Guo et al., 2015; John et al., 2008; Li et al., 2013; Spandler & Hermann, 2006; Taetz et al., 2016, 2018), whereas pervasive fluid infiltration often results in only microscopic alteration of the original minerals in the rock (e.g., Giuntoli, Lanari, Brun, et al., 2018; Giuntoli, Lanari, & Engi, 2018; Halama et al., 2014; Konrad-Schmolke et al., 2011; Liu, Massonne, Wu, et al., 2017). Both focused and pervasive fluid advectations were observed in this study. The focused fluid advection led to the formation of the quartz-garnet veins, which are interpreted as leached fracture zones (Liu et al., 2018) instead of a fracture filled with newly precipitated minerals. The pervasive fluid advection is reflected by the pervasive distribution of the albite rims (Figures 3h, 3i, 5b, and 5c) and the extensive alteration of relict peak minerals in the eclogite.

For the formation of the quartz-garnet vein, advective mass transport was calculated using the following equation (Ague, 2003):

$$q_{TI} \approx L(M_e/\Delta C_e) \quad (5)$$

where q_{TI} (m³/m²) is the time-integrated fluid flux, L (m) is the geochemical alteration distance along the fluid flow direction, M_e (mol/m³) is the moles of element e added (+) or removed (−) per volume rock, and ΔC_e is the concentration difference (mol/m³) of element e between the input and equilibrium fluids.

L cannot be estimated here so that only the term $M_e/\Delta C_e$ was calculated. Such a term is equivalent to the fluid-rock ratio in Bickle (1992), that is, the volume of reactive fluid that was needed to alter a unit volume of rock. The calculations were conducted in reference to the mass changes of SiO₂, Al₂O₃, and Na₂O in the quartz-garnet vein. Recent solubility experiments have revealed that aqueous fluids in equilibrium with albite/jadeite + quartz + paragonite could contain 8.25 wt.% SiO₂, 1.14 wt.% Al₂O₃, and 1.18 wt.% Na₂O at 1.75 GPa and 600 °C (Wohlers et al., 2011). At somewhat higher temperatures, under which the fluid-

eclogite interaction probably happened, the contents of these oxides should be higher in aqueous fluids but this will not significantly change our estimates. A density of 3.45 and 1.25 g/cm³ was chosen for the eclogite and the solute-rich fluid, respectively. In combination with the solubility experimental results mentioned above, the fluid was calculated to contain 1.72×10^{-3} mol/cm³ SiO₂, 0.14×10^{-3} mol/cm³ Al₂O₃, and 0.24×10^{-3} mol/cm³ Na₂O, which were assumed to be the ΔC_e s. According to this assumption, the calculated $M_e/\Delta C_e$ ratios are 2.97 cm³/cm³ (SiO₂), 13.8 cm³/cm³ (Al₂O₃), and 4.76 cm³/cm³ (Na₂O), respectively (Table 3), which represents a minimum estimate and indicates a high fluid flux (Bickle, 1992).

11. Summary and Conclusions

The eclogite-vein system from the Dabie UHP terrane documents complex HP fluid-rock interactions during exhumation. Relict peak minerals, including garnet, phengite, and apatite in the system, were chemically altered by the HP fluid through a coupled dissolution and reprecipitation mechanism, giving rise to variable and characteristic zoning patterns for these minerals. Peak garnet in the eclogite was replaced first by a Mg-rich zone and then by a Ca-rich zone, which suggests a nearly isothermal exhumation from the peak P-T conditions of c. 3.3 GPa and 665–680 °C to the P-T conditions of the amphibolite-facies. The Mn and HREE-Y contents remained unchanged in the two replacing garnet zones since the modal content of garnet changed little in the eclogite during the HP fluid-rock interaction. Garnet in the quartz-garnet vein is a relict phase from the precursor eclogite, which was partially dissolved by the HP fluid. Back incorporation of Mn and HREEs-Y elevated the contents of these elements significantly in the altered garnet zone. Altered phengite is commonly characterized by a Ba-rich rim. In response to fluid-aided alteration, the LREE contents were reduced and oriented monazite, calcite, and pyrrhotite inclusions formed in apatite, reflecting mobilization and redistribution of LREEs, CO₃²⁻, Fe, and S between these minerals. In addition to monazite, secondary epidote group minerals accommodated part of LREEs released from apatite.

Sodic plagioclase rims and plagioclase + quartz associations in the eclogite-vein system do not represent melt pseudomorphs. Instead, they indicate that the active HP fluid was a Si-Al-Na-rich aqueous fluid which formed close to the wet solidus. The aqueous fluid was also rich in Ba, as suggested by the altered phengite composition and the precipitation of Ba-rich K-feldspar. Mass balance calculations show that SiO₂, P₂O₅, LREEs, MREEs, and Zr-Hf-Th-U were added to and Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, Li, LILEs, TMEs, and Ti-Nb were removed from the quartz-garnet vein during the HP fluid-rock interaction. The net growth of quartz-apatite-epidote group minerals-zircon and the dissolution of omphacite-phengite-dolomite-pyrite governed such compositional changes. In case of fluid advection, a high fluid flux was needed to interpret the observed mass transfer. To sum up, this study contributes to understanding the nature and behavior of HP fluids and their key role in resetting mineral compositions and facilitating mass transfer in subduction zone metamorphic environments.

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