# UHP eclogite from western Dabie records evidence of polycyclic burial during continental subduction

BIN XIA<sup>1,\*</sup>, YUNFENG SHANG<sup>1</sup>, XIANBIN LU<sup>1</sup>, AND YUANBAO WU<sup>1</sup>

<sup>1</sup>School of Earth Sciences, State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China

#### Abstract

Understanding the behavior of continental crust during subduction is important for investigating dynamic processes at convergent plate margins. Although simulations have predicted continental crust may experience multiple burial-partial exhumation cycles during subduction, petrological evidence of these cycles is scarce. In this study at Sidaohe, western Dabie, we combine microstructural observations and mineral chemistry with phase equilibrium modeling, Amp-Pl thermobarometry and Zr-in-rutile thermometry to constrain the *P*-*T* evolution for three eclogite samples. All samples have a similar mineral assemblage of garnet + omphacite + symplectite (amphibole + plagioclase  $\pm$  clinopyroxene) + quartz, with accessory rutile/ilmenite. Element mapping and analytical traverses across large garnets from two samples show obviously systematic variations in Ca and, less strongly, Mg, Fe, and  $X_{Me}$  [Mg/(Mg+Fe<sup>2+</sup>)]. Based on phase equilibrium modeling and calculated isopleths for grossular, pyrope and  $X_{Mg}$  in garnet, we show that P first increased from 23.0 to 28.5 kbar, then decreased to 24.0 kbar, before increasing again to a maximum of 30.5 kbar ( $\pm 1.0$  kbar, 2 sigma error) concomitant with a small increase in T from 580 to 605 °C ( $\pm 20$  °C, 2 sigma error) at the late prograde stage. These data are interpreted to indicate multiple burial cycles and partial exhumation of eclogite during ongoing continental subduction. After the Pmax stage, T first increased to a maximum of 664-644 °C at 25.0-20.0 kbar, then decreased to 581-561 °C (±30 °C, 2 sigma error) at 15.0-10.0 kbar based on results of Zr-in-rutile thermometry. Further decompression and cooling occurred across P-T fields of 590-567 °C at 12.0-10.0 kbar and 520-504 °C (±40 °C, 2 sigma error) at 8.0 kbar. Fine-grained symplectite (clinopyroxene + plagioclase  $\pm$  amphibole) in the matrix is interpreted to have formed after omphacite due to dehydroxylation of nominally anhydrous minerals during decompression from the  $P_{\text{max}}$  stage. By contrast, formation of coarse-grained symplectite (amphibole + plagioclase) and a veinlet of rutile + quartz that crosscuts one sample may be related to influx of externally sourced H<sub>2</sub>O. This study shows that: (1) evidence of cyclic burial and partial exhumation may be retained in low-T eclogite during continental subduction, and (2) fluid contributing to widespread retrogression of eclogite during exhumation may be internally and/or externally sourced.

Keywords: Eclogite, phase equilibrium modeling, multiple burial cycles, continental subduction, western Dabie

#### INTRODUCTION

Subduction zones play a key role in material recycling between Earth's surface and its interior (Zheng et al. 2012). Based on geological and geophysical observations, and on numerical simulations, a model was developed to understand the dynamics of ocean slab subduction beneath arcs or continents into the mantle (Shreve and Cloos 1986; Cloos and Shreve 1988; Gerya et al. 2002). In this model, a subduction channel develops between the upper and lower plates where a mélange of sediments, crustal fragments and fluid accommodates deformation, metamorphism and metasomatism (Shreve and Cloos 1986). Subsequently, the model was applied to interpret geodynamic processes in continental collision zones (e.g., Zheng et al. 2012; Butler et al. 2013). Similar to the model for oceanic subduction, during continental subduction detached fragments of continental crust were predicted to undergo multiple burial-exhumation cycles due to convective flow (Gerya et al. 2002; Gerya and Stöckhert 2006; Zheng et al. 2009). However, direct petrological evidence for this behavior is sparse (e.g., Beltrando et al. 2007; Rubatto et al. 2011) and the detailed movements of detached fragments of continental crust during subduction are poorly known.

To understand geodynamic processes operating in continental subduction channels we need a robust determination of the *P*-*T* evolution of high-pressure (HP) and ultrahigh-pressure (UHP) rocks (Wei et al. 2010; Li et al. 2016; Xia et al. 2018a; Bovay et al. 2021). Using phase equilibrium modeling and compositional isopleth thermobarometry (Wei et al. 2010; Groppo et al. 2015), we can constrain *P*-*T* conditions from rock-forming minerals in eclogite (e.g., garnet, phengite) under the assumption that the chemical composition was not reset, or was only slightly reset, during the post-peak metamorphic evolution (Caddick et

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<sup>\*</sup> E-mail: xiabin@cug.edu.cn

al. 2010; Rubatto et al. 2011; Bovay et al. 2021). For instance, studies of garnet with growth zonation from eclogite in the Chinese SW Tianshan (Li et al. 2016) and from schists in the Sevier hinterland, U.S.A. (Harris et al. 2007) revealed episodes of sharp increases and decreases in *P*, interpreted to represent multiple burial-exhumation cycles. In both cases, the garnet occurs in rocks with relatively low *T* at the peak stage (<550 °C), which is beneficial for the retention of *P*-*T* information in compositionally zoned garnet. However, eclogite in continental subduction zones commonly records higher a *T* at the peak or during the retrograde stages (>650 °C; Carswell and Zhang 1999), which may result in the removal of early-stage *P*-*T* information due to compositional re-equilibration (Liu et al. 2006; Caddick et al. 2010; Groppo et al. 2015; Xia et al. 2018a).

The Sulu-Dabie belt, which formed during the Triassic collision between the Yangzi and Sino-Korean cratons, has been regarded as the typical example for continental subduction (Fig. 1a; Zheng et al. 2012, 2019). However, no petrological evidence supporting a polycyclic burial-exhumation process has been reported from HP-UHP rocks from the Sulu-Dabie belt. In western Dabie, peak temperature for HP-UHP eclogite was constrained to 520-670 °C at 26.0-31.0 kbar (Zhang and Liou 1994; Liu et al. 2004, 2006; Wei et al. 2010), distinctly lower than eclogite from the eastern Dabie (average of  $700 \pm 50$  °C at >28.0 kbar) and Sulu (average of 750  $\pm$  50 °C at 29.0–43.0 kbar) belts (Zhang et al. 2009; Suo et al. 2012; Wu and Zheng 2013; Li et al. 2018; Zheng et al. 2019). In addition, previous studies have shown that garnet from eclogite in western Dabie commonly has growth zoning (Liu et al. 2004, 2006; Wei et al. 2010). Therefore, we infer that early-stage P-T information may have



**FIGURE 1. (a)** Tectonic framework of the Sulu-Dabie orogen in central China. It is located between the Yangtze craton to the south and the Sino-Korean craton to the north. (b) Geological map of the western Dabie (modified from Wei et al. 2010). Based on lithologies and metamorphic grade, western Dabie is subdivided into 6 units. From south to north, they are: the Mulanshan greenschist-blueschist unit, the Hong'an HP eclogite unit, the Xinxian UHP eclogite unit, the Huwan HP eclogite unit, the Balifan mélange unit and the Nanwan flysch unit. (Color online.)

been retained in garnet from these eclogites. In this study, we determine P-T conditions for the prograde, peak and retrograde stages and construct a complete P-T path for eclogite at Sidaohe, western Dabie. Based on phase equilibrium modeling using compositional isopleth thermobarometry, we report changes in P from eclogite, which we interpret to represent polycyclic burial-partial exhumation processes during continental subduction.

#### **GEOLOGICAL BACKGROUND**

In western Dabie (Fig. 1b; also known as the Hong'an block), various types of metabasite (blueschist, greenschist, and eclogite) and serpentinite are mainly enclosed in volumetrically dominant metasedimentary rocks and granitic gneiss as blocks, lenses and occasionally, intercalated layers (Liu et al. 2004). From south to north, based on systematic variations of lithologies and metamorphic grade, six lithotectonic units are subdivided (Fig. 1b; Wei et al. 2010), which are: the Mulanshan greenschistblueschist unit (peak P-T conditions for garnet-bearing blueschist at 5.0-11.0 kbar, 319-427 °C; Liu et al. 2004), the Hong'an HP eclogite unit (peak P-T conditions for eclogite at 19.0-26.0 kbar, 485-585 °C; Liu et al. 2004; Lou et al. 2013), the Xinxian UHP eclogite unit (P<sub>max</sub> stage P-T conditions for eclogite at 28.0-32.0 kbar, 520-670 °C; Zhang and Liou 1994; Liu et al. 2004, 2006; Wei et al. 2010), the Huwan HP eclogite unit (peak P-T conditions for eclogite at 18.0-23.0 kbar, 540-630 °C; Liu et al. 2004; Ratschbacher et al. 2006), the Balifan mélange unit (P-T conditions for a mylonitized quartz-feldspathic schist at 9.0-10.0 kbar, 458-516 °C; Liu et al. 2004) and the Nanwan flysch unit. The variation of metamorphic grade and the architecture of units has been interpreted to represent a huge anticline with UHP rocks at the core and HP rocks at the two limbs, similar to the eastern Dabie belt (Hacker et al. 2000; Liu et al. 2004).

In western Dabie, geochronological studies on eclogite and country rocks have constrained the prograde stage metamorphism to occur at 239–226 Ma, the peak UHP eclogite facies metamorphism at ~226 Ma, the early retrograde eclogite facies metamorphism at 216–213 Ma and the later retrograde amphibolite facies metamorphism at ~212 Ma (Wu and Zheng 2013 and references therein). These ages are comparable to the eastern Dabie and Sulu belts, indicating they are a huge continuous Triassic orogenic belt. However, in the western segment of the Huwan HP eclogite unit, late Carboniferous ages of ~310 Ma have been reported for eclogite and its country rock gneisses (Wu et al. 2009; Liu et al. 2011). Based on geochemical signatures of some eclogite showing oceanic crust affinity, these ages were interpreted to represent an early oceanic subduction prior to the Triassic continental collision (Wu and Zheng 2013).

#### ANALYTICAL METHODS AND SAMPLING

# Analytical methods

Initial mineral analyses and element mapping for symplectite were performed using a JEOL-8230 electron probe microanalyzer with 4 wavelength-dispersive spectrometers (WDS) at the Center for Global Tectonics, School of Earth Sciences, China University of Geosciences (Wuhan). The operating conditions were 15 kV acceleration voltage, 20 nA beam current, and 1 µm beam diameter for garnet and clinopyroxene and 5–10 µm beam diameter for amphibole and plagioclase. Raw X-ray intensities were corrected using a ZAF (atomic number, absorption, fluorescence) correction procedure. A series of natural and synthetic standard peak intensity (SPI) standards were used and changed based on the analyzing minerals. The following standards were used: sanidine (K), pyrope garnet (Fe, Al), diopside (Ca, Mg), jadeite (Na), rhodonite (Mn), olivine (Si), rutile (Ti). Elements in unknown samples were all determined within about 2% relative based on analyses of secondary standards. Representative results are given in Online Materials<sup>1</sup> Tables OM1 and OM2.

Backscattered electron (BSE) images and energy-dispersive spectrometer (EDS) analyses were obtained using an FEI Quanta 200 scanning electron microscope (SEM) equipped with an EDAX EDS system at the State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences (Wuhan). The images were obtained at an accelerating voltage of 20 kV with a spot size of 200–400 nm, an emission current of ~100  $\mu$ A, and a working distance of 11–12 mm.

Trace element analyses of rutile grains were performed by the laser ablationinductively coupled plasma-mass spectrometry (LA-ICP-MS) method at Wuhan Sample Solution Analytical Technology Co. Ltd. Laser sampling was performed using a GeolasHD laser ablation system (wavelength of 193 nm). We used 80 mJ laser energy, 32 µm spot size, and a 5 Hz frequency for the analyses. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. NIST610, BHVO-2G, BIR-1G, and BCR-2G were used as external standards for trace element analysis. Off-line selection and integration of background and analyzed signals, time-drift correction and quantitative calibration for trace element analysis and U-Pb dating were performed by ICP-MSDataCal (Liu et al. 2008). For the detailed procedure, please reference Liu et al. (2008). For inclusions and matrix rutile the microbeam analyses were focused on their central part, for megacrystal rutile two profile analyses were performed. The results are shown in Online Materials<sup>1</sup> Table OM3.

The whole rock compositions were analyzed at the State Key Laboratory of Geological Processes and Mineral Resources. China University of Geosciences (Wuhan) using X-ray fluorescence (XRF) of fused glass disks. The samples were first crushed to <60 mesh in a corundum jaw crusher, then to <200 mesh in an agate mill. Then, 0.5 g of rock powder, together with 5 g of flux (Li2B4O2:LiBO2 = 12:22) were fused in a high-frequency melting furnace for 11 min at ~1050 °C in 95% Pt-5% Au crucibles. The melt was swirled repeatedly to ensure complete dissolution and homogenization of the material, and then poured into a mold to form a thin, flat-surfaced disk (34 mm diameter). The loss-on-ignition (LOI) was measured on dried rock powder by heating in a pre-heated corundum crucible to 1000 °C for 90 min and recording the weight loss. XRF analysis was carried out on a Shimadzu XRF-1800 sequential X-ray fluorescence spectrometer, using a Rh-anode X-ray tube with a voltage of 40 kV and current of 70 mA. Calibration curves used for quantification were produced by bivariate regression of data from ~63 reference materials encompassing a wide range of silicate compositions. The measurement procedure and data quality were monitored by repeated samples (one in eight samples), USGS standard AGV-2 and Chinese National standards GSR-1 and GRS-7.

#### Sampling

In this study, eclogite samples were collected at Sidaohe (115°3'37.33"E, 31°20'32.67"N) in the Xinxian UHP eclogite unit (Fig. 1b). Eclogite occurs as block (4–6 m in diameter) and is enclosed in garnet-bearing felsic gneiss (Fig. 2a). From center to rim, it was more severely retrograded with more abundant quartz veins developed at the edge (Figs. 2a and 2b).

To qualify *P-T* evolution of the eclogite at Sidaohe, we chose three samples (Sdh-1, Sdh-2, and DB17-06) for detailed petrological analysis. Sdh-1 and Sdh-2 were selected for phase equilibrium modeling, while Sdh-1 and DB17-06 were chosen for rutile trace element analysis.

#### Petrology

All samples at Sidaohe, western Dabie show various retrogression in thin sections (Figs. 2c, 2d, and 3). Both eclogite Sdh-1 and Sdh-2 show a granoblastic texture in the scanned thin section (Fig. 2c) and have a similar mineral assemblage of garnet (43–48 vol%) + omphacite (1–3%) + symplectite of Pl  $\pm$  Amp  $\pm$ Cpx (37–42%) + quartz (10–15%) and accessory rutile/ilmenite (2–3%) (Fig. 2c) [note that mineral abbreviations in this study follow Whitney and Evans (2010)]. The eclogite Sdh-1 has slightly more quartz but less symplectite than Sdh-2. Sample DB17-06, with the quartz veinlet, has been more severely retrogressed with less garnet relics but more Pl  $\pm$  Amp  $\pm$  Cpx symplectite in the matrix (Fig. 2d). The veinlet mainly consists of oriented coarse quartz and rutile and  $Pl \pm Amp \pm Cpx$  symplectite (Fig. 2d).

Porphyroblastic garnet (anhedral to subhedral, 0.5-3.0 mm in diameter) is cut by fractures filled with dominantly fine-grained amphibole and/or fibrous  $Amp + Pl \pm Rt/Ilm$  symplectite (Figs. 3a, 3b, 3f, and 3h). Coronas of  $Amp \pm Pl$  develop along garnet rims (Figs. 3h and 3i). Inclusions in garnet are mainly omphacite, quartz,  $Pl \pm Amp \pm Cpx$  symplectite, with rare epidote, amphibole, rutile/ilmenite, and apatite (Figs. 3a-3e and 3k). Traverses from core to rim (Figs. 4a and 4b) and element mapping (Fig. 4c-4f) across a large porphyroblastic garnet from both Sdh-1 and Sdh-2 show obvious zoning of Ca and, less strongly, Mg, Fe, and  $X_{Me}$ , but no Mn zoning. For Sdh-1, Grs first decreases from 31 to 25-26 mol% from core to mantle, then increases to 28-29 mol% before decreasing again to 20-21 mol% from mantle to rim. Alm varies antithetically with Grs but consistently with Pyr (Fig. 4a). From core to rim, Alm first slightly increases from 50 to 52 mol%, then decreases to 50 mol% before increasing again to 55 mol%; Prp first increases from 18 to 21-22 mol%, then decreases to 18-20 mol% before increasing again to 23 mol%;  $X_{Mg}$  varies from 0.26 to 0.30. For Sdh-2, from core to rim, Grs first decreases from 29 to 24-25 mol%, then increases to 28-29 mol% before decreasing again to 23-24 mol%; Alm first increases from 50 to 52-53 mol%, then decreases to 50 mol% before increasing again to 54 mol%; Prp first increases from 18 to 21-22 mol%, then decreases to 20 mol% before increasing again to 22 mol%.  $X_{Mg}$  varies from 0.25 to 0.29–0.30. Sps varies little from core to rim (1–2 mol%) for both samples (Figs. 4a and 4b).

Omphacite is only preserved as inclusions in garnet (Figs. 3c and 3e). In the matrix, it was completely replaced by  $Pl \pm Amp$ ± Cpx symplectite showing short prismatic or granular shapes (Figs. 2c, 3g, and 3h). The reaction was inferred to be  $Omp \pm H_2O$  $\rightarrow$  Pl ± Amp ± Cpx, as has been evidenced by the symplectite partially replacing omphacite in garnet (Fig. 3c). Intergrowths of Cpx, Pl, and/or Amp are generally perpendicular to the reaction front (Figs. 3c, 3g, and 5a-5g). Previous studies have shown that symplectite usually grew from the original omphacite margins to the reaction front and the thickness of the lamellaes usually decreases with decreasing temperature (Joanny et al. 1991; Waters 2003; Lanari et al. 2013). Therefore, in the matrix, we define Cpx-bearing symplectites of Cpx1+Amp1+Pl1 (mineral grain sizes 50–100 µm in diameter; Figures 3d, 3e, 3g, 3h, 3j, 5a, 5b, and 5d-5k) as Sym1 and Cpx2 + Pl2 (commonly <20 µm in diameter; Figs. 3g, 3h, 5a, and 5b) as Sym2. For the Cpx-absent symplectite of Amp3 + Pl3 (commonly >100 µm; Figs. 3h and 3i) formed at later amphibolite facies metamorphism (Martin 2019), we define it as Sym3. For both Sdh-1 and Sdh-2, omphacite included in garnet has constant X<sub>Jd</sub> of 42-45 mol% while Cpx1 in Sym1 has lower X<sub>Jd</sub> of 12-26 mol% (Fig. 6a). Composition of Cpx2 in Sym2 was not measured due to its small dimensions (<10 µm in diameter).

Amphibole in eclogite is found in three textural positions. (1) As inclusions in garnet (Figs. 3a and 3i). For Sdh-1 and Sdh-2, Amp has comparable  $^{c}(Al + Fe^{3+} + 2Ti)$  of 1.29–1.93 apfu and  $^{A}(Na + K + 2Ca)$  of 0.35–0.70 apfu (23 O basis), mostly ranging from sadanagaite to tschermakite, with only one pargasite (Fig. 6b; Hawthorne et al. 2012). (2) Together with Pl constituting Sym1 (Amp1; Figs. 5a and 5b) and Sym3 (Amp3; Figs. 3g, 3h,

and 3i). For Sdh-1, Amp1 has  ${}^{c}(A1 + Fe^{3+} + 2Ti)$  of 0.89–1.41 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.46–0.58 apfu, ranging from pargasite to magnesiohornblende; Amp3 has  ${}^{c}(A1 + Fe^{3+} + 2Ti)$  of 0.79–0.94 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.15–0.27 apfu, is magnesiohornblende. For Sdh-2, Amp1 has  ${}^{c}(A1 + Fe^{3+} + 2Ti)$  of 1.48 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.50 apfu, is magnesiohornblende; Amp3 has  ${}^{c}(A1 + Fe^{3+} + 2Ti)$  of 0.59–1.03 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.59–1.03 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.07–0.21 apfu, is magnesiohornblende (Fig. 6b). And (3) rimming garnet (Figs. 3i and 3j) or together with Pl and Rt/Ilm in cracks in garnet (Fig. 3f), has  ${}^{c}(A1 + Fe^{3+} + 2Ti)$  of 1.61–1.77 apfu and  ${}^{A}(Na + K + 2Ca)$  of 0.66–0.71 apfu, belonging to Sadanagaite (Fig. 6b).

Plagioclase in both Sym1 and Sym3 is albite with  $Ab_{0.92-0.99 \,(mean \, 0.96)}$ . Epidote is included in garnet but absent in the matrix (Fig. 3a). It has  $Fe^{3+}$  of 0.61.

Rutile shows various occurrences in thin sections: as inclusions in garnet (30–100  $\mu$ m; inclusion Rt as type 1; Fig. 3i); in the matrix (100–300  $\mu$ m; matrix Rt as type 2; Figs. 3j and 3k) and as megacrystals in the veinlet (500–4000  $\mu$ m; megacrystal rutile as

FIGURE 2. (a) Eclogitic block enclosed in the host garnet-bearing felsic gneiss. Eclogite is strongly retrogressed from the center toward the rim. Abundant quartz veins are at the edge of the block, with less in its interior. (b) Small veinlets in the center of the block where eclogite Sdh-1 was sampled. Close to veinlet, eclogite was more strongly retrogressed. (c) Thin section for Sdh-1 showing bimineralic texture with omphacite in the matrix completely replaced by Pl  $\pm$ Amp  $\pm$  Cpx symplectite. (d) Thin section for DB17-06 with veinlet of megacrystal rutile and quartz cross-cutting eclogite. (Color online.) type 3; Figs. 2d and 31). Most of rutile grains have been partially replaced by ilmenite along rims or fractures (Figs. 3j, 3k, and 31).

Based on the above petrographic observations and mineral compositions, several stages in the metamorphic evolution of the eclogite at Sidaohe, western Dabie may be inferred. Evidence of the prograde metamorphic stage (M0) is recorded by garnet and its inclusions of omphacite, amphibole, quartz, epidote and rutile (type 1).  $Pl \pm Amp \pm Cpx$  symplectite in the matrix is interpreted to represent former omphacite and is a typical decompressionrelated texture in eclogite (Joanny et al. 1991). The peak stage (M1) mineral assemblage is inferred to be Grt + Omp + Qtz + Rt (type 2). The retrograde metamorphic stage (M2) is represented by the breakdown of Omp to form Sym1 (Cpx1+Amp1 + Pl1) and Sym2 (Cpx2 + Pl2). The late retrograde metamorphic stage (M3) is represented by Sym3 (Amp3 + Pl3) replacing Sym1 and Sym2 (Fig. 3e), amphibole/plagioclase and chlorite replacing garnet (Figs. 3c and 3g). Megacrystal rutile (type 3) in veinlets may be formed prior to stage M3, whereas ilmenite replacing rutile in the matrix may form at this stage.





**FIGURE 3.** Photomicrographs showing the mineralogy and microstructures of eclogite in BSE images (**a**, **b**, **c**, **f**, **l**), under cross-polarized light (**e**) and plane-polarized light (**d**, **g**, **h**, **i**, **j**, **k**). (**a**) Subhedral garnet porphyroblast from Sdh-1 with inclusions of Ep, Amp, Omp, and Qtz; cracks in garnet are mainly filled with Amp + Pl + Rt/Ilm. Traverses of point analyses roughly follow the solid white line. (**b**) Subhedral garnet porphyroblast from Sdh-2. Traverses of point analyses roughly follow the solid white line. (**b**) Subhedral garnet porphyroblast from Sdh-2. Traverses of point analyses roughly follow the solid white line. (**c**) Omphacite inclusion in garnet of **a**. Omphacite was partly replaced by Cpx + Pl symplectite (Sym2) which was rimmed by coarse Amp. (**d** and **e**) Omphacite inclusion in garnet. In the matrix, Pl ± Amp ± Cpx symplectite shows short prismatic or granular shapes interpreted to be pseudomorphs after omphacite. (**f**) Fractures in garnet filled with fibrous Amp + Pl ± Rt/Ilm symplectite. (**g** and **h**) Cpx + Pl + Amp (Sym1), Cpx + Pl (Sym2) and Amp + Pl (Sym3) symplectites in the matrix showing short prismatic shape; (**i**) Rutile inclusions in garnet (type 1). (**j**) Rutile as single grains in the matrix abutting garnet (type 2). (**k**) Rutile in the matrix surrounded by Qtz + Amp or Pl ± Amp ± Cpx symplectite (type 2). (**l**) Megacrystal rutile in quartz veinlet crosscutting eclogite (type 3). Rutile has been partially replaced by ilmenite along rims or fractures. (Color online.)

#### PHASE EQUILIBRIUM MODELING

To constrain peak *P*-*T* conditions and metamorphic processes for the eclogite at Sidaohe, western Dabie, phase equilibrium modeling was performed using THERMOCALC software (version 3.40, updated in March 2014) and the associated internally consistent thermodynamic data set ds62 (Holland and Powell 2011; updated in November 2016). The chemical system used for modeling is (Mn)NCFMASHTO [(MnO-)Na<sub>2</sub>O-CaO-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-TiO<sub>2</sub>-O] system. A–x relationships used in the modeling are as follows: garnet (White et al. 2014); clinopyroxene and amphibole (Green et al. 2016); plagioclase (Holland and Powell 2003); and epidote (Holland and Powell 2011). Rutile, sphene, lawsonite, kyanite, quartz, and H<sub>2</sub>O are considered to be pure phases.

In the modeling to constrain the prograde to peak *P*-*T* evolution for the eclogites Sdh-1 and Sdh-2, the whole-rock compositions obtained by XRF were used after correction of the CaO content for the P<sub>2</sub>O<sub>3</sub> contained in apatite (Table 1). The O content (equals to Fe<sub>2</sub>O<sub>3</sub> in molar percent) was calculated from the whole-rock composition of eclogite sampled in the same locality of this study by Yan et al. (2005). In their study using wet chemistry, eclogite and retrograded eclogite gave a consistent Fe<sub>2</sub>O<sub>3</sub> (in molar percent)/ FeO<sup>T</sup> (in mol%) ratio of 7.5%. H<sub>2</sub>O was set to be in excess based on the assumption that the prograde evolution may be H<sub>2</sub>O saturated



**FIGURE 4.** Traverses of point analyses for garnet from (**a**) Sdh-1 and (**b**) Sdh-2. Half A and B represent analyses for one half and the other half of the garnet, respectively. (**c**–**d**) Element mapping of Ca and Mg for a large porphyroblastic garnet from Sdh-1; the dotted lines may represent garnet zoning patterns. (**e**–**f**) Ca and Mg element mapping for a large porphyroblastic garnet from Sdh-2; the dotted lines represent suggested garnet zoning patterns. (Color online.)



**FIGURE 5.** Photomicrographs showing the microstructures of symplectite in Sdh-1 under plane-polarized light (**a**) and in BSE images (**b** and **c**). Element maps of Sym1 ( $\mathbf{d}$ - $\mathbf{f}$ ) and Sym2 ( $\mathbf{h}$ - $\mathbf{k}$ ) showing intergrowths of Cpx, Pl, and/or Amp generally oriented perpendicular to the reaction front. From Sym1 to Sym2, Amp (in volume content) decreases while Cpx increases ( $\mathbf{d}$ - $\mathbf{k}$ ). (Color online.)

considering the progressive transition from a mineral assemblage dominated by hydrous minerals (e.g., epidote, lawsonite, chlorite, and glaucophane) to one dominated by anhydrous minerals (e.g., garnet and omphacite), and the observed abundance of hydrous minerals as inclusions in garnet. To constrain *P*-*T* conditions for the retrograde stage forming Cpx + Pl + Amp symplectites after omphacite, the effective bulk-rock composition calculated from the equilibrated reaction combined with mineral compositions was used in the phase equilibrium modeling. The balanced reaction forming Sym1 after omphacite using the least square method (software PCalc2.3 by Godard 2009) applied to compositions of Omp, Cpx1, Pl1, and Amp1 is as follows:

$$1.00 \text{ Omp} + 0.25 \text{ Qtz} + 0.02 \text{ H}_2\text{O} = 0.59 \text{ Cpx}2 + 0.32 \text{ Pl2} + 0.02 \text{ Amp2}.$$
(1)

 $TiO_2$  in the effective bulk composition is same as the value for modeling in Figure 7a and H<sub>2</sub>O was set to be in excess (Table 1). Sample compositions (in wt%) and corrected or modified bulk compositions (in mol%) used for phase equilibrium modeling are given in Table 1.

#### Prograde to peak metamorphic stages

P-T pseudosections constraining the prograde to peak P-T evolution for the eclogites Sdh-1 (Fig. 7a) and Sdh-2 (Fig. 7b) were calculated in the MnNCFMASHTO system using the bulk

compositions in Table 1 for the *P*-*T* range 12.0–32.0 kbar and 500–700 °C. Both calculations show similar topology for phase relations. For instance, lawsonite is present in the top-left phase assemblage fields and is replaced by epidote at P <21.0 kbar at T <610-615 °C, and by Grt + Omp ± Ky at T>610 °C; glaucophane/hornblende is replaced by Grt + Omp ± Ky at P>20.5 kbar and T >590-595 °C. However, kyanite is modeled to be present at P of 19.5–26.0 kbar at T>610 °C in Figure 7a, but is absent in Figure 7b; epidote is modeled to be present at T>640 °C in Figure 7b.

Isopleths for Grs (18–38 mol%), Prp (7–26 mol%), and  $X_{Mg}$ (0.25-0.30) in garnet and j(o) [Na/(Na+Ca), 0.45-0.54] in omphacite have been calculated for most of the modeled P-T range (Figs. 7c and 7d). The results show that Grs values in garnet roughly decrease while Prp and  $X_{Mg}$  values roughly increase with increasing pressure and temperature (Figs. 7c and 7d). In the phase assemblage fields of Grt + Omp + Lws + Gln + Coe/Qtz + Rt + H<sub>2</sub>O, the measured Grs, Prp and  $X_{Mg}$  in garnet from Sdh-1 (Grs = 0.31–0.21, Prp = 0.18–0.23, and  $X_{Mg}$  = 0.26–0.30) and Sdh-2 (Grs = 0.29–0.23, Prp = 0.18–0.22, and  $X_{Mg}$  = 0.25–0.30) define comparable P-T fields of 23.0-30.5 kbar, 585-605 °C, and 24.5-29.5 kbar, 580-600 °C, respectively (Figs. 7c and 7d). From garnet core to rim, P first increases from 23.0 to 28.5 kbar, then decreases to 24.0 kbar before increasing again to 30.5 kbar concomitant with a small increase in T from 580 to 605 °C (Figs. 7e and 7g). In the phase assemblage fields of Grt + Omp + Lws  $\pm$ 



FIGURE 6. Compositions of omphacite and amphibole from the eclogite Sdh-1 and Sdh-2. (a) Compositions of omphacite. WEF represents end-members for Wo (wollastonite), En (enstatite), and Fs (ferrosilite) after Morimoto et al. (1988). (b) Classification of amphibole with various occurrences (after Hawthorne et al. 2012). Ing = as inclusions in garnet; rimg = rimming garnet. (Color online.)

TABLE 1. Whole-rock compositions (in wt%) together with modified bulk compositions (in mol%) used for phase diagram calculations for eclogite at Sidaohe, western Dabie

Samples	Figures	H₂O	SiO <sub>2</sub>	$AI_2O_3$	CaO	MgO	FeO (FeO <sup>7</sup> )	K₂O	Na₂O	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub> (O)	P <sub>2</sub> O <sub>5</sub>
					Primary b	ulk-rock co	omposition (wt	%)					-
Sdh-1		*	50.99	13.97	9.54	5.52	14.28	0.03	2.87	2.46	0.22	*	0.39
Sdh-2		*	48.02	13.73	9.99	6.04	14.85	0.04	2.87	2.32	0.21	*	0.43
					Corrected b	oulk-rock co	omposition (mo	ol%)					
Sdh-1	7a and 7c	excess	54.53	8.80	10.34	8.80	11.49	0.02	2.97	1.98	0.19	0.86	
	8a	excess	57.59	6.18	11.82	10.98	4.80	0.00	5.65	1.99	0.00	0.98	
	8b	0.00	57.59	6.18	11.82	10.98	4.80	0.00	5.65	1.99	0.00	0.98	
		2.00	56.43	6.06	11.59	10.76	4.71	0.00	5.54	1.95	0.00	0.96	
Sdh-2	7b and 7d	excess	52.22	8.80	10.98	9.79	12.15	0.03	3.02	1.90	0.19	0.91	
Note: For	the modified b	oulk compo	sitions. FeO <sup>7</sup>	represents	total iron. C	)xvaen (in m	nol%) is equal to	Fe <sub>2</sub> O <sub>2</sub> (in m	nol%), * nul	l values			

 $Gln + Coe/Qtz + Rt + H_2O$ , isopleths for j(o) of omphacite have steep positive slopes with j(o) values increasing with temperature. In these fields, the measured j(0) of omphacite correspond to T ranges of 600–650 °C for Sdh-1 [j(o) = 0.52–0.55] and 595–630 °C for Sdh-2 [j(o) = 0.49–0.51] at 25.0–30.0 kbar, respectively. The inferred peak stage (M1) mineral assemblage characterized by Grt + Omp (represented by  $Pl \pm Amp \pm Cpx$  symplectite) + Coe/Qtz + Rt corresponds to the modeled phase assemblage fields of Grt + Omp + Coe/Qtz + Rt + H<sub>2</sub>O, defining temperatures of >640 °C in Figure 7a and >615 °C in Figure 7b at P>19.5 kbar, respectively. In combination with the P-T conditions constrained by isopleths of Grs and Prp in garnet and j(o) of omphacite, a heating process after the  $P_{\text{max}}$  stage may be inferred (Fig. 7f).

### Retrograde metamorphic stage

A P-T pseudosection constraining the retrograde P-T evolution was calculated for the eclogite Sdh-1 in the NCFMASHTO system using the effective bulk composition in Table 1 for the P-T range 5.0-25.0 kbar and 450-650 °C (Fig. 8a). In Figure 8a, the observed mineral assemblage in Sym1 corresponds to the modeled phase assemblage fields of O/Dio + Hbl + Pl  $\pm$  Qtz +  $Rt + H_2O$ , defining P of 5.0–13.0 kbar at the modeled T range. In these fields, j(o) values in omphacite increase with increasing pressure and the maximum j(o) content in the symplectitic Cpx2 from Sdh-1 (0.28) and Sdh-2 (0.30) corresponds to pressures of 10.5-11.5 kbar and 11.0-12.0 kbar at 580-650 °C, respectively. The lower j(o) content (0.10–0.27) in omphacite may indicate

► FIGURE 7. (a and c) P-T pseudosection for the eclogite Sdh-1. (1) Grt Dio Gln Lws Spn, (2) Grt Gln Lws Ep Spn, (3) Grt Gln Lws Dio Omp Ep, (4) Grt Gln Lws Dio Omp Ta, (5) Grt Lws Omp Ky, (6) Grt Gln Omp Ky, (7) Grt Gln Omp Ky Ep, (8) Grt Gln Omp Ep Spn, (9) Grt Gln Lws Dio. (b and d) P-T pseudosection for the eclogite Sdh-2. 1) Grt Dio Gln Lws Spn, 2) Grt Gln Lws Ep Spn, 3) Grt Gln Lws Dio Ep, 4) Grt Dio Gln Ep Spn, (5) Grt Gln Dio Omp Lws Ep, (6) Grt Gln Dio Ep, (7) Grt Gln Dio Omp Lws Ta, (8) Grt Gln Dio Lws, (9) Grt Omp Lws. (e) Variations of P defined by isopleths of Grs in Grt from core to rim. (f) Compilation of the inferred P-T evolution from the later prograde to the  $P_{max}$ , then to the T<sub>max</sub> stages for both P-T pseudosections for Sdh-1 and Sdh-2. The whole rock compositions are given in Table 1. "cg" represents calculated isopleths for Grs in garnet, "mg" represents calculated isopleths for Prp in garnet, xmg represents calculated isopleths for X<sub>Mg</sub> in garnet, and "jo" represents calculated isopleths for j(o) of omphacite. Lws-Ec represents lawsonite eclogite facies, Ep-Ec represents epidote eclogite facies, Amph-Ec represents amphibolite facies, Ep-Bs represents epidote blueschist facies, EA represents epidote amphibolite facies, AM represents amphibolite facies, HGR represents high-pressure granulite facies (after Liou et al. 2004). In this study, according to a-x models of amphibole for modeling phase diagram using Thermocalc, glaucophane is defined to have high z (0.8–1, Na on the M4 site) and y (0.9–1, octahedral Al) combined with low a (0–0.2, A-site Na) and c (0–0.2, Ca), whereas hornblende is defined to have high a (0.2–0.6), y (0.2–0.6), and c (0.6–0.9). (Color online.) (See next page.)



a decrease of P during further exhumation retrogression.

To evaluate H<sub>2</sub>O influence on the formation of Sym1, we calculated a *P*-*M*<sub>H<sub>2</sub>O</sub> pseudosection for the eclogite Sdh-1 in the NCFMASHTO system using the bulk composition in Table 1 at *T* = 580 °C for the *P* range of 5.0–25.0 kbar (Fig. 8b). The H<sub>2</sub>O content ranges from 0.00 to 2.00 mol%. In Figure 8b, free H<sub>2</sub>O is present in fields with *M*<sub>H<sub>2</sub>O</sup> above 1.12 mol% and *P* below 21.5 kbar (the red solid line as the H<sub>2</sub>O-saturation boundary). The phase assemblage fields of Dio + Hbl + Pl ± Omp ± Qtz ± H<sub>2</sub>O develop at *P* below 11.0 kbar and *M*<sub>H<sub>2</sub>O</sup> above 0.56 mol%. Along decompression process during retrogression, eclogite may evolve along the yellow dotted line from A to D with *M*<sub>H<sub>2</sub>O in the bulk rock saturating Sym1 may be ~1.12 mol%, corresponding to 0.4 wt%.</sub></sub></sub>

# **AMP-PL THERMOBAROMETRY**

In this study, we use Amp-Pl thermobarometry to constrain *P-T* conditions for the formation of Sym1 with Cpx and Sym3 without Cpx during retrogression. In this study, we calculate temperature for the formation of Sym1 at 12.0 kbar based on the modeling results in Figure 8a. On the other hand, considering the lower Al<sub>2</sub>O<sub>3</sub> content in Amp3 than Amp1 in Sym1 which may yield a *P* difference of ~4.0 kbar using the barometry of Schmidt (1992), we calculate *T* for the formation of Sym3 at 8.0 kbar, similar to that of Martin (2019). The calculation uses the Amp-Pl thermometry B (edenite + albite = richterite + anorthite) by Holland and Blundy (1994). The results show that *T* for Sym1 (calculated at fixed Ab of 0.96) ranges from 567–590 °C and for Sym3 (calculated at fixed Ab of 0.97) ranges from 504–520 °C, respectively. Uncertainties for these results could be ±40 °C within 2 sigma error (Holland and Blundy 1994).

### TRACE ELEMENT COMPOSITION OF RUTILE AND ZR-IN-RUTILE THERMOMETRY

Trace element analyses were applied to rutile from the samples Sdh-1 and DB17-06. Figure 9 shows Nb/Ta vs. Nb, Ta, and Zr, and Zr vs. Sc, U and Hf characteristics for rutile in various occurrences. The inclusion rutile (type 1) has limited variations of Nb/Ta ratios (14.9-17.2) and Nb (322.4-362.6 ppm), Ta (15.5–26.8 ppm), Zr (75–124 ppm), and Hf (2.8–3.7 ppm) contents (Figs. 9a, 9b, 9c, and 9f; Online Materials<sup>1</sup> Table OM3). The matrix rutile (type 2) has relatively higher Nb/Ta ratios (15.4-21.0) and Nb (324.3-483.8 ppm), Zr (96-248 ppm), and Hf (3.1–7.1 ppm) contents (Figs. 9a and 9f) than type 1 rutile. The megacrystal rutile in the veinlets (type 3) has slightly more scattered Nb/Ta ratios (13.9-22.5) and Ta contents (15.5-26.8 ppm; Fig. 9b), but relatively consistent Zr (72-105 ppm), Sc (1.1-2.4 ppm), Hf (3.3-4.5 ppm), and U (0.3-0.9 ppm, except for two analyses 6.1, 4.6 ppm) contents (Figs. 9d, 9e, and 9f; Online Materials<sup>1</sup> Table OM3).

We use the *P*-dependent Zr-in-rutile thermometry by Tomkins et al. (2007) to calculate temperature for rutile in various occurrences. Beforehand, *P* should be primarily constrained. The inclusion rutile (type 1) armored by garnet has a relatively consistent Zr content (Fig. 9c and may imply a system closed to Zr (Zhang et al. 2010). Therefore, we use a *P* of 25.0–30.0 kbar at the late prograde stage (Fig. 7f) for further calculation. The Zr content of 75.2–124.3 ppm results in *T* of 608–664 °C with the upper limit of the interquartile *T* range of 634–654 °C (Figs. 10a, 10c, and 10d). Matrix rutile (type 2) has been interpreted to coexist with the main rock-forming minerals (e.g., garnet and omphacite) at  $T_{max}$  or near  $T_{max}$  stages. Therefore, we calculate *T* for type 2 rutile at 25.0–20.0 kbar and the Zr content of 95.7–247.8 ppm resulting in *T* of 698–605 °C with the upper limit of the interquartile *T* 



FIGURE 8. (a) P-T and (b) P- $M_{H_{2O}}$  pseudosections for the eclogite Sdh-1. The whole-rock compositions are given in Table 1. "jo" represents calculated isopleths for j(o) of omphacite. (Color online.)





range of 664–644 °C (Figs. 10a, 10c, and 10d). The megacrystal rutile (type 3) in the veinlet may be formed at a later stage at the transition of eclogite to amphibolite facies metamorphism (Zheng et al. 2011a). Therefore, we calculate *T* at 15.0–10.0 kbar and the Zr content of 71.9–105.0 ppm results in *T* of 592–548 °C with the upper limit of the interquartile *T* range of 581–561 °C (Figs. 10b, 10c, and 10d). The LA-ICP-MS analytical error for Zr in rutile is 4.7–16.6 ppm (within 2 sigma), corresponding to *T* uncertainties of 4–6 °C. However, following the recommendation of Tomkins et al. (2007), the uncertainty on *T* could be ~30 °C (within 2 sigma) using Zr-in-rutile thermometry. In this study, we adopt the upper limit of the interquartile *T* range for further discussion as recommended by Taylor-Jones and Powell (2015).

# DISCUSSION

#### *P-T* evolution

Compositional isopleths including Grs, Prp, and  $X_{Mg}$  in garnet and j(o) of omphacite in eclogite are commonly used as *P*-*T* constraints in phase equilibrium modeling (Powell and Holland 2008; Wei et al. 2010; Groppo et al. 2015; Wang et al. 2021; Xia et al. 2018b, 2020). Although compositional re-equilibration could be expected at *T*>700 °C (Caddick et al. 2010), modified garnet growth zonation has been identified in MT-UHP eclogite or even in granulite undergoing UHT metamorphic conditions

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(e.g., O'Brien 1997; Schmid et al. 2000; Jiao et al. 2021). In this study, because of intense fluid activity during exhumation, the eclogites at Sidaohe in western Dabie have been retrograded during exhumation. However, in carefully selected samples, there are vestiges of prograde information preserved in large refractory porphyroblastic garnet. We interpret the obvious zoning of Ca in garnet to be original, thus, the fluctuations in Ca contents from core to rim may be due to *P* variations according to our phase equilibrium modeling. On the other hand, the weaker zoning of Mg, Fe, and  $X_{Mg}$  and lack of Mn zoning may be ascribed to partial diffusional re-equilibration during retrogression. The more obvious zoning of Ca than Mg, Fe, and Mn in large garnets may be due to the larger ionic radius of Ca and significantly more sluggish volume diffusion, according to numerical modeling (Chakraborty and Ganguly 1991; Schwandt et al. 1996; Vielzeuf et al. 2007).

When interpreting the results of phase equilibrium modeling, it is important to estimate the uncertainties which may comprise systematic and random uncertainties (Powell and Holland 2008; Xia et al. 2020). The systematic uncertainties on *P* and *T* propagated from each end-member enthalpy in the data set are calculated to be  $\pm 0.4$  kbar and  $\pm 12$  °C (2 sigma error) using Thermocalc, respectively. On the other hand, the random uncertainties propagated from the analytical uncertainties for EPMA (within ~2% relative) and the AX software for calculating mineral formulas (~1–2% relative) could be ~0.6 kbar on P and ~10 °C on T (2 sigma error; Xia et al. 2020). Therefore, the absolute uncertainties on P are  $\pm 1.0$  kbar and on T are  $\pm 20$  °C (2 sigma error). However, we should take these values as minima if considering other systematic uncertainties propagated from a-x models and random uncertainties from the bulk rock composition.

By combining the P-T results from phase equilibrium modeling, Amp-Pl thermobarometry and Zr-in-rutile thermometry, a complete P-T path is proposed for the eclogite at Sidaohe, western Dabie (Fig. 11), from the prograde stage to the peak stage, and then through several retrograde stages.

The prograde to  $P_{\rm max}$  stages. Based on inclusions of Omp + Amp + Ep + Qtz + Rt/Ilm in garnet and the composition of garnet and omphacite, we propose that the prograde P-T evolution (M0) passed through the modeled phase assemblage fields of Grt + Omp + Lws  $\pm$  Gln + Coe/Qtz + Rt + H<sub>2</sub>O. Lawsonite and glaucophane have not been observed in the thin section, and most likely were replaced by epidote and calcium-rich amphibole (pargasite to tschermakite), respectively, during exhumation (Wei et al. 2010; Lou et al. 2013). Fractures around epidote and amphibole inclusions in garnet (Figs. 3a and 3b) may have acted as pathways for fluid infiltration to trigger retrogression. Based on garnet compositional isopleth thermobarometry, we propose an increase of P from 23.0 to 28.5 kbar, then a decrease to 24.0 kbar, before an increase to 30.5 kbar (±1.0 kbar, 2 sigma error) concomitant with a small increase in T from 580 to 605 °C (±20 °C, 2 sigma error; Figs. 7c, 7d, and 7e). However, since we are uncertain about the extent to which the Prp and  $X_{Mg}$  zoning profiles in garnet have been flattened, the T results based on Prp and  $X_{Mg}$  isopleths in

garnet should be treated with appropriate caution. Nevertheless, we infer two periods of compression separated by a period of decompression during the prograde evolution of the eclogite at Sidaohe, western Dabie (Figs. 7e and 7f). A compression path with a steep positive slope that reached P-T conditions for the  $P_{\text{max}}$  stage of 29.0–30.5 kbar/590–605 °C are consistent with the results from an eclogite at Sibian about 20 km to the northwest in the same Xinxian UHP unit (Fig. 1b; Wei et al. 2010). This type of prograde evolution is similar to that modeled for oceanic crust in modern subduction zones due to coupling between the subducting slab and the overlying mantle wedge (e.g., model W1300; Syracuse et al. 2010), but at lower T and has been interpreted to represent fast subduction (Wei et al. 2010). The UHP metamorphism for the  $P_{\rm max}$  stage is consistent with the report of coesite pseudomorphs in eclogite at Sidaohe (Yan et al. 2005) and coesite in eclogite and the country rock gneisses in the Xinxian UHP unit (e.g., at Guojiahe and Chengmagang, Fig. 1; Zhang and Liou 1994; Liu et al. 2004, 2006). In the modeled phase assemblage field of Grt+Omp+Lws+Coe/Qtz+Rt+H2O (Fig. 7d), a T of 595-650 °C (±20 °C, 2 sigma error) at 25.0-30.0 kbar is constrained by isopleths of j(o) of omphacite and is comparable to the T range of 634-654 °C (±30 °C, 2 sigma error; here and subsequently, we use the upper limit of the interquartile range in T for the Zr-in-rutile thermometry results) recorded by rutile included in garnet (type 1), indicating a T increase after the  $P_{\text{max}}$  stage (Fig. 10c).

The  $T_{\text{max}}$  stage. Initial exhumation to the  $T_{\text{max}}$  stage (M1) produced an inferred mineral assemblage of Grt + Omp + Coe/Qtz + Rt, which indicates the *P*-*T* evolution passed through the modeled phase assemblage fields of Grt + Omp + Coe/Qtz + Rt + H<sub>2</sub>O after

**FIGURE 10.** The calculated *T* using the Zr-in-rutile thermometer by Tomkins et al. (2007) for rutile with various occurrences. (a) Calculated at 25.0-30.0 kbar for type 1 rutile. (b) Calculated at 25.0-20.0 kbar for type 2 rutile. (c) Calculated at 15.0-10.0 kbar for type 3 rutile and summary of the *T* calculated for rutile with various occurrences. (d) The interquartile *T* range for rutile with various occurrences. The thick black line in the rhombic field from **a**–**c** represents the upper limit of the interquartile *T* range. (Color online.)



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FIGURE 11. Summary of *P*-*T* paths from this and previous studies of eclogite from western Dabie. The purple arrows represent the *P*-*T* path from our study. The solid arrow was inferred from garnet compositional isopleth thermobarometry; the dashed arrow was inferred from a combination of phase equilibrium modeling, Zr-in-rutile thermometer (blue rhombus) and Hb-Pl thermobarometry (green diamond). (Color online.)

the  $P_{\text{max}}$  stage (Figs. 7a and 7b). In these fields, the calculated modal contents of Grt and Omp are 47.0 and 36.7%, respectively, typical of the biomineral eclogite as observed in thin sections (Fig. 2c). For type 2 rutile in the matrix, using Zr-in-rutile thermometry we have calculated *T* of 664–644 °C (±30 °C, 2 sigma error) at 25.0–20.0 kbar, interpreted to represent *P*-*T* conditions for the  $T_{\text{max}}$  stage (Figs. 10c and 10d), similar to the results obtained using conventional thermobarometry by previous researchers (Zhang and Liou 1994; Liu et al. 2004). Along the *P*-*T* path from the  $P_{\text{max}}$  stages, Gln and Lws disappear via the reactions Lws + Omp + Gln = Grt + Qtz + H<sub>2</sub>O, respectively (Fig. 7f).

The retrograde stages. During subsequent exhumation, rock-forming omphacite in the matrix broke down to form Amp + Pl + Cpx symplectite (Sym1). Based on phase equilibrium modeling and conventional Amp-Pl thermometry, we estimate that Sym1 formed at 567–590 °C/12.0 kbar. This *T* range is similar to the *T* of 581–561 °C calculated at 15.0–10.0 kbar for type 3 rutile in the veinlets (Fig. 11). These *P*-*T* estimates are interpreted to represent a decrease of *T* during the retrograde stage M2 decompression. Late retrogression (M3) led to the formation of Sym3 at *T* of 504–520 °C, calculated at 8.0 kbar using Amp-Pl thermometry.

**Summary.** For eclogite at Sidaohe, western Dabie, we propose a *P*-*T* path with a prograde segment showing two cycles of *P* increase to the  $P_{\text{max}}$  stage, then a *T* increase during initial exhumation to the  $T_{\text{max}}$  stage, before a decrease in both *P* and *T* during subsequent retrograde stages. The clockwise, open convex *P*-*T* path is similar to those in the studies of Zhang and Liou (1994) and Liu et al. (2004, 2006) on eclogite from western Dabie, but differs from those in the studies of Wei et al. (2010) and Cheng and Cao (2015) who inferred isothermal decompression after the  $P_{\text{max}}$  stage.

# H<sub>2</sub>O behavior along the *P-T* evolution

From the prograde to the  $P_{max}$  stage. H<sub>2</sub>O contents in the bulk rock are mainly controlled by the stability of hydrous minerals and the P-T fields related to various continuous and discontinuous reactions rock crossed during subduction (Schmidt and Poli 2014; Zheng and Chen 2016). In this study, P-T fields at 23.0-31.0 kbar (with Qz then Coe), 580-600 °C were constrained for a segment of the *P*-*T* evolution from the late prograde to  $P_{\text{max}}$ stages (Fig. 7f). In these fields, previous experimental studies on metabasite compositions suggest that the hydrous minerals are mainly Lws, Ctd, Ph, and Ep/Zoi with Gln decomposed at P > 23.0 kbar (Schmidt and Poli 2014), while Wei and Zheng (2020) considered the stable minerals to be Lws, Ph, Amp, and Ta. In our study, due to the absence of significant K<sub>2</sub>O and the low-MgO content in the bulk composition (Online Materials<sup>1</sup> Table OM3), Ph and Ta were not formed and H<sub>2</sub>O in the bulk rock was retained only in Lws and Gln. Along the P-T path from A to B in Figure 7f, calculated modals of Gln decrease from 12.5 (A) to 0.3 (B) mode% whereas Lws slightly increase from 7.2 to 8.3 mode%. Accordingly, calculated H<sub>2</sub>O content in the bulk rock slightly decreases from 0.92 to 0.88 wt%, implying the release of H<sub>2</sub>O by the Gln-out reaction is compensated by an increase in modal Lws. Therefore, in subduction zones with low-thermal gradients (5-7 °C/Km), Lws in eclogites could be the most important H<sub>2</sub>O reservoir. Indeed, it may take H<sub>2</sub>O to 40.0 kbar at T < 700 °C, before destabilizing to form normally anhydrous garnet and omphacite (Schmidt and Poli 2014; Zheng and Chen 2016; Wei and Zheng 2020). In addition, numerous studies in Sulu-Dabie and elsewhere have shown that at UHP conditions, nominally anhydrous minerals (NAMs) such as Grt and Omp can incorporate a considerable amount of structural hydroxyl (OH<sup>-</sup>) and molecular water (H<sub>2</sub>O) in point defects within the crystal lattice (Chen et al. 2007), allowing fluid to be carried into the deeper mantle (>200 km), and even to the mantle transition zone (Katayama and Nakashima 2003; Zheng 2009).

From the  $P_{\text{max}}$  to  $T_{\text{max}}$  stages. In Figure 7f, the *P*-*T* evolution from B to C sequentially crosses the Gln- and Lws-out curves and the modeled H<sub>2</sub>O content for relevant assemblages rapidly decreases from 0.88 to 0 wt% (in the modeled assemblages there is no structural hydroxyl in the NAMs). Without considering hydroxyl/H<sub>2</sub>O contained in NAMs, the eclogite would become bimineralic and be effectively dry, consistent with our observations (Fig. 2c). The released H<sub>2</sub>O may migrate out of the local rock system to promote crust-mantle interactions, the exhumation of deeply subducted continental crust, and the retrogression of HP/UHP rocks in continental subduction channels (Chen et al. 2007; Zheng and Chen 2016).

The retrograde stage. Strong fluid activity during the retrograde exhumation is evidenced by pervasive retrogression and the development of quartz veins/veinlets (Figs. 2c and 2d). During this process, H<sub>2</sub>O may act as a kinetic facilitator for the destabilization of omphacite, as a component of the reaction to form amphibole in symplectite or as a carrier for components required to precipitate minerals in veinlets (Joanny et al. 1991; Martin 2019). For UHP eclogite, numerous studies have shown that H<sub>2</sub>O may be released from the NAMs during retrograde exhumation (e.g., Chen et al. 2007; Zheng et al. 2011a). In Sulu-Dabie, the amount of structural hydroxyl could be 115–1300 ppm in omphacite and 92–1735 ppm



in garnet (Xia et al. 2005; Chen et al. 2007). The total  $H_2O$  concentration including fluid inclusions, hydrous mineral inclusions and structural hydroxyl could even be up to 1170–20745 ppm in Omp and 522–1584 ppm in garnet (Chen et al. 2007).

In this study, Sym2 at the reaction front with only rare or no Amp (Figs. 5c–5k) may require very little H<sub>2</sub>O for its formation. By contrast, our modeling shows that Sym1, which has Amp several tens of micrometers in diameter (Figs. 5d-5g), requires a H<sub>2</sub>O content of 0.4 wt% (or 4000 ppm) to hydrate the mineral assemblage (Fig. 8b). Considering Sym1 only developed at limited places around Sym2 (assumed <10 vol% in thin sections; Figs. 2c and 3g), we assume that a maximum H<sub>2</sub>O content of 400 ppm in the bulk rock may be sufficient to the formation of Sym1. Such an amount of H<sub>2</sub>O may be provided by H<sub>2</sub>O released from the NAMs during decompression. Therefore, we interpret that the H<sub>2</sub>O to trigger the formation of both Sym1 and Sym2 was internally sourced. A similar conclusion was reached by Anderson and Moecher (2007) and Martin (2019) in their studies of symplectite. In support of this interpretation in our study, rutile in the matrix (type 2) has comparable Ta, Sc, and U contents to rutile included in garnet (type 1; Figs. 9b, 9d, and 9e), implying the properties of fluid at this stage had an affinity with that forming type 1 rutile. The high-Zr and -Hf contents of the matrix rutile may be related to the breakdown of garnet.

The coarse-grained rutile (type 3) in veinlets has more scattered Nb/Ta ratios and Ta contents, but limited variation in Nb, Zr, and Hf contents, distinctly different from the inclusion rutile and the matrix rutile (Figs. 9a, 9b, and 9f), which may imply different properties of the metamorphic fluid compared with that at the prograde to peak stages (Zheng et al. 2011a). We interpret the rutile in veinlets to be formed from an external fluid source with constant Nb, Zr, and Hf contents but varied Ta content and Nb/Ta ratios. More abundant quartz veins developed at the transition zone of the eclogite block and the country rock gneisses may support this conclusion (Fig. 2a). The shear zone between the main interface of the eclogitic block and the country rock may act as a preferential path for fluid entering the rock during retrogression (cf. Martin 2019). Fluid may also promote the formation of Sym3 with coarse-grained Amp and Pl of comparable amount in the matrix, as has been evidenced by its more abundant development near the veinlets (Figs. 2b and 2d).

### IMPLICATIONS

# Polycyclic burial of eclogite in continental subduction channel

In this study, our modeling results show that eclogite within a single unit at Sidaohe records two cycles of P increase during the prograde metamorphic stage. The first cycle records a P increase from 23.0 to 28.5 kbar, followed by partial exhumation, and then a second cycle records a P increase from 24.0 to 30.5 kbar (Figs. 7e and 7f). Variations of the minimum to maximum P conditions for each cycle are up to 6.5 kbar, implying the two cycles of prograde P increase are a reliable result. The result is distinctly different from a single P-T loop commonly described for eclogite in Sulu-Dabie by previous studies (Zhang and Liou 1994; Liu et al. 2004; Cheng and Cao 2015; Wei et al. 2010; Xia et al. 2018a; Zheng et al. 2019).

In other places in the world, rocks showing *P* cycles during a single orogenic event have been reported and interpreted to repre-

sent burial-partial exhumation cycles (Brueckner 2006; Beltrando et al. 2007; Blanco-Quintero et al. 2011; Rubatto et al. 2011; Li et al. 2016). Overall, two scenarios have been proposed to interpret these cycles: (1) they are related to orogenic-scale shorteningextension switches mostly developed in the continental subduction environment (Brueckner 2006; Rubatto et al. 2011), and (2) they are developed within Franciscan-type subduction channels in oceanic subduction zones (Blanco-Quintero et al. 2011; Gerya et al. 2002; Li et al. 2016). In the first case, rocks showing short-term, multiple eclogite facies metamorphism from the Sesia zone in the Italian Western Alps were interpreted to be formed due to oblique subduction along the convergent plate margin. Episodic switches from transpressional to transtensional deformation led to alternating burial and partial exhumation for rocks in the subduction zone (Rubatto et al. 2011). In the second case, convective movement of rocks occurs within a thin and rapidly sheared layer of unconsolidated sediments (Lister et al. 2001) or serpentinites (Blanco-Quintero et al. 2011) mixed with fluid along the plate interface in the subduction channel (Cloos and Shreve 1988; Zheng et al. 2011b). The driving forces could be competing drag and buoyancy combined within a convecting fluid (Gerya et al. 2002; Blanco-Quintero et al. 2011; Zheng et al. 2012). For instance, eclogite from the Chinese western Tianshan records a polycyclic burial-partial exhumation evolution that was interpreted to be due to convective flow in the subduction channel (Li et al. 2016).

In this study, we interpret the multiple burials and partial exhumation cycles of eclogite at Sidaohe to be formed in a continental subduction channel. A crustal slice containing the eclogite may have been detached from the surface of the descending lower plate due to fracturing. After the crust had been subducted to a depth of ~100 km, a slice was detached and partially exhumed to ~82 km depth before being subducted again to a depth of ~107 km. This polycyclic movement may have proceeded due to convective flow in the channel. Metasedimentary rocks, well exposed in western Dabie, may have acted as a weak, low-viscosity material along the plate interface (Cloos and Shreve 1988; Lister et al. 2001; Gerya et al. 2002). In addition, dehydroxylation of NAMs and fluid ingress into eclogite, as discussed above, may facilitate convective movement of rock fragments in the continental subduction channel (Zheng et al. 2011b).

Our study indicates that information for polycyclic P-T evolution could be potentially preserved in garnet from low-T eclogite. Especially Ca may preserve prograde chemical variations considering its larger ionic size and lower diffusivity than the other divalent cations. By combining garnet zoning profiles and phase equilibrium modeling, we propose that more rocks showing polycyclic P-T evolution could be revealed in further studies.

# Thermal relaxation during exhumation

The exhumation *P*-*T* path shows an increase in *T* from the  $P_{\text{max}}$  to  $T_{\text{max}}$  stages, followed by a decrease of both *P* and *T* (Fig. 11). The exhumation path depends on the balance between the rates of exhumation and temperature increase (Carswell and Zhang 1999). In the early stages of exhumation, unless the exhumation rate is exceedingly fast, deeply subducted rocks may continue to experience heating, resulting in the  $T_{\text{max}}$  after the  $P_{\text{max}}$  along the exhumation path (Carswell and Zhang 1999). Such a process has been anticipated by thermal modeling of subducted crustal

slabs (England and Thompson 1984). The increase in T after the  $P_{\text{max}}$  is generally interpreted to be due to thermal relaxation by conductive heat transfer (Carswell and Zhang 1999; Winter 2013). For the deeply subducted continental crust, conductive heating driven by the relaxation of isotherms may operate on timescales of tens of millions of years (England and Thompson 1984). Large UHP terranes with ancient crustal protoliths may experience UHP metamorphism over long timescales with slow exhumation rates, while small UHP terranes commonly with juvenile crustal protoliths may experience UHP metamorphism over short timescales with rapid exhumation rates (Kylander-Clark et al. 2008; Zheng et al. 2019). As one of the largest UHP terranes on Earth, the Dabie-Sulu orogen has a metamorphic duration of  $15 \pm 2$  Ma at subarc depths (Wu and Zheng 2013; Zheng et al. 2019). Therefore, in western Dabie, the relatively long duration of HP/UHP rocks at mantle depths may be sufficient for thermal relaxation during initial exhumation.

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#### Endnote:

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