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## Favorable $P-T-fO_2$ conditions for abiotic CH<sub>4</sub> production in subducted oceanic crusts: A comparison between CH<sub>4</sub>-bearing ultrahigh- and CO<sub>2</sub>-bearing high-pressure eclogite



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## ABSTRACT

Subduction is a key element in the carbon cycle between the Earth's surface and deep interior. In addition to pressure (P) and temperature (T), oxygen fugacity  $(fO_2)$  is an intensive variable that can change the speciation, stability, and mobility of carbon-bearing phases in subduction zones. However, tracking redox evolution and associated carbon speciation in high-pressure metamorphic rocks from subduction zones remains challenging. In this study, we identified CH<sub>4</sub>-rich fluid inclusions in ultra-high-pressure (UHP; i.e., coesite-bearing) eclogites (the UHP-CH<sub>4</sub> eclogite) and CO<sub>2</sub>-rich fluid inclusions in high-pressure (HP; i.e., quartz-bearing) eclogites (the HP-CO<sub>2</sub> eclogite) from the Chinese southwestern (SW) Tianshan palaeosubduction zone, respectively. Combining the garnet-clinopyroxene oxybarometry and comprehensive thermodynamic calculations, we revealed that the  $fO_2$  of the UHP-CH<sub>4</sub> eclogite decreases to a minimum of  $\sim$ FMQ – 3 at peak P-T conditions (2.8 GPa, 525 °C) and CH<sub>4</sub> is expected to form in graphite-saturated C-H-O fluids. Whereas during the early-exhumation stage (2.5 GPa, 600 °C), the UHP-CH<sub>4</sub> eclogite is predicted to buffer higher  $fO_2$  conditions of  $\sim$ FMQ - 0.9. In contrast, the HP-CO<sub>2</sub> eclogite, which has a higher bulk CO<sub>2</sub> content (~10 wt%) and elevated Fe<sup>3+</sup>/ $\Sigma$ Fe ratio (0.24) than the UHP-CH<sub>4</sub> eclogite, suggesting a stronger oxidative seafloor alteration of the HP-CO<sub>2</sub> eclogite protolith before subduction, stabilizes graphite and  $CO_2$ -rich fluids at peak  $fO_2$  conditions between FMQ and FMQ + 1 (2.6 GPa, 500 °C). These data demonstrate that the thermal structure (P-T conditions) of the subduction zone and the composition of the slab are first-order controls on the redox evolution of subducting slabs and the changing speciation of carbon in slab fluids buffered by the metamorphic rock system. Therefore, we propose that the cold subduction of a weakly altered oceanic crust (e.g., UHP-CH<sub>4</sub> eclogites from the SW Tianshan) provides ideal conditions for the formation of ultra-deep abiotic CH<sub>4</sub>.

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## 1. Introduction

Volatile elements (e.g., C, H, O, N, and S) are normally redoxsensitive and play a critical role in the formation and evolution of the atmosphere, ocean, and biosphere on the Earth's surface (Berner, 2003; Suarez et al., 2019). For example, carbon (C) exists in a wide range of oxidation states from C<sup>4–</sup> in CH<sub>4</sub> to C<sup>4+</sup> in CO<sub>2</sub>. Globally, ~82 Mt/year of Earth's surface carbon is recycled into deep Earth in the process of plate subduction (Plank and Manning, 2019). Investigating the fate of subducted carbon is crucial for constraining the carbon cycle between Earth's surface and

\* Corresponding author. E-mail address: lfzhang@pku.edu.cn (L. Zhang). deep mantle reservoirs. Previous studies have shown that prograde fluid-induced dissolution of carbonate and carbonaceous materials may represent an essential process by which C-bearing fluids are released from subducting slabs (Frezzotti et al., 2011; Ague and Nicolescu, 2014; Facq et al., 2014; Kelemen and Manning, 2015; Menzel et al., 2020; Tumiati et al. 2020; Vitale et al., 2020a). However, whether slab fluids are dominated by reduced (e.g.,  $CH_4$ ,  $H_2S$ ,  $HS^-$ ) or oxidized (e.g.,  $CO_2$ ,  $HSO_4^-$ ,  $SO_4^{2-}$ ) species remains controversial, and this dynamic has significant implications for constraining the redox evolution of subducting slabs, mantle wedges, and related volcanic arcs (e.g., Debret and Sverjensky, 2017; Gerrits et al., 2019; Walters et al., 2019; 2020; Vitale et al., 2017; Piccoli et al., 2019; Li et al., 2020; Li et al., 2021, 2022). Determining the mobility and speciation of carbon-bearing phases in subduction zone fluids remains an active and challenging research frontier (e.g., Debret et al., 2021).

The speciation and properties of C-bearing fluids in the subduction zone depend not only on P-T but also on the composition of the slab from which the fluids are derived (Evans et al., 2017; Piccoli et al., 2019; Walters et al., 2020) or locally equilibrated mineral assemblages in subduction channels (Debret and Sverjensky, 2017). The redox capacity (i.e., redox budget (RB), Evans 2006) of a rock system is controlled by the amount and oxidation state of all redox-sensitive major elements (e.g., Fe, C, and S). Carbon and sulfur are present at very low concentrations in the fresh ocean crust, and iron is primarily found in its reduced state as Fe<sup>2+</sup> (see review in Evans and Tomkins, 2021). Initially, fresh mid-ocean ridge basalt (MORB) displayed an average Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of  $\sim$ 0.14 (Cottrell and Kelley, 2011; Zhang et al., 2018). Hydrothermal circulation at the seafloor can oxidize the oceanic crust and underlying lithospheric mantle by introducing oxidized species, such as  $O_2$ .  $CO_2$ , and  $SO_4^{2-}(aq)$ , as well as through hydrolysis (Bach and Edwards, 2003; Alt et al., 2012; Alt et al., 2013). For example, the average  $Fe^{3+}/\Sigma Fe$  ratios of the altered oceanic crust (AOC) vary with depth from  $\sim$ 0.35 in the upper volcanic section to  $\sim$ 0.20 in the sheeted dike complex (Bach and Edwards, 2003). The oxidation degree of the oceanic crust and lithospheric mantle during hydrothermal alteration is a function of temperature, sedimentation rate at the seafloor, time-integrated water-rock ratio, fluid flow geometry, and porosity-permeability relationships (Bach and Edwards, 2003; Evans and Tomkins, 2021). In fact, the most oxidized regions of the AOC are restricted to narrow alteration haloes adjacent to fractures and other fluid pathways (Bach and Edwards, 2003). Combined, these observations demonstrate that the distribution of multivalent elements within the oceanic lithosphere, as well as their oxidation states, are highly heterogeneous prior to subduction (Tumiati and Malaspina, 2019). The extent to which such inherited redox heterogeneities may affect C speciation in slab fluids derived from the subducting oceanic crust remains unclear (Evans et al. 2017; Evans and Tomkins, 2021).

On the other side, the redox state of the slab might also evolve over the subduction process. For example, Debret et al. (2014, 2015, 2016, 2020) found that the high pressure serpentinite dehydration process (<2 GPa) was accompanied by a reduction in the bulk rock  $Fe^{3+}/\Sigma Fe$  ratio (e.g., a decrease in magnetite mode), which may be coupled with the release of oxidized fluids (e.g., SO<sub>x</sub>, H<sub>2</sub>O, CO<sub>x</sub>). Similarly, the thermodynamic models of Walters et al. (2020) predicted that the subduction of pervasively altered oceanic crust in subduction zones with low slab-top geothermal gradients generates SO<sub>x</sub>-bearing slab fluids, whereas fluids from subduction zones with high slab-top geothermal gradients and/or less altered crust generate slab fluids dominated by reduced sulfur species. The oxidation of S<sup>1-</sup> in pyrite to S<sup>4+</sup> in sulfate is balanced by the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> in the eclogitic slab residuum. However, if slab fluids carry primarily reduced species, as proposed by previous studies such as Lee et al. (2010), Piccoli et al. (2019), and Li et al. (2020), the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of the crust will remain constant or even increase. Reconciling studies predicting reduced fluids with the general observation that arc magma  $fO_2$ 's is elevated relative to other tectonic settings, Ague et al. (2022) proposed that reduced slab fluids may be oxidized as they are filtered through sediments at the slab-top. In summary, the large potential variation in the slab redox budget and contrasting predictions regarding multivalent elements speciation in slab fluids warrant further investigation.

Historically, most studies have focused on oxidized carbon species (e.g.,  $CO_2$ ,  $CO_3^{2-}$ ,  $HCO_3^{-}$ ) in fluids released from subducting slabs (e.g., Frezzotti et al., 2011; Ague and Nicolescu, 2014; Kelemen and Manning, 2015). In contrast, fluxes of reduced carbon, transported

as  $CH_4$ , may also be possible at sufficiently low  $fO_2$  (e.g., Vitale et al., 2017; Tao et al., 2018a). Notably, CH<sub>4</sub>-bearing fluids are expected to be distributed more broadly than previously recognized as both high-pressure experiments (Scott et al., 2004; Chen et al., 2008; Lazar et al., 2014; Li, 2016; Tao et al., 2018a) and petrological studies (e.g., Galvez et al. 2013; Tao et al., 2018a) have demonstrated that carbonate can be reduced during subduction. Furthermore, thermodynamic modeling using the Deep Earth Water model (DEW) has predicted the increased stability of organic acids at high pressures (≥30 kbar) (Sverjensky et al., 2014; Sverjensky and Huang, 2015; Huang et al., 2017). Correspondingly, reduced hydrocarbons are increasingly being recognized in fluid inclusions from high-pressure metamorphic rocks in subduction zones. For example, Frezzotti (2019) found that the surfaces of diamonds, in fluid inclusions hosted in metasediments from Lago di Cignana, Italy, were coated by functional groups of carboxylic acids. Vitale et al. (2017, 2020b) observed CH<sub>4</sub>-H<sub>2</sub>S-NH<sub>3</sub>-rich fluid inclusions in high pressure (HP)-low temperature (LT) ultramafic rocks from Alpine Corsica and the western Italian Alps, demonstrating that deep serpentinization (40-80 km) in subduction zones may generate significant amounts of reduced C-O-H-N-S fluids. Coincidentally, olivine-hosted CH<sub>4</sub>-H<sub>2</sub>-N<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>S fluid inclusions in metamorphosed ultramafic rocks from the Appalachian belt were also identified by Boutier et al. (2021). Similarly, Peng et al. (2021) identified CH<sub>4</sub>-H<sub>2</sub> fluid inclusions in dolomite in HP serpentinite from SW Tianshan (Fig. 1), which were associated with retrograde serpentinization at 7-9 kbar. Based on field observations and geochemical evidence reported by these studies, the formation of CH<sub>4</sub> is, so far, primarily associated with the serpentinization of ultramafic rocks in subduction zones.

In contrast to serpentinites, the origin and evolution of reduced carbon-bearing fluids in the subducted mafic crust remains more enigmatic. Methane-bearing fluid inclusions were identified in ultra-high pressure (UHP) continental-type eclogites and were interpreted as remnants of prograde and peak metamorphic fluids (Fu et al., 2003; Mukherjee and Sachan, 2009), but the mechanisms by which the reduced fluids were stabilized were not constrained. Tao et al. (2018a) reported CH<sub>4</sub>-rich fluid inclusions in omphacite in HP oceanic-type eclogite from the SW Tianshan orogenic belt (Fig. 1) and proposed a mechanism by which  $CH_4$  can be produced from Fe-carbonate reduction in water, as demonstrated in highpressure experimental simulations. However, several questions remain: (1) Can CH<sub>4</sub>-bearing fluids become entrapped in minerals other than omphacite? (2) What are the genetic relationships between abiotic CH<sub>4</sub> and  $P-T-X-fO_2$  evolution of the bulk rock system? (3) What is the significance of abiotic CH<sub>4</sub> in the redox evolution of the subducting oceanic crust?

In this study, we reported CH<sub>4</sub>-rich fluid inclusions in garnet and omphacite in coesite-bearing eclogites (the UHP-CH<sub>4</sub> eclogite) from the SW Tianshan subduction zone, which is the first petrological observation to unequivocally report the formation of primary CH<sub>4</sub> in the oceanic-type supra-subducted mafic system. Based on the distribution of CH4 in garnet and omphacite, garnetclinopyroxene oxybarometry, and comprehensive thermodynamic calculations, the detailed metamorphic  $P-T-X(\text{fluid})-fO_2$  evolution for the UHP-CH<sub>4</sub> eclogite during supra-subduction and early exhumation processes was investigated. The UHP-CH<sub>4</sub> eclogite sample was compared with an HP eclogite sample having CO<sub>2</sub>rich fluid inclusions (the HP-CO2 eclogite) collected from elsewhere in SW Tianshan. We found that lower-P conditions combined with greater oxidized bulk composition stabilized CO<sub>2</sub> over CH<sub>4</sub> in the slab fluids. As a consequence, we (1) highlight the important role of the redox budget and metamorphic P-T on  $fO_2$ for a dehydrating rock-buffered system; (2) suggest that cold subduction (e.g., low-temperature conditions) of weakly altered ocea-



**Fig. 1.** Geological background of the Chinese southwestern Tianshan. (a) Schematic geological map of the S.W. Tianshan HP-UHP metamorphic belt associated with the coeval low-P and high-T metamorphic belt; (b) Yellow stars show sampling localities of the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites in this study. Grey stars show localities of CH<sub>4</sub>-fluid inclusions that have been reported earlier (Modified after Zhang et al., 2019; Peng et al., 2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nic crust is more favorable for reducing species formation in slab fluids.

### 2. Geological setting and sample selection

The South Tianshan is a near east-west oriented HP-UHP subduction metamorphic belt in N.W. China extending 200 km along the South Central Tianshan Fault (SCTF, Fig. 1a; see review in Tan et al., 2019). The HP-UHP complexes in China are correlated in the west with the Atbashi and Chatkal HP complexes in Kyrgyzstan (e.g., Loury et al., 2016; 2018) and Fan-Karategin (U)HP complex in Tajikistan (Volkova and Budanov, 1999). The HP-UHP complexes contain mafic and ultramafic rocks which are interpreted as relicts of the palaeo-Tianshan oceanic lithosphere (Volkova and Budanov, 1999; Gao and Klemd, 2003; Ai et al., 2006; Simonov et al., 2008; Zhang et al., 2019). The Akeyazi Metamorphic Complex (AMC) in the Chinese section of the belt is comprised of HP-UHP schistose meta-sedimentary to meta-volcaniclastic rocks which host boudins, pods, blocks, and layers of marble, eclogite, blueschist, and rare serpentinite (Gao et al., 1999; Zhang et al., 2002a, b; Li et al., 2007). The eclogites locally show well-preserved pillow structures and exhibit geochemical signatures consistent with OIB, E-MORB, and *N*-MORB protoliths (Zhang et al., 2001; Gao and Klemd, 2003; Ai et al., 2006), whereas the meta-sediments and meta-volcaniclastic rocks exhibit continental crustal to pelagic characteristics (Liu et al., 2014; Meyer et al., 2016; Tan et al., 2017; Bayet et al., 2018).

Eclogites experienced peak *P*–*T* conditions estimated between 430 and 630 °C at 14–30 kbar at a regional scale. Two types of eclogites are identified in this area: (1) coesite-bearing ultrahigh-pressure (UHP) lawsonite eclogite are exposed in the north of the Muzhaerte, Habutengsu, Kebuerte sections with a structural thickness of ~10 km; (2) high-pressure (HP) eclogite occurs throughout the rest of the section (Lü et al., 2009, 2012a, 2012b, 2019) (see HP and UHP units in Fig. 1). Some lawsonite-bearing eclogites reached a peak pressure of 30 kbar at a temperature of  $\leq$ 500 °C with a ~5 °C/km prograde geothermal gradient, indicating that the SW

Tianshan orogenic belt may be the coldest UHP subduction zone preserved in the global rock record (Zhang et al., 2019).

Carbonated eclogites are widespread in the HP and UHP sections of SW Tianshan (e.g., Zhang et al., 2002b, 2003; Tao et al., 2014, 2018b, 2020; Zhu et al., 2018, 2020; Li et al., 2012, 2014; This study). Carbonate minerals are mainly dolomite, observed as inclusions or coarse-grained porphyroblast in the matrix. Relict magnesite and aragonite inclusions in dolomite are consistent with prograde (U)HP metamorphism during subduction (Tao et al., 2014), showing the decomposition of Fe-dolomite under high pressure. Retrograde calcite is also widely observed. Fine-grained graphite in eclogites are ubiquitously found in veins, the result of abiotic precipitation from CO<sub>2</sub>-bearing fluids during the exhumation process (Zhu et al., 2020). In addition, graphite can also be observed as inclusions in garnet, dolomite, and omphacite, and is formed by the reduction of carbonate or decomposition of Fedolomite during prograde metamorphism (Lü et al., 2012a, 2012b; Tao et al., 2018a, 2020). Previous research suggested that the protoliths of eclogite (mafic oceanic crustal rocks) were mainly carbonated during seafloor alteration prior to subduction, as opposed to a syn-metamorphic addition during metamorphism: (1) Mg-Sr-Nd isotopes measured on the carbonates in eclogites display typical signatures associated with seawater alteration of oceanic basalts and homogeneous Sr isotopic ratios suggest equilibration with an internally generated fluid released during metamorphism, as opposed to an external fluid (Zhu et al., 2018; Tao et al., 2018b); (2) The positive  $\delta^{34}$ S values of pyrite cores in eclogite from the SW Tianshan also record a seawater sulfate from pre-subduction seafloor hydrothermal alteration (Li et al., 2021).

In this study, two exhumed carbonate-bearing eclogites (i.e., carbonated eclogite) were selected from the SW Tianshan (U)HP subduction orogenic belts (see sample locality in Fig. 1) for a comparative study. The coesite- and CH<sub>4</sub>-bearing (UHP-CH<sub>4</sub>) eclogite was sampled from the northern UHP section exposed along the Akesayi River, whereas the quartz and CO<sub>2</sub>-bearing (HP-CO<sub>2</sub>) eclogite was collected from the southern HP section exposed along the Habutengsu River.

## 3. Methods

## 3.1. Sample analysis

### 3.1.1. Scanning electron microscopy

An FEI Quanta 650 scanning electron microscope (SEM) equipped with an Oxford INCA X-MAX50 250 + energy dispersive X-ray spectrometer at the School of Earth and Space Sciences (SESS), Peking University was used for back-scattered electron (BSE) image acquisition. The running conditions were 15 kV acceleration voltage, 5 nA beam current, and ~10 mm working distance. Qualitative X-ray intensity-composition maps were recorded with an integration time of ca. 600 min under these operating conditions.

## 3.1.2. Raman spectroscopic analyses

Confocal Laser-Raman spectroscopy was performed on a HOR-IBA JY LabRAM HR Evolution Raman system at SESS, Peking University. A laser beam with a wavelength of 532 nm was focused on the fluid/solid inclusions through  $100 \times$  objectives of a light microscope. A laser power of 50 mW was used with a spot size of 1 µm, with accumulation times varying from 15 s to 300 s. The estimated spectral resolution was >0.7 cm<sup>-1</sup>. Raman spectrometer was calibrated by using synthetic single-crystal silicon. Gas/liquid phases (e.g., CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and N<sub>2</sub>) and solid phases (e.g., coesite and calcite) were identified with the peak assignments from Frezzotti et al. (2012) and RRUFF database (Lafuente et al., 2015), respectively.

### 3.1.3. Minerals compositional micro-analysis

3.1.3.1. Major element compositions. Chemical compositions of minerals in carbonated eclogites were analyzed using a JEOL-8230 electron probe microanalyzer at SESS, Peking University. The operating conditions were accelerating voltage of 15 kV, beam current of 10-20 nA, and beam size of 2 µm for silicates except for muscovite (5  $\mu m)$  and for carbonates (10  $\mu m)$ . Counting times were 10-30 s. The instrument is equipped with four spectrometers (S1–S4): K, Ca, and Ti were analyzed using a PETI crystal (S1), and two TAP crystals (S2 and S4) were used for Na, Si, Mg, and Al, and a LIFH crystal (S3) was used to analyze Cr, Mn, Fe, and Ni. SPI 53 minerals (USA) were adopted for the quantitative analysis (following Li et al., 2018): sanidine was employed for K: diopside for Ca and Mg; rutile for Ti; jadeite for Na, Al, and Si; chromium oxide for Cr; rhodonite for Mn; hematite for Fe; and nickel silicide for Ni. Finally, a PRZ correction was performed and the mineral formula was calculated by using the MinPlot program (Walters 2022).

3.1.3.2. WDS elemental maps. The X-ray maps for selected elements in garnet (Fe, Ca, Mg, Mn) and omphacite (Cr, Fe, Al, Na) were conducted by wavelength dispersive spectra (WDS) on a JEOL JXAiSP100 Electron Probe Microanalyzer at Nanjing Hongchuang Geological Exploration Technology Service Co. ltd (NHGETS). The accelerating voltage, beam current, pixel interval and dwell time were 15 kV, 200 nA, 1.0  $\mu$ m, and 30 ms, respectively. The following characteristic X-rays and analyzing crystals were used: Al (K $\alpha$ , TAP crystal), Ca (K $\alpha$ , PETJ crystal), Fe (K $\alpha$ , LIFL crystal), Mg (K $\alpha$ , TAPH crystal), Mn (K $\alpha$ , LIFH crystal), Cr (K $\alpha$ , LIFH crystal), Na (K $\alpha$ , TAPH crystal).

3.1.3.3. Measurement of  $Fe^{3+}$  in garnet by using "Flank method". Garnets containing both  $Fe^{3+}$  and  $Fe^{2+}$  are potentially  $fO_2$  sensors to estimate the redox state of the eclogitic rocks (Stagno et al., 2015; Tao et al., 2018a). Therefore, we determined  $Fe^{3+}/\Sigma Fe$  profiles (from core to rim) of several garnet grains in the UHP-CH<sub>4</sub> eclogites by the "Flank method" using a JEOL JXA-8530F Plus electron microprobe at the Institut für Geowissenschaften, Goethe-Universität (Höfer et al., 1994; Höfer and Brey, 2007). The "Flank method" and simultaneous quantitative elemental analyses were conducted at 15 kV and 120 nA, with a beam diameter defocused to 1 µm. For the flank method measurements, two spectrometers with large TAP crystals and the smallest detector slit (300  $\mu$ m) were used. The counting time at the flanks of FeL $\alpha$  and FeL $\beta$  was 100 s each. Fe<sup>3+</sup>/ $\Sigma$ Fe was determined by applying the correction for self-absorption using four natural garnets with variable total Fe and  $Fe^{3+}/\Sigma Fe$  known from Mössbauer "milliprobe" (Höfer and Brey, 2007). The remaining three spectrometers were used to carry out the simultaneous elemental analyses of Si, Ti, Al, Cr, Fe, Mn, Ni, Mg, Ca, Na, K, and P. Appropriate silicates (pyrope (Mg, Al, Si), albite (Na), CaSiO<sub>3</sub> (Ca)), phosphate (KTiOPO<sub>4</sub> (Ti, K, P)), and metals or metal oxides (iron metal (Fe), MnTiO<sub>3</sub> (Mn), Cr<sub>2</sub>O<sub>3</sub> (Cr), NiO (Ni)) were used as standards, and a ZAF routine was used for the matrix correction. Peak and background measuring times varied between 20 and 60 s. Each quantitative  $Fe^{3+}/\Sigma Fe$  value is the mean of two sets of 25 single measurements in a 5  $\mu m \times$  5  $\mu m$  wide grid with a 1.3 µm step size between the single points, independently determined on two spectrometers at the same measuring spot; each quantitative elemental composition is the mean of one set of 25 single measurements. The uncertainty in Fe<sup>3+</sup>/ $\Sigma$ Fe determination is about  $\pm 0.01 (1\sigma)$ .

#### 3.1.4. Bulk-rock major and trace element analysis

Bulk rock powders ( $\sim$ 500 g) for major and trace elemental analysis were milled using an agate mortar to a mesh size of  $<200 \,\mu m^2$ . Powders were analyzed at the NHGETS, Nanjing, China. The major element analyses were conducted by X-ray fluorescence spectrophotometry (XRF) on fused glass disks using a Malvern Panalytical Axios<sup>MAX</sup> instrument. The loss on ignition (LOI) and  $H_2O^+$ ,  $H_2O^$ were determined prior to major element analyses by P124S electronic analytical balance. CO<sub>2</sub>, FeO, and Fe<sub>2</sub>O<sub>3</sub> were obtained by titration analyses. The parallel analysis of standard reference rock materials (AGV-2, W-2a, and GBW07316) indicated that analytical standard errors for major oxides were <2%, and totals of 100 ± 1% were calculated. The bulk-rock trace elements, including rare earth elements (REEs), were analyzed on Agilent Technologies 7700x quadrupole inductively coupled plasma mass spectrometers (ICP-MS) at NHGETS. About 50 mg powders were mixed with 0.5 ml HNO<sub>3</sub> and 1.0 ml HF in high-pressure PTFE bombs. These bombs were steel-jacketed and placed in the oven at 195 °C for 72 h to completely dissolve refractory minerals. Evaporation and acid dissolution steps were repeated twice, followed by dilution (50 ml) and injection into the ICP-MS. For transition metal elements, powders were dissolved in HNO<sub>3</sub>, HF, and HClO<sub>4</sub>, followed by heatinduced evaporation and the second stage of digestion with aqua regia. Geochemical reference materials (USGS) were analyzed, including basalt (BIR-1, BCR-2, BHVO-2), andesite (AVG-2), rhyolite (RGM-2), and granodiorite (GSP-2). Standard errors were better than  $\pm 10\%$  for the elements with concentrations of 10–50  $\mu$ g·g<sup>-1</sup> and better than  $\pm 5\%$  for the elements of >50 µg·g<sup>-1</sup>.

#### 3.2. Thermodynamic modeling

## 3.2.1. Metamorphic P-T paths constraint from pseudosection

To reconstruct the P-T evolution of the investigated samples, phase equilibrium diagram modelings in closed systems (i.e., no component fractionation) were undertaken with the Perple\_X software package (version 6.9.1, Connolly, 2005) and the internally consistent thermodynamic database of Holland and Powell (2011) (i.e., HP62). During pseudosection modeling, element (instead of oxide) components (Na-K-Ca-Fe-Mg-Mn-Al-Si-C-H<sub>2</sub>-O<sub>2</sub>) were preferred because (1) COH solvents in the fluid have a strong tendency to order for certain bulk compositions at low temperature (Connolly and Galvez, 2018), and (2) Perple\_X will automatically reject any phase/species in which the sum of the components is less than or equal to zero (e.g., the composition of graphite is  $1CO_2 - 1O_2$  and graphite will be rejected from the calculation). Titanium is predominantly hosted in rutile at high pressure and was neglected. Calcium in apatite was also removed from the bulk since apatite is stable in the eclogite  $H_2O$  was set to be in excess (5 wt%) to make free fluid present in all phase regions (Li et al., 2013; Chen et al., 2013), which is consistent with fluidsaturated conditions in cold subduction zone rocks (Okamoto and Maruyama, 1999). The bulk-rock  $Fe^{3+}/\Sigma Fe$  and  $CO_2$  values of the eclogite measured by the titration method were used for the calculation. Although pyrite has been observed, S was not considered in the thermodynamic modeling to make treatment more tractable. Combined with the XRF analysis for other elements (Table EA1), the effective bulk-rock compositions are provided in Table 1.

The solid-solution models of garnet, omphacite, amphibole, glaucophane, phengite, chlorite, epidote, and dolomite were used and listed in Table EA2. C—O—H fluid behavior in equilibrium with solid rocks was modeled using the "generic hybrid molecular fluid" EoS solution models (GFSM), and the neutrally charged molecules considered in the fluid were  $H_2O-H_2$ —CO<sub>2</sub>—CO—CH<sub>4</sub> with linear subdivision (Connolly and Galvez, 2018). The EoS for  $H_2O$  and CO<sub>2</sub> are PS EoS (Pitzer and Sterner, 1995), whereas other species

use the MRK EoS (Connolly and Cesare, 1993). The fluid composition is calculated in equilibrium with the predicted solid mineral phases, consistent with the rock-buffered conditions where a fluid is generated by devolatilization (Galvez et al., 2015; Galvez et al., 2016; Connolly and Galvez, 2018; Piccoli et al., 2019).

#### 3.2.2. Calculation of the $fO_2$ conditions

The equilibrium,  $5CaFeSi_2O_6$  (in Cpx) +  $1/3Ca_3Al_2Si_3O_{12}$  (in Grt) +  $O_2 = 2Ca_3Fe_2Si_3O_{12}$  (in Grt) +  $1/3Fe_3Al_2Si_3O_{12}$  (in Grt) +  $4SiO_2$  (in Coe) (Stagno et al., 2015), was used for determining the  $fO_2$  of the UHP-CH<sub>4</sub> eclogites from the compositions of the paired garnet and clinopyroxene at different metamorphic stages, including the Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of garnet from the "Flank method". *P* and *T* values were estimated from pseudosections, the standard state Gibbs free energy change was derived from Holland and Powell (2011), and the activity–composition relations for the garnet solid solution are compiled by Gudmundsson and Wood (1995).

To verify the results of the Grt-Cpx oxybarometry, the T-Log  $fO_2$  diagram for the UHP-CH<sub>4</sub> eclogite was also modeled with the Perple\_X software package (version 6.9.1) in the Na-K-Ca-Fe-Mg-Mn-Al-Si-C-H<sub>2</sub>-O<sub>2</sub> system considering the actual mineral assemblage. The T-Log  $fO_2$  diagram was calculated for the temperature and log  $fO_2$ , respectively, of 400–600 °C and  $-26 \sim -14$  at a given metamorphic peak P of 2.8 GPa.

Considering that the "Flank method" of Fe<sup>3+</sup> in garnets measurements were not performed on the HP-CO<sub>2</sub> eclogite sample, we extract the chemical potential of O<sub>2</sub> ( $\mu$ O<sub>2</sub>) of the modeled closed system for the HP-CO<sub>2</sub> eclogite by the "werami" routine in Perple\_X (version 6.9.1) and computed the phase diagram of log fO<sub>2</sub> relative to the fayalite-magnetite-quartz (FMQ) buffer as a function of pressure and temperature. The predicted chemical potential of O<sub>2</sub> ( $\mu$ O<sub>2</sub>) is converted to oxygen fugacity (fO<sub>2</sub>) by the equation  $fO_2^{T, P} = \exp \left( \left[ \mu O_2^{T, P} - \mu O_2^{T, 1} \frac{\text{bar}}{\text{purel}} \right] / [\text{RT}] \right)$ . For consistency, we also calculated the fO<sub>2</sub> of the FMQ buffer over the same range of *P*-*T* conditions using the Holland and Powell (2011) database. In our model, fO<sub>2</sub> conditions are not fixed, but are a function of the bulk compositions (e.g., Fe<sup>3+</sup>/\SigmaFe) and metamorphic *P*-*T* conditions.

All  $P-T-fO_2$  calculations for phase relations are conducted with the same bulk compositions (Table 1), activity-composition models (Table EA2), databases, and EoS of fluid species as described in Section 3.2.1.

Moreover, the  $fO_2$  contours of the "max  $aH_2O$ " (i.e., C— $H_2O$  join,  $X_0 = 1/3$ ) in *P*–*T* space, which separates CH<sub>4</sub>- and CO<sub>2</sub>-dominant aqueous fluid in the C—H—O system (H<sub>2</sub>O—H<sub>2</sub>—CO<sub>2</sub>—CO—CH<sub>4</sub>—C<sub>2</sub>-H<sub>6</sub>), were also calculated using the COH model (Zhang and Duan, 2009) for understanding the basic changing laws of main fluid species. Below this  $fO_2$ , abiotic CH<sub>4</sub> is the predominant phase in the graphite/diamond saturated fluid system, whereas, above it, CO<sub>2</sub>-rich aqueous fluids are stable (Malaspina et al., 2010; Schmidt and Poli, 2014; Tao et al., 2018a; Tumiati and Malaspina, 2019).

## 3.2.3. Calculation of potential original speciation of the fluid in equilibrium with the UHP-CH<sub>4</sub> eclogite

Pseudosections were computed by assuming a molecular fluid model (Walters et al., 2020; Spránitz et al., 2022), whereas the electrolytic model was calculated at the two representative P-T-f $O_2$  conditions (3 GPa, 525 °C, FMQ – 3 and 2.5 GPa, 600 °C, FMQ – 1) estimated from both petrographic records and pseudosection calculations to infer the potential original carbonic fluid in equilibrium with the graphite-bearing UHP-CH<sub>4</sub> eclogite (Grt + Omp + Law + Mus + Gln + Coe/Qtz, set excess). The full electrolytic speciation calculations were done with the Deep Earth Water (DEW) model (Huang and Sverjensky, 2019; Sverjensky et al., 2014) and the EQ3 software (Wolery, 1992; Wolery and

 Table 1

 Bulk-rock compositions (wt.%) of the UHP-CH<sub>4</sub> (H19-43) and HP-CO<sub>2</sub> (H19-01) eclogites.

Effective bulk-rock compositions used for thermodynamic modeling with Perple_X																	
Sample	Si	Al	Fe	Ca	Mg	К	Na	Mn	С	$H_2$	02	Total					
H19-43 H19-01	25.22 19.10	6.70 4.41	6.73 10.22	5.71 10.20	3.59 3.32	1.18 0.01	2.19 1.46	0.12 0.28	0.29 2.78	0.56 0.56	47.71 47.66	100.00 100.00					
Measurements obtained by XRF, electronic analytical balance, and titration analyses																	
Sample	SiO <sub>2</sub>	$Al_2O_3$	TiO <sub>2</sub>	TFe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	MnO	$P_{2}O_{5}$	LOI	Total	$H_2O$	FeO	$Fe_2O_3$	$Fe^{3+}/\Sigma Fe$	CO <sub>2</sub>
H19-43 H19-01	55.46 41.25	13.10 8.42	0.58 1.36	9.20 13.64	8.45 14.87	6.11 5.57	1.47 0.01	3.01 1.98	0.16 0.36	0.21 0.34	2.08 11.33	99.83 99.13	1.46 2.11	6.64 9.32	1.82 3.39	0.198 0.247	1.10 10.27

Daveler, 1992) with modified Berman thermodynamic database (Berman, 1988, Berman, 1990). K<sup>+</sup> activity was fixed by muscovite, Ca<sup>2+</sup> activity by diopside in clinopyroxene, Mg<sup>2+</sup> activity by pyrope in garnet,  $Fe^{2+}$  activity by almandine in garnet,  $Al^{2+}$  activity by glaucophane, H<sup>+</sup> activity by lawsonite, aqueous H<sub>4</sub>SiO<sub>4</sub> activity by coesite/quartz, and Na<sup>+</sup> was used for all electrical balance and Cl<sup>-</sup> was used to estimate the activity coefficient in EQ3 (Sverjensky et al., 2014; Sverjensky and Huang, 2015). Since graphite is an important saturated carbon phase in our mineral paragenesis and may constrain  $O_2$  activity (2C + H<sub>2</sub>O  $\leftrightarrow$  CO<sub>2</sub> + CH<sub>4</sub>),  $CO_3^{2-}$  activity is buffered by graphite (Sverjensky et al., 2014). Considering the approximate treatment of mineral solid solution in the DEW model database, garnet and omphacite were approximated as solid solutions consisting of pyrope 0.12/0.25, almandine 0.7/0.54, grossular 0.18/0.21, and diopside 0.29/0.26, hedenbergite 0.26/0.27, jadeite 0.45/0.47 based on the mineral compositions analyzed in the samples under the corresponding  $P-T-fO_2$  conditions. Some phases (MgSiC<sup>+</sup>, Mg (OH)<sub>2</sub> (aq), paragonite, phlogopite) that did not extrapolate plausibly were excluded from calculations.

## 4. Results

#### 4.1. Petrological observations

### 4.1.1. The UHP-CH<sub>4</sub> eclogite

The UHP-CH<sub>4</sub> eclogite sample (H19-43) consisted predominantly of garnet (20%), omphacite (40%), phengite (20%), quartz (12%), amphibole (4%), and minor zoisite + graphite + rutile + carbo nates + albite + apatite + sulfides (<5 %). Amphibole bands were observed in association with phengite and defined foliation (Fig. 2a). Garnet (0.5–1 mm in size) were typically euhedral with reddish inclusion-rich cores overgrown by nearly colorless rims (Fig. 2b). Inclusions in the garnet cores included coesite/quartz, omphacite, dolomite, zoisite, paragonite, and rutile. Two coesite inclusions ( $\sim$ 50  $\mu$ m) in the garnet cores were optically identified and confirmed by Raman spectroscopy (Fig. 2c), indicating that this eclogite underwent UHP metamorphism. The Raman spectra displayed diagnostic coesite Si-O stretching bands at 521, 427, 356, 325, 271, and 205 cm<sup>-1</sup>. Quartz rims replacing coesite were not optically observed and no characteristic peaks of quartz were detected by Raman spectroscopy (e.g., 467 cm<sup>-1</sup>). Fe-bearing dolomite was also identified near coesite inclusions. We observed rectangle-shaped zoisite-paragonite inclusion assemblages consistent with pseudomorphs after lawsonite (Fig. EA1a; Tian and Wei, 2013). Omphacite exhibited subhedral-euhedral porphyroblasts (0.1-0.5 mm across) in the matrix and was oriented parallel to foliation (Figs. EA1b-c). Minor albite was observed as a retrograde phase along garnet grain boundaries.

Dolomite mineral inclusions were observed in garnet and rutile (Fig. 2c and EA2b), whereas the carbonate in the matrix was calcite in textural equilibrium with hornblendic amphiboles (Figs. EA2c-d). Dolomite inclusions in rutile grains were also encased in calcite

(Fig. EA2b). These observations suggest that dolomite was formed in the prograde (U)HP metamorphic stage, whereas calcite grew in the retrograde amphibolite-facies stage. Dotted graphite was observed in garnet and omphacite or encased in later calcite (Fig. 2d–e). The sulfides were predominantly pyrite (Py, FeS<sub>2</sub>) and chalcopyrite (Ccp, CuFeS<sub>2</sub>). Rare sphalerite (Sp, ZnS) and galena (Gn, PbS) were found in pyrite (Figs. EA2a–b). Porphyroblastic pyrite and chalcopyrite (after bornite during retrogression, Li et al., 2016a, 2021) crystals contained omphacite, phengite, and rutile inclusions, which could be cut by hornblendic amphibole. This phenomenon meant that most, if not all, sulfide grains were recrystallized and in equilibrium with (U)HP mineral assemblages during subduction. In addition, the replacement of chalcopyrite with magnetite and rutile by ilmenite was observed.

The UHP-CH<sub>4</sub> eclogite (H19-43) is named for the ubiquitous presence of CH<sub>4</sub> ± H<sub>2</sub> ± N<sub>2</sub> bubbles in the fluid inclusions. The small (<1–10  $\mu$ m) fluid inclusions (FIs) in this sample were predominantly aqueous and consisted of two to three phases (L + V ± S) (Fig. 2f–g). Isolated amorphous FIs were found in garnet cores and mantles, along with dolomite and coesite inclusions, suggesting prograde-to-peak entrapment. In contrast, the garnet rims were inclusion-poor and compositionally distinct. Meanwhile, some oriented tubular two/three-phase fluid and rutile inclusions occur in omphacite cores with their long dimensions parallel to the c-axis of the host crystals (Fig. 2g). These features suggest that they are primary fluid inclusions trapped during the growth of the omphacite cores (Gao and Klemd, 2001). Calcite (5–30 vol%) is the only observed daughter mineral phase in fluid inclusions (Fig. EA1d).

### 4.1.2. The HP-CO<sub>2</sub> eclogite

The HP-CO<sub>2</sub> eclogite sample (H19-01) consisted of garnet (25%), omphacite (45%), dolomite (10%), glaucophane (5%), sulfide (5%), quartz (5%), and minor rutile, titanite, graphite, magnetite, and apatite (Fig. 3a-c). Porphyroblastic garnet (1-2.5 mm sized) preserved two sets of mineral inclusion assemblages. Garnet-I (core) contained primarily omphacite and some quartz, whereas Garnet-II (rim) contained omphacite, euhedral dolomite, and quartz (Fig. 3c). Dolomite (0.2-1 mm diameter), omphacite, and quartz in the matrix appeared texturally equilibrated (Fig. 3f and EA2g). The matrix dolomite grains were idioblastic/subidioblastic and rich in fluid inclusions oriented parallel to the cleavage plane (Fig. 3g). Furthermore, oriented multiphase FIs were widespread in omphacite (Fig. 3f). Small calcite grains were scattered around the rims of the dolomite grains, which is interpreted as a retrograde texture (Figs. EA2g-h). Graphite was distributed along the crystal cleavage in dolomite and is associated with fluid pockets and magnetite, representing the redox decomposition of Fedolomite. Epidote is rare in the HP-CO<sub>2</sub> eclogite. The other matrix phases included glaucophane and pyrite. Some glaucophane grains were rimmed by secondary barroisite. Pyrite grains occurred in the matrix (homogeneously distributed with dolomite and omphacite)



**Fig. 2.** Representative petrological observations for the UHP-CH<sub>4</sub> eclogites. (a) Hand specimen of UHP-CH<sub>4</sub> eclogites (sample H19-43), which consists mainly of garnet, omphacite, amphibole, phengite and quartz. (b) Garnet porphyroblasts with omphacite, phengite, and quartz. White lines across garnet grains show the locations of the zoning profile presented in Fig. 4a. (c) Coesite and dolomite inclusions in garnet cores and the Raman spectrum of coesite with typical bands denoted. (d) Dotted spherulitic graphite is included in garnet and omphacite. (e) Retrograde calcite wraps dotted graphite formed earlier. Raman spectra of (f) isolated, amorphous primary FIs in the garnet cores and (g) orientated tubular two-phase FIs in the omphacite cores with prominent CH<sub>4</sub> (2917 cm<sup>-1</sup>) and H<sub>2</sub> (4155 cm<sup>-1</sup>) peaks. Mineral abbreviations: FIs, fluid inclusions; Grt, garnet; Phn, phengite; Omp, omphacite; Qtz, quartz; Amp, amphibole; Dol, dolomite; Coe, coesite; Cal, calcite; Gph: graphite.

(Fig. 3b and EA2f) and as inclusions in garnet porphyroblasts (Fig. EA2e). The pyrite in the matrix displayed magnetite rims, which were not observed around pyrite grains included in the garnet. High-*P* mineral phases (rutile, glaucophane, and dolomite) were included within the pyrite.

The HP-CO<sub>2</sub> eclogite (H19-01) is also named for the ubiquitous presence of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O, instead of CH<sub>4</sub>, in the fluid inclusions (<10  $\mu$ m) in both omphacite and dolomite. FIs are predominantly aqueous and also contain two or three phases (L + V ± S). The vapor bubble, when present in dolomite, usually consists of CO<sub>2</sub> (1285 and 1388 cm<sup>-1</sup>) along with magnetite and graphite (Fig. 3d–e and g), whereas N<sub>2</sub> + H<sub>2</sub>O is common in omphacite-hosted inclusions (Fig. 3f).

#### 4.2. Geochemical analysis

#### 4.2.1. Bulk rock geochemistry

The bulk rock major and trace element compositions of the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites are presented in Table EA1. The UHP-CH<sub>4</sub> eclogite (H19-43) exhibits elevated SiO<sub>2</sub>, K<sub>2</sub>O, H<sub>2</sub>O, and lower CaO content compared to the average MORB (White and Klein, 2014). The chondrite-normalized REE pattern (Fig. EA3a) had a negative slope, with a (La/Sm) N value of 3.02, (La/Yb) N value of 6.06, and Nb/La ratio of 1.02, indicating an enriched mantle

source for the protolith. The *N*-MORB-normalized trace element pattern showed an irregular distribution (Fig. EA3b): The large ion lithophile elements (LILEs) (Cs, Rb, Ba, K, Pb, Sr, and Li) displayed prominent positive anomalies, whereas some high field strength elements (HFSEs) (Ti, Nb, Ta) showed negative anomalies. The Nb/Ta ratio (14.45) and Zr/Hf ratio (36.28) were within the known range for oceanic basalts (Pfänder et al., 2007).

The HP-CO<sub>2</sub> eclogite displayed lower SiO<sub>2</sub> (~40 wt%), K<sub>2</sub>O (0.01 wt%), Rb (0.84  $\mu$ g·g<sup>-1</sup>), and Ba (11.65  $\mu$ g·g<sup>-1</sup>) content compared to both average MORB and the UHP-CH<sub>4</sub> sample. In contrast, the CaO (~15 wt%), Li (~20  $\mu$ g·g<sup>-1</sup>), and Pb (3.26  $\mu$ g·g<sup>-1</sup>) concentrations were significantly higher than those of MORB and ocean island basalts (OIBs) (Fig. EA3b). In agreement with the high carbonate content, the HP-CO<sub>2</sub> eclogite samples exhibited high LOI values of 11.33 wt%. The HP-CO<sub>2</sub> eclogite had a (La/Sm) <sub>N</sub> ratio of 4.59, (La/Yb) <sub>N</sub> ratio of 21.33, Nb/Ta ratio of 12.46, and Zr/Hf ratio of 38.57. The REE concentrations and patterns of the HP-CO<sub>2</sub> eclogite (Fig. EA3a).

## 4.2.2. Mineral chemistry

4.2.2.1. Garnet. Garnet grains in eclogites display significant compositional and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio zonation from core to rim. In the UHP-CH<sub>4</sub> eclogite, garnet grains display core-to-rim increases in



**Fig. 3.** Representative petrological observations for the HP-CO<sub>2</sub> eclogite. (a) Hand specimen of HP-CO<sub>2</sub> eclogites (sample H19-01). (b) Overview photomicrograph showing garnet, dolomite, omphacite, and pyrite. (c) A garnet porphyroblast shows two stages of growth from core to rim. (d) Graphite is distributed in dolomite. (e) Graphite is associated with fluid pockets and magnetite, surrounded by Fe-dolomite. Raman spectra of primary fluid inclusions in (f) omphacite and (g) dolomite, show peaks at 1285 cm<sup>-1</sup> (CO<sub>2</sub>), 1388 cm<sup>-1</sup> (CO<sub>2</sub>), and 2330 cm<sup>-1</sup> (N<sub>2</sub>). Mineral abbreviations: Py, pyrite; Gln, glaucophane; P-Fl, primary fluid inclusions; S-Fl, secondary fluid inclusions.

Mg (Prp\_{0.08} to Prp\_{0.25}), whereas the Fe content and Fe  $^{3+}\!/\Sigma Fe$  ratios showed a core-to-rim decrease (Alm<sub>0.71</sub> to Alm<sub>0.52</sub>; Fe<sup>3+</sup>/ $\Sigma$ Fe 0.06– 0.02). In contrast, the Ca content decreased from the core to the mantle and increased from the mantle to the rim (Figs. 4a and 5), where the mantle exhibited the lowest Ca content (Grs<sub>0.16</sub>) and likely recorded the peak pressure. In lawsonite-bearing eclogite facies, the Ca in garnet was strongly influenced by lawsonite partitioning, and the increased abundance of lawsonite as P increased in the low-T region may have resulted in a decrease in grossular in garnet. Contouring grossular and pyrope concentrations in the P-T pseudosection can be applied to determine the peak P-T conditions (Tian and Wei, 2013; Du et al., 2014; Lü et al., 2019). According to all compositional zoning profiles of CH<sub>4</sub>-bearing garnets, the composition changes continuously from the core to the mantle, which represents the prograde to peak stage (low Ca and Mg, high FeO<sub>T</sub> and Fe<sup>3+</sup>/ $\Sigma$ Fe; Figs. 4c and 6), while the narrow rim (red edge in the Mg X-ray intensity map in Figs. 5 and 6) may represent early retrogressive heating during the exhumation stage (high Ca and Mg, low FeO<sub>T</sub> and Fe<sup>3+</sup>/ $\Sigma$ Fe; Fig. 4c).

Garnet from the HP-CO<sub>2</sub> eclogite exhibited higher Ca (Grs<sub>0.24<sup>-0.29</sup></sub>) and lower Mg (Prp<sub>0.03<sup>-0.09</sup></sub>) compared to the UHP sample (Figs. 4b and 9a). Fe and Ca were almost constant from the core (Grt-I) to the rim (Grt-II) (Grs<sub>0.26</sub>, Alm<sub>0.66</sub>), whereas Mg displayed a slight continuous increase (Prp<sub>0.03</sub> to Prp<sub>0.09</sub>), which may reflect a prograde metamorphic process with near-isobaric heating.

4.2.2.2. Omphacite. All clinopyroxene grains were chemically identified as omphacite (Fig. 4e) based on the classification presented by Morimoto (1988). Systematic compositional variations were also observed. In the UHP-CH<sub>4</sub> eclogite, cores were elevated in Fe<sup>3+</sup> (calculated using the charge balance option in MinPlot, see Walters 2022) and total FeO relative to rims (Mean: Fe<sup>3+</sup>/ $\Sigma$ Fe: 0.53 to 0.35; FeO<sub>T</sub>: 7.82 to 3.75; Fig. 4f–g; Table EA3), correspond-



**Fig. 4.** Chemical compositions of garnet, muscovite, omphacite, carbonates, and amphibole. Representative garnet compositional zoning profiles in the UHP-CH<sub>4</sub> (a) and HP-CO<sub>2</sub> (b) eclogite samples. (c) The plot of garnet X(pyrope) or FeO\* (total, EPMA measured) vs Fe<sup>3+</sup>/ $\Sigma$ Fe (Flank method measured) highlights compositional distinct between core and rim in the UHP-CH<sub>4</sub> eclogite. (d) Plots of Si (p.f.u.) vs Al (p.f.u.) for phengite compositions in the UHP-CH<sub>4</sub> eclogite. The paragonite analysis is from the box-shaped pseudomorph after lawsonite in Fig. EA1a. (e-g) Composition diagram for clinopyroxene, showing two types of omphacite. (g) Plots of Fe<sup>3+</sup>/ $\Sigma$ Fe (calculated by charge balance) vs FeO\* (total, EPMA measured) of omphacite. (g) Plots of Fe<sup>3+</sup>/ $\Sigma$ Fe (calculated by charge balance) vs FeO\* (total, EPMA measured) of omphacite. (h) Compositional ternary classification diagram for carbonate analyses. (i) Amphibole classification plot after Leake et al. (1997). Mineral abbreviations: Ank, ankerite; Arg, aragonite.



**Fig. 5.** EPMA elemental X-ray maps of garnet and omphacite in the UHP-CH<sub>4</sub> eclogite. It clearly shows two sets of garnet-omphacite pairs (omphacite cores-garnet cores, omphacite rims-garnet rims) that were used to constrain the *f*O<sub>2</sub> condition by the Grt–Cpx oxybarometry.

ing to compositional zoning on the BSE images (bright core: high Fe and Cr, low Al vs dark rim: low Fe and Cr, high Al; Fig. 5). Small and extremely rare omphacite inclusions were found in garnets, and limited data suggest that they have the same compositional evolution as the matrix omphacite (Fig. 4e). Omphacite grains in the HP-CO<sub>2</sub> eclogite sample exhibited elevated Na, Fe<sup>3+</sup>, and total FeO contents compared to those in the UHP-CH<sub>4</sub> eclogite (Fig. 4f–g). The matrix omphacite, omphacite inclusions in garnet cores, and omphacite inclusions in dolomite encased in garnet rims had similar compositions.

4.2.2.3. Carbonates. Carbonates in the UHP-CH<sub>4</sub> eclogite sample (H19-43) were Fe-bearing dolomite and pure calcite (Fig. 4h), whereas those in the HP-CO<sub>2</sub> eclogite sample (H19-01) were Ferich dolomite and minor Mg and Fe-bearing calcite. The Fe<sup>2+</sup>/ (Mg + Fe<sup>2+</sup>) ratio of dolomite in the HP-CO<sub>2</sub> eclogite ranged from 0.27 to 0.46 (Mean: 0.32), which was much higher than that of those in the UHP-CH<sub>4</sub> eclogite (~0.08). The Fe content in the dolomite-ankerite solid solution may decrease with pressure at a constant temperature, which is consistent with the lower dolomite X<sub>Fe</sub> content in the UHP-CH<sub>4</sub> eclogite (Tao et al., 2014; Li et al., 2014).

4.2.2.4. Other minerals. Phengite porphyroblasts (0.5–1 mm across) with Si = 3.3–3.6p.f.u. (Fig. 4d) were observed in the UHP-CH<sub>4</sub> eclogite. Rare paragonite (Si  $\leq$  3.2p.f.u.) occurs with zoisite and quartz in rectangle-shaped aggregates included in garnet, which were interpreted as pseudomorphs after lawsonite (Fig. EA1a). In the matrix, several zoisite porphyroblasts (0.5–0.7 mm) cutting

the phengite and omphacite foliations exhibited  $Fe^{3+}/(Fe^{3+}+AI)$  ratios of 0.06 to 0.15. Rare epidote ( $Fe^{3+}/(Fe^{3+}+AI)$  ratio of ~0.19) also occurred in the HP-CO<sub>2</sub> eclogite. Amphibole exhibited significant compositional variation in all samples and could be grouped into glaucophane, barroisite (after glaucophane during retrogression; Li et al., 2016b), hornblendic amphibole, and actinolite using the classifications reported by Leake et al. (1997) and Diener et al. (2007) (Fig. 4i). Rims of barroisite were observed on euhedral porphyroblasts of glaucophane in the HP-CO<sub>2</sub> eclogite.

#### 4.3. Thermodynamical modeling

4.3.1. Metamorphic  $P-T-fO_2$  conditions of the UHP-CH<sub>4</sub> eclogite 4.3.1.1. P-T path constraints. In the P–T pseudosection calculated for the UHP-CH<sub>4</sub> eclogite (Fig. 6), the prograde to peak assemblage garnet, omphacite, phengite, glaucophane, Fe-dolomite, lawsonite, graphite, and coesite/quartz were stable at > 2.6 GPa and < 550 °C. The graphite-out isograd (graphite activity in the model is 1) was largely isothermal and occurs between 550 °C and 600 °C. Garnet core to mantle compositions constrained a continuously prograde to peak conditions of  $\sim$ 500 °C at  $\sim$ 2.6 GPa to  $\sim$ 550 °C at  $\sim$ 2.9 GPa (Mean: 525 °C, 2.8 GPa), which was consistent with observations of coesite and graphite (not diamond) and wellpreserved CH<sub>4</sub>-rich fluid inclusions. In addition, it can be speculated that as deeper subduction (increasing *P* and *T*), dolomite decomposes into magnesite and glaucophane disappears in the bulk rock. Garnet rim compositions record an early-retrograde/ exhumation condition of  $\sim$ 600 °C at  $\sim$ 2.5 GPa. The retrograde P-T path crosses the lawsonite-out reaction, which is consistent with



**Fig. 6.** *P*–*T* pseudosections for the UHP-CH<sub>4</sub> eclogite calculated with Perple\_X based on the effective bulk composition (Table 1). The insert image has shown the Mg X-ray map of the garnet in Fig. 2b and the location of CH<sub>4</sub> fluid inclusions identified by Raman which are marked with red stars. Pseudosections are contoured with isopleths of grossular and pyrope to constrain the *P*–*T* path. Mineral abbreviations: Mica, muscovite; Mgs: magnesite; Sid: siderite; Law, lawsonite; Dia: diamond. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the observed pseudomorphs of zoisite and paragonite after the lawsonite (Fig. 6 and EA1a). Our P-T path matches closely with previous estimates for the whole UHP units (see review in Zhang et al., 2019).

4.3.1.2. fO<sub>2</sub> determination and C-O-H fluid speciation. Precise and accurate in situ garnet  $Fe^{3+}/\Sigma Fe$  analysis (Table EA3) allowed us to calculate the  $fO_2$  conditions of peak and early-retrograde metamorphism using garnet-clinopyroxene oxybarometry (Stagno et al., 2015; Tao et al., 2018a). Omphacite cores, which can occur in the garnet core and mantle domains, have  $\text{FeO}_{T}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that are much higher than the omphacite rim and are rich in primary CH<sub>4</sub> fluid inclusions (Figs. 4e-g, 5 and EA1b-c). Garnet cores and mantles were also observed to contain CH<sub>4</sub> fluid inclusions as well as high FeO<sub>T</sub> and Fe<sup>3+</sup>/ $\Sigma$ Fe ratios (Fig. 4a and c). These data demonstrate that omphacite cores are likely to be in chemical equilibrium with the garnet core-mantle during prograde to peak garnet growth. In particular, for garnet, relative to the mantle and rim, the cores, which not only account for most of the garnet volume but also the most abundant fluid and mineral inclusions as omphacite cores (Fig. 2b and 5–6), are believed to preserve original compositions without being altered by retrogression or kinetically inhibited due to Rayleigh fractionation (caused by the feedstock supply) during crystal growth. Therefore, two sets of garnet-omphacite pairs (the average component of omphacite cores – garnet cores and omphacite rims – garnet rims; Fig. 5, Table EA3) were used to constrain the  $fO_2$  condition at 2.8 GPa, 525 °C (average prograde to peak P–T) and 2.5 GPa, 600 °C (average early-exhumation P–T), respectively. The calculated log  $fO_2$  yielded values for FMQ – 2.9 and FMQ – 0.9 (Table EA3), correspondingly.

We compared the results of Grt-Cpx oxybarometry and petrography of the peak mineral assemblage (Grt + Omp + Gln + Law + Coe + Phn + Dol) with the T-Log  $fO_2$  diagram for UHP-CH<sub>4</sub> eclogites at 2.8 GPa (Fig. 7). The model predicts CH<sub>4</sub>-rich fluids at FMQ – 2.9, consistent with Grt-Cpx oxybarometry results and the observed CH<sub>4</sub>-bearing inclusions in the garnet and omphacite cores. Our calculations further reveal that small differences in the redox budget (RB) (which is here mainly dependent on Fe<sup>2+</sup>-Fe<sup>3+</sup> and C<sup>4+</sup>-C<sup>4-</sup> ratios), here calculated as excess  $O_2$ , will result in drastically different  $fO_2$  (Fig. EA4). These jumps in  $fO_2$  occur following the disappearance of one buffering assemblage and the appearance of another at higher or lower  $fO_2$ , such as the formation of methane (C<sup>4-</sup>) following the disappearance of carbonate (C<sup>4+</sup>) and stabilization of graphite (C<sup>0</sup>) (Fig. 7 and EA4). In our model,  $fO_2$  and  $O_2$  (wt.



**Fig. 7.** T-Log *f*O<sub>2</sub> diagram at 2.8 GPa for the UHP-CH<sub>4</sub> eclogite. The isopleths of grossular (Ca/(Ca + Mg + Fe + Mn)), pyrope (Mg/(Ca + Mg + Fe + Mn)), referenced FMQ oxygen fugacity buffer, and CH<sub>4</sub>/(CH<sub>4</sub> + CO<sub>2</sub>) ratios are shown. Mineral abbreviations: Hem, hematite; Wnc, winchite.

%) are positively correlated, as changes in  $fO_2$  induce changes in buffering capacity of the multi-variant system of solid solution phases.

Aqueous fluid is likely to be a major agent in slab-mantle carbon transfer. Here, we quantitatively predicted the carbon speciation in fluids calculated using the DEW model at the *P*–*T*–*f*O<sub>2</sub> conditions estimated by our pseudosection predictions and Grt-Cpx oxybarometry (prograde to peak stage *vs* early-exhumation stage; Fig. 8). Results show that the most important C-bearing aqueous species are CH<sub>4</sub> (~1.25 mol/kg-H<sub>2</sub>O), CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup>, and C<sub>2</sub>H<sub>6</sub> with minor H<sub>2</sub> at the prograde UHP conditions, while in the early-exhumation/retrograde stage, the fluids are dominated by H<sub>2</sub>CO<sub>3</sub> (~1.64 mol/kg-H<sub>2</sub>O), CO<sub>2</sub>, HCO<sub>3</sub> and a small amount of CH<sub>4</sub> (~0.15 mol/kg-H<sub>2</sub>O).

Together, the garnet-clinopyroxene oxybarometry and the thermodynamic calculations were consistent with the finding of CH<sub>4</sub> dominant aqueous fluid detected in the FIs in garnet and omphacite cores by Raman spectroscopy.

#### 4.3.2. Metamorphic P-T-fO<sub>2</sub> conditions of the HP-CO<sub>2</sub> eclogite

According to the isopleths for garnet compositions, the P-Tpseudosection calculated for the HP-CO<sub>2</sub> eclogite (Fig. 9a) showed that the assemblage garnet, omphacite, glaucophane, phengite, dolomite, lawsonite, and quartz ± graphite was stable between 2.5 and 2.7 GPa at 475-550 °C (near isobaric heating; Mean: 500 °C, 2.6 GPa). These estimates were within the range of uncertainty of previous estimates for peak metamorphic conditions of the central HP unit (see review in Tan et al., 2019). The graphiteout isograd (graphite activity in the model is 1) was largely isothermal and occurred between 475 °C and 500 °C. The pseudosection revealed that the lawsonite and glaucophane modes decreased whereas the garnet and omphacite modes increased during prograde metamorphism (increasing *T*), but that lawsonite and glaucophane remained stable under peak conditions (Figs. EA5a-c). The stable dolomite region in the HP-CO<sub>2</sub> eclogite was much wider than that in UHP-CH<sub>4</sub> eclogite, because the bulk composition was rich in Ca and CO<sub>2</sub>. The expanded dolomite stability was consistent



**Fig. 8.** Aqueous fluid compositions in equilibrium with the mineral assemblage of the UHP-CH<sub>4</sub> eclogite at prograde to peak stage (a–c) and early-exhumation stage (d–f), respectively. Numbers are by mol % and only species with concentrations >10<sup>-5</sup> mol/kg-H<sub>2</sub>O are shown.



**Fig. 9.** Pseudosections for the HP-CO<sub>2</sub> eclogite calculated with Perple\_X based on the effective bulk composition (Table 1). (a) P-T pseudosections and the insert image shows the Si X-ray intensity map of the garnet in Fig. 3c. Pseudosections are contoured with isopleths of grossular and pyrope to constrain the P-T path. (b) The plot of log  $fO_2$  relative to FMQ as a function of pressure and temperature. The  $fO_2$  is more sensitive to changes in temperature under high pressure.

with the phase diagram calculated for similar carbonated eclogites by Zhu et al. (2020). Interestingly, the abundance of  $CO_2$  in the solid assemblage has a steep rise, followed by a gradual decrease with increasing temperature, suggesting a small *P*–*T* window where carbon remained locked within the solid assemblage (Fig. EA5d): Hydrous phases are consumed prior to significant carbonate breakdown to produce aqueous fluid; when lawsonite decomposes at higher *T*, the liberated Ca combines with the  $CO_2$ in the fluid to form carbonates, which induces transient carbon sequestration from the remaining fluid, or at minimum preserves the remaining carbonate, and forms the abundant dolomite that is preserved as inclusions in garnet-II (rim).

The  $fO_2$  contoured P-T pseudosection for the HP-CO<sub>2</sub> eclogite sample (high CO<sub>2</sub> content and elevated Fe<sup>3+</sup>/ $\Sigma$ Fe in bulk than the UHP-CH<sub>4</sub> eclogite) is shown in Fig. 9b and used to estimate  $fO_2$ , assuming closed-system conditions and bulk rock equilibrium. The predicted lowest  $fO_2$  is at low *T* and high *P* conditions. The prograde to peak path was predicted to traverse an  $fO_2$  range of FMQ to FMQ + 1.0, thus buffering a higher  $fO_2$  relative to the UHP-CH<sub>4</sub> eclogite. The elevated  $fO_2$  conditions were consistent with observed CO<sub>2</sub>-bearing FIs and magnetite stability in dolomite.

## 4.4. Key reactions inducing CH<sub>4</sub> or CO<sub>2</sub> formation in eclogite

#### 4.4.1. Specific CH<sub>4</sub> formation reactions in the UHP-CH<sub>4</sub> eclogite

The low  $fO_2$  of  $\sim$ FMQ – 3 buffered from prograde to peak evolution of the UHP-CH<sub>4</sub> yielded by adjusting ferric (Fe<sup>3+</sup>) and ferrous (Fe<sup>2+</sup>) iron (i.e.,  $O_2$  + (Fe<sup>2+</sup>O)<sub>mineral</sub>  $\leftrightarrow$  (Fe<sup>3+</sup>O<sub>3</sub>)<sub>mineral</sub>) in the silicate mineral assemblage (e.g., Grt + Omp + Gln), and is electrochemically balanced by the transformation of carbon species (CO<sub>2</sub> + 2H<sub>2</sub>O  $\leftrightarrow$  CH<sub>4</sub> + 2O<sub>2</sub>):

$$8(Fe^{2+}O)_{mineral} + CO_2 + 2H_2O \leftrightarrow 4(Fe^{3+}_2O_3)_{mineral} + CH_4$$
 (A)

This reaction results in elevated  $Fe^{3+}$  in the garnet and omphacite cores, along with the formation of CH<sub>4</sub>-rich fluids that are preserved as inclusions. Combined, dehydration (producing H<sub>2</sub>O from Gln and Law) and redox reactions between C and Fe occur to produce the peak UHP-CH<sub>4</sub> eclogite assemblage:

$$\begin{array}{l} \mbox{Gln + Law + Dol $\rightarrow$ Grt + Omp + Qtz/Coe + C^0$} \\ \mbox{+ C-H-O fluids} \end{array} \tag{B}$$

The graphite-saturated C–H–O fluid evolves into a CH<sub>4</sub>dominated fluid (Fig. 11b, c) as dolomite is consumed because  $fO_2$  is the chemical link between the solids and fluids in the rock and carbonic fluid can be rock-buffered to a reduced state ( $fO_2$  values between "max  $\alpha$ H<sub>2</sub>O" (C-H<sub>2</sub>O join; Fig. 10b, c) and "pure-CH<sub>4</sub>", Fig. 7). Lawsonite pseudomorphs and dolomite can be found in garnet cores along with graphite and CH<sub>4</sub> inclusions, showing remnants of the reactant minerals, as well as the products. Dolomite was not predicted to be in equilibrium with a CH<sub>4</sub>-dominant fluid (Fig. 7), suggesting that the reaction did not fully reach equilibrium.

## 4.4.2. Specific CO<sub>2</sub> formation reactions in the HP-CO<sub>2</sub> eclogite

Based on variations in modal abundances in the phase diagram (Fig. 9) and the petrological observations that graphite is observed with fluid pockets and magnetite within Fe-dolomite (rich in CO<sub>2</sub> fluid inclusions) (Fig. 3d–e and g), this assemblage could also be encapsulated by garnet rims. This texture indicates a redox reaction between Fe-dolomite and H<sub>2</sub>O (produced from Gln and Law) under peak P-T (Tao et al., 2018a), and the generalized reactions along the prograde P-T path (increasing T at an almost constant pressure) are estimated follows:

$$Law + Gln \rightarrow Grt + Omp + H_2O \qquad (C)$$

Dol-1 (high Fe) + 
$$H_2O \rightarrow Fe_3O_4$$
 + Dol-2 (low Fe) +  $C^0$  + C–H–O fluid (D)

The graphite-saturated C—H—O fluid is expected to evolve into a CO<sub>2</sub>-dominated fluid at the high  $fO_2$  (FMQ ~ FMQ + 1, between "CCO" and "max  $aH_2O$ " (C-H<sub>2</sub>O join)) buffered by the mineral assemblage of HP-CO<sub>2</sub> eclogites at the peak (Fig. 11b and d).

#### 5. Discussion

## 5.1. Distinguishing a rock- or fluid-buffered metamorphic system

Carbon speciation in the slab may be governed (buffered) by the host system, yielding either a rock- or external fluid-buffered system. The dilemma of "what controls what" can be overcome only by considering the degree of  $fO_2$  buffering by the reactive bulk composition inherited from the protolith relative to modification

by an external fluid (Galvez et al., 2015; Galvez et al., 2016; Cannaò and Malaspina, 2018; Connolly and Galvez, 2018; Piccoli et al., 2019). The degree to which an external fluid may buffer a rock depends on the time-integrated fluid flux and the final fluid-rock ratio (e.g., Ague et al., 2022). Rocks subjected to intense fluid metasomatism in SW Tianshan have been examined in previous studies (e.g., John et al., 2012; van der Straaten et al., 2012; Li et al., 2013, 2017) and exhibit the following characteristics: (1) Metasomatism during prograde to peak metamorphism is largely channelized and limited to cm-scale metasomatic selvages on the scale of cm surrounding veins; (2) Textures consistent with garnet and omphacite dissolution-reprecipitation are observed, such as rounded and lobate grain shapes (see Fig. 6 in Lü et al., 2012a, 2012b) or relict prograde-peak garnet overgrown by secondary garnet (see Fig. 8 in Li et al., 2013); (3) Chlorite, epidote, and titanite are widely distributed; (4) Hornblendic amphibole or actinolite extensively replaces omphacite; (5) Prograde to peak phengite is replaced by paragonite.

In our samples, we did not observe textural, petrological, or geochemical evidence showing the infiltration of an external fluid during (U)HP metamorphism, which would produce new hydrous phases such as talc and chlorite (Supplementary material, Fig. EA6). Instead, prograde to early retrograde metamorphic minerals were well-preserved and internally buffered (including solids and fluids) by reactive bulk composition. For example, in UHP-CH<sub>4</sub> eclogites: (1) garnet and omphacite are >60% in volume; (2) phengite was observed in the matrix rather than paragonite; (3) only rare euhedral epidote was observed in the matrix; (4) coesite inclusions were not retrogressed to quartz, which occurs rapidly in the presence of water (Frezzotti 2019); (5) "Bell-shaped" Mn profiles were observed in garnet, which has been referred to as prima facies evidence for preservation of growth zoning (see review in Kohn, 2014). For HP-CO<sub>2</sub> eclogites: (1) the assemblage mainly consisted of garnet, omphacite, dolomite, and quartz; (2) epidote in the matrix was rare (although this may reflect lower bulk  $Al_2O_3$ ; and (3) there was also no significant Mn diffusion in garnet. Additionally, the observed major and trace element compositions of the bulk rock were also consistent with those of a rockbuffered system. For example, (1) the measured H<sub>2</sub>O values were low in the rocks (1.46 wt% for the UHP-CH<sub>4</sub> eclogite and 2.11 wt % for the HP-CO<sub>2</sub> eclogite) and were too low to saturate the rocks in fluid at peak or early-retrograde conditions; (2) The infiltration of serpentinite-derived fluids was expected to increase Ni and Cr concentrations (e.g., Spandler et al., 2011; Walters et al., 2021) or enrich strong fluid-mobile elements such as Cs and Rb; however, the concentrations measured here were low or even depleted (Table EA1, Fig. EA3b). Combined, these data demonstrate that prograde to early-exhumation metamorphism occurred in a rockbuffered system at a low fluid-rock ratio. As a result, the CH<sub>4</sub>- vs CO<sub>2</sub>-producing reactions in our two samples were driven internally by differences in bulk-rock compositions and *P*–*T* conditions. The proposed mechanism of CH<sub>4</sub> production is based on the premise of intra-plate metamorphism under low fluid-rock ratio conditions during internally driven metamorphic devolatilization.

## 5.2. Pre-subduction alteration: First-order control of heterogenous fO<sub>2</sub> of subducting slabs

Heterogenous seafloor alteration processes significantly modulate the distribution of redox-sensitive elements (e.g., Fe, C, and S) in the oceanic lithosphere prior to subduction. This distribution may be further modified in response to high-*P* and high-*T* metamorphism and fluid metasomatism during subduction (Evans and Tomkins, 2021). Therefore, it is necessary to consider presubduction alteration of the Paleo-Tianshan oceanic crust.



**Fig. 10.** (a) Plot of log  $fO_2$  relative to FMQ as a function of pressure and temperature using the effective bulk composition (Table 1) of the UHP-CH<sub>4</sub> eclogite but assuming no  $CO_2$  and  $Fe^{3+}/\Sigma$ Fe ratio of 0.1. Also shown are the subduction P-T paths of the northeast Japan (cold subductions, from Peacock and Wang, 1999), the Cascadia (hot subductions, from Walters et al., 2020), the UHP-CH<sub>4</sub> eclogite calculated in this study, and the coldest P-T path recorded in S.W. Tianshan (from Zhang et al., 2016). (b) The  $fO_2$  contours of the "max  $\alpha H_2O$ " (i.e.,  $C-H_2O$  join,  $X_0 = 1/3$ ) in P-T space. (c) Isobaric-isothermal phase diagram for the C-O-H system at 2.8 GPa, 525 °C, showing the position of the "max  $\alpha H_2O$ " (separating CH<sub>4</sub>- and CO<sub>2</sub>-dominant aqueous fluid) and C (graphite) saturation curve (above this curve, graphite can be stable) and corresponding  $fO_2$  values.

The contrasting  $fO_2$  histories of our two samples are partially driven by differences in pre-subduction alteration histories, which are reflected in the bulk characteristics of their protoliths. The metabasalts exhibited geochemical characteristics (e.g., (La/Sm)  $_{\rm N}$ and (La/Yb) N) consistent with the OIB affinity for the protoliths (Table EA1, Fig. EA3). However, both samples exhibited some geochemical characteristics that were not typical MORB- or OIB-like. For example, the UHP-CH<sub>4</sub> eclogite was greatly enriched in K<sub>2</sub>O (1.47 wt%), Li (45.50 µg•g<sup>-1</sup>), Rb (38.50 µg•g<sup>-1</sup>), and Cs  $(1.53 \,\mu g \cdot g^{-1})$  relative to unaltered basalt. Enrichments in these elements were commonly observed in low-temperature seaflooraltered basalts (e.g., Kelley et al., 2003; Bouman et al., 2004). In contrast, the K<sub>2</sub>O and SiO<sub>2</sub> (0.01 and 41.25 wt%, respectively) were depleted in the HP-CO<sub>2</sub> eclogite, whereas CaO (14.87 wt%) was enriched. Potassium may be removed during high-T seafloor alteration (>150 °C), whereas low-T alteration results in K addition (Edmond et al., 1979; Seyfried and Bischoff, 1979; von Damm

et al., 1985). The elevated CaO,  $Fe_{Total}$ , and  $Fe^{3+}/\Sigma Fe$  ratio in the HP-CO<sub>2</sub> eclogite relative to MORB and OIB were also consistent with hydrothermal calcite and/or epidote/saponite in the protolith (e.g., Alt et al., 2010; Banerjee et al., 2000).

According to our previous Mg-Sr-Nd isotopic analysis of carbonates in carbonated eclogites from SW Tianshan (Zhu et al., 2018; Tao et al., 2018b, and references therein), (1) the bulk  $\delta^{26}$ Mg of all carbonated eclogites (-0.19% to +0.24%) is higher than that of unaltered MORB and OIB; (2) carbonate in eclogites have higher Sr isotopic compositions ( $^{87}$ Sr/ $^{86}$ Sr<sub>(i)</sub> = 0.7077–0.708 2) than depleted mantle values; and (3) positive  $\epsilon$ Nd<sub>(t = 320 Ma)</sub> values (7.6–8.2) were consistent with oceanic basalts as the precursor. First, seawater alteration can shift the bulk  $\delta^{26}$ Mg of oceanic basalt to higher values, and because limited Mg isotopic fractionation is expected during dehydration metamorphism, the measured values likely reflect the alteration of the protolith. Second, while the Nd isotopic compositions were consistent with an



**Fig. 11.** Schematic view of the condition of  $P-T-X-fO_2$  for a mafic oceanic slab in the S.W. Tianshan subduction zone. (a) Bulk-composition modification of oceanic slab prior to subduction. During heterogeneous hydrothermal alteration, water, sulfate, sulfide (pyrite-chalcopyrite parageneses, Li et al., 2021), and carbonate (especially CaCO<sub>3</sub>) are added to the oceanic crust and underlying lithospheric mantle (Schmidt and Poli, 2014; Evans and Tomkins, 2021), leading to different initial redox budget (RB). The pink and brown circles represent the possible positions of our UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> samples in the lithosphere before subduction respectively. (b) A schematic model showing devolatilization behavior at different positions of the slab. The release of oxidized or reduced slab fluids depends on both the *P*-*T* conditions and the composition of the slab (in response to the protolith alteration before subduction and the total redox budget evolves as mobile elements are extracted during subduction) in the rock-budget decreases, prograde redox reactions may stabilize different carbon species in the C-H-O fluid at variable depth levels during subduction. (c) The UHP-CH<sub>4</sub> ecolgite, combined with moderate bulk CO<sub>2</sub> content and low Fe<sup>3+</sup>/SFe, stabilizes CH<sub>4</sub>-rich fluids at their peak. (d) The HP-CO<sub>2</sub> ecolegient, combined with higher bulk CO<sub>2</sub> content and elevated Fe<sup>3+</sup>/SFe, stabilizes CO<sub>2</sub>-rich fluids at their peak. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oceanic basalt protolith, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios showed evidence of perturbation by seafloor hydrothermal fluids. Therefore, the narrow range of <sup>87</sup>Sr/<sup>86</sup>Sr values measured in carbonate reflects homogenization with an internally derived fluid during metamorphic dehydration rather than an external fluid. As a result, carbonates were introduced into the protolith during the pre-subduction alteration. The high carbonate abundance and high LOI of the carbonated eclogites (e.g., H19-01, Table EA1) indicated relatively significant seafloor alteration. In addition, the eclogite samples contained carbonates both as idioblastic matrix grains and inclusions in garnet and rutile (Fig. 2c, 3b-c and EA2b, g-h). Porphyroblastic dolomite grains also hosted omphacite and rutile inclusions. These textures implied that carbonates were present early and in equilibrium with garnet and omphacite during the prograde evolution of the rock. Finally, metasomatic textures were not present in our samples (see Section 5.1). Thus, we concluded that carbonate was introduced to the eclogite protoliths prior to subduction rather than by metasomatism in the subduction channel.

Sulfides were also present in the samples. Mineral inclusions (rutile, omphacite, glaucophane, phengite, lawsonite, and dolomite) formed during (U)HP metamorphism occurred within the pyrite grains. Additionally, pyrite grains can also occur as inclusions in garnet porphyroblasts or are in textural equilibrium with homogeneous dolomite and omphacite in the matrix. Primary magmatic sulfide parageneses, that is pyrrhotite–chalcopyrite–pen tlandite in oceanic basalts and gabbros (e.g., Patten et al., 2012), were not observed in our samples. In contrast, pyrite (Figs. EA2a–b and e–f) observations were consistent with hydrothermal sulfides formed during the alteration of the oceanic crust (e.g., Alt et al., 1989; Patten et al., 2016; Li et al., 2021). These textures indicated that sulfides were present throughout the pro-

grade to peak metamorphic history of the rock, which is consistent with textural observations of pyrite in unmetasomatized eclogite by Li et al. (2016a, 2016b, 2020) from SW Tianshan. The pyrite with (U)HP inclusions in our samples may have recrystallized in the presence of fluids produced by prograde to peak dehydration reactions, but the pyrite inclusions in the garnet may have been inherited from earlier stages of metamorphism or the protolith. Li et al. (2021) measured in-situ  $\delta^{34}$ S values of sulfides in similar eclogites from SW Tianshan and suggested that positive  $\delta^{34}$ S values of pyrite cores and pyrite inclusions in garnet were inherited from presubduction seafloor hydrothermal alteration.

Petrographic, textural, and isotopic signature evidence suggests that sulfides (e.g., pyrite) and carbonates were added to oceanic basalt during seafloor alteration and underwent HP/UHP metamorphism. Alt and Teagle (1999) found that the bulk CO<sub>2</sub> content of the crust decreased with depth and increased with the formation age of oceanic crust. Additionally, seafloor alteration may mobilize and concentrate sulfides as well as increase  $Fe^{3+}/\Sigma Fe$  (e.g., Bach and Edwards, 2003; Patten et al., 2016). Therefore, based on the above petrological and geochemical features (CO2 and FeS2 concentrations, LOI, Fe<sup>3+</sup>/ $\Sigma$ Fe, etc.; Table 2), we suggest that the protolith of the HP-CO<sub>2</sub> eclogite sample (H19-01) was more strongly altered, or at least under more oxidizing conditions, than that of the UHP-CH<sub>4</sub> eclogite sample (H19-43). The protolith of the HP-CO<sub>2</sub> eclogite may have originated in a more fractured portion of the oceanic crust or closer to the seawater, and thus have been more readily exposed to oxidative seawater-rock interaction, prior to subduction (Fig. 11a). The contrasting  $P-T-fO_2$  behavior of the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites indicated that the heterogeneous alteration of the seafloor before subduction, resulting in different protolith bulk compositions (especially the redox budget), is a first-order control on the speciation of C in slab fluids.

#### Table 2

Comparison between the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites.

Sample	UHP-CH <sub>4</sub> Ec. (H19-43)	HP-CO <sub>2</sub> Ec. (H19-01)				
Petrological observations						
Locality	Akesayi, UHP belt	Habutengsu, HP belt				
Mineral assemblage	Grt (20%) + Omp (40%) + Phn (20%) + Qtz (12%) + Amp (4%),	Grt (25%) + Omp (45%) + Dol (10%) + Gln (5%) + Qtz (5%) + Py (5%),				
	Gph + Zo + Rt + Ttn + Dol + Cal + Ap + Py < 5%	Brs + Gph + Ep + Rt + Cal + Ttn + Mt + Ilm + Ap < $5\%$				
Relicts at Pre to peak Stage	Grt-(core-mantie) + Omp-core + Fo Dol + Cpb + Dbp + Coo + Pt + Dv (+Low providemorph)	Grt-(core to rim) + Omp + Doi + Gin + Qtz + Rt + Py + Mt (+Law providemorph)				
Exhumation Stage	$\operatorname{Grt-rim}$ + $\operatorname{Omp-rim}$ + $\operatorname{Hb}$ + $\operatorname{Zo}$ + $\operatorname{Pa}$ + $\operatorname{Chl}$ + $\operatorname{Ttn}$ + $\operatorname{Ab}$ + $\operatorname{Cal}$	(+Law pseudomorph) Brs + Ep + Ttp + Cal + Hb + Otz + Mt + Ilm + Mt				
	+ Qtz + Mt					
Fluid inclusions at peak	$CH_4 + H_2O + H_2$	$CO_2 + H_2O$				
Characteristics of the minerals that encase $CH_4/CO_2$						
Trap position	Crt-(core-mantle); Omp-core	Dol				
Composition	Grt-(core-mantle): High FeO <sub>T</sub> and High Fe <sup>3+</sup> / $\Sigma$ Fe;	Fe-Dol				
characteristics	Omp-core: High FeO <sub>T</sub> and High Fe <sup>3+</sup> / $\Sigma$ Fe					
Characteristics of the bulk rock						
H <sub>2</sub> O (wt.%)	1.46	2.11				
CO <sub>2</sub> (wt.%)	1.10	10.27				
SiO <sub>2</sub> (wt.%)	55.46	41.25				
$Fe^{3+}/\Sigma Fe$ (mol.)	0.20	0.24				
Peak P-T conditions	$\sim$ 2.8 GPa, $\sim$ 525 °C	$\sim$ 2.6 GPa, $\sim$ 500 °C				
Estimate $fO_2$ of rock at	-2.9	$\geq 0$				
peak (Log <sub>10</sub> fO <sub>2</sub> (FMQ))						

## 5.3. Evolution of slab P-T-fO<sub>2</sub> during subduction

5.3.1. Comparison of redox evolutions between the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites

Petrologic observations and thermodynamic calculations allowed us to reconstruct the metamorphic  $P-T-fO_2$  evolution during the subduction-exhumation processes for different slices from the slab. For the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites, the predicted  $fO_2$  was shown to be a function of buffering phase assemblage (Figs. 5, 7, and 9b), which are in turn controlled by P-T and initial bulk composition.

For the UHP-CH<sub>4</sub> eclogite, we predict that  $fO_2$  will decrease to a minimum of ~FMQ – 2.9 at peak *P*–*T* conditions (2.8 GPa, 525 °C), and CH<sub>4</sub> is expected to form in graphite-saturated C–H–O fluids under the control of such low  $fO_2$  in the system. This event was recorded by fluid/solid inclusions (C<sup>0</sup> + CH<sub>4</sub>) in garnets and omphacites (Fig. 2). Whereas during the early-exhumation stage (2.5 GPa, 600 °C), the rock is predicted to buffer higher  $fO_2$  conditions of ~FMQ – 0.9. And the late-exhumation/retrograde petrological characteristics of the opaque phases, including the replacement of pyrite-chalcopyrite by magnetite and rutile by ilmenite, further indicated an oxygen fugacity above the FMQ buffer (Tao et al., 2017).

For the HP-CO<sub>2</sub> eclogite,  $fO_2$  conditions between FMQ and FMQ + 1 (2.6 GPa, 500 °C) were predicted. The  $fO_2$  contoured P-T pseudosection phase diagram shows that oxygen fugacity is more sensitive to changes in temperature. The HP-CO<sub>2</sub> eclogite contained higher FeO<sub>T</sub> and exhibited a higher Fe<sup>3+</sup>/ $\Sigma$ Fe ratio compared to that of the UHP-CH<sub>4</sub> eclogite (0.24 vs 0.20, respectively) and contained significant carbonate ( $C^{4+}$ ). The higher redox budget of the HP-CO<sub>2</sub> eclogite (more Fe<sup>3+</sup> and C<sup>4+</sup>, unless stated otherwise, the RB referred to here is relative to a mantle-like reference state of Fe as  $Fe^{2+}$ , C as C<sup>0</sup>, and S as S<sup>2-</sup>) stabilized a higher  $fO_2$  in the rock buffered equilibrium system compared to the UHP-CH<sub>4</sub> eclogite. As a result, graphite-saturated CO<sub>2</sub>-bearing aqueous fluid was produced instead of a CH<sub>4</sub>-bearing fluid (fO<sub>2</sub> values fall between "CCO" and "max  $aH_2O$ "). If  $fO_2$  is high in a system, and the system remains rock-buffered; then, comparatively reduced material added to that system will become oxidized, and vice versa:  $O_2$  +  $(Fe^{2+}O)_{mineral} \leftrightarrow (Fe_2^{3+}O_3)_{mineral}, O_2 + C^0 \leftrightarrow CO_2$ . Therefore, we suggest that the elevated initial carbonate (C<sup>4+</sup>) and Fe<sup>3+</sup>/ $\Sigma$ Fe provided the conditions necessary to maintain relatively high  $fO_2$  in the HP-CO<sub>2</sub> eclogite.

It is important to note that when considering the measured bulk composition for the UHP-CH<sub>4</sub> eclogite alone, as used to model the P-T history for the UHP-CH<sub>4</sub> eclogite (Fig. 6), the  $fO_2$  conditions predicted were not low enough to stabilize CH<sub>4</sub> (Fig. EA7). Instead, CO<sub>2</sub>-rich fluid was calculated under graphite-saturated conditions. These results are inconsistent with the observation of CH<sub>4</sub>-bearing FIs, as well as the Grt-Cpx oxybarometry and  $T - \log fO_2$  models, suggesting that open system modification of the bulk composition may have impacted the RB, and consequently  $fO_2$ . Therefore, we hypothesize that retrograde oxidation and loss of a reduced CH<sub>4</sub>bearing fluid at peak conditions resulted in a more oxidized silicate residuum. However, we can demonstrate the impact of different initial RB might have had on the buffering silicate assemblage. For this scenario, we assumed an extreme case in which no CO<sub>2</sub> is present in the protolith and the rock has an  $Fe^{3+}/\Sigma Fe$  ratio of 0.1 (same as the average MORB Fe<sup>3+</sup>/ $\Sigma$ Fe ratio, Berry et al., 2018). Our results are shown in a plot of  $\log fO_2$  relative to FMQ as a function of pressure and temperature (Fig. 10a). Such a composition can buffer a sufficiently low  $fO_2$  to cross the C-H<sub>2</sub>O join at peak conditions (Fig. 10b–c). The overall  $fO_2$  was low compared with that of the HP-CO<sub>2</sub> eclogite; the lower oxygen fugacity conditions correspond to low-T and high-P conditions at the peak of UHP metamorphism. In contrast, early-retrograde metamorphism was predicted to stabilize the higher  $fO_2$  relative to the peak. While the exact  $fO_2$  values are speculative, the shapes of the  $fO_2$  isolines are similar to those of the HP-CO<sub>2</sub> eclogite but at lower  $fO_2$ . The predicted prograde trend is also consistent with the prograde decrease in fO<sub>2</sub> measured by Tao et al. (2018a) using Grt-Cpx oxybarometry (from FMQ - 1.9 to FMQ - 2.5) and Li et al. (2016a, 2020) using sulfide-oxide equilibria and thermodynamic calculations ( $fO_2$  conditions at 60 km (FMQ), 90 km (FMQ - 1), 120 km (FMQ - 2), and 150 km (FMQ - 3) for eclogites in SW Tianshan). These results suggest, that even if open-system modification resulted in a higher measured bulk rock RB, decreasing  $fO_2$  is expected along the prograde path.

Our models also show a slight pressure dependence in the  $fO_2$  gradient, with decreasing  $fO_2$  at higher *P* at a fixed *T*. Moreover,

the  $fO_2$  contours of the "max  $aH_2O$ " in P-T space (Fig. 10b, c) demonstrated that the low-T region can more easily achieve low  $fO_2$  compared with the high-T part to stabilize CH<sub>4</sub> in a rock-buffered system. These data suggest that higher  $fO_2$  conditions may have occurred along the hotter subduction geotherm. A relatively cold subduction path (e.g., the Paleo-Tianshan subduction zone) aided in permitting sufficiently reducing conditions to form abiotic CH<sub>4</sub>.

# 5.3.2. Comprehensive progress: redox couples and redox transfers in a rock-buffered system

The  $fO_2$  of the subducted materials is likely very inhomogeneous, both between subduction zones and within a single slab, thus complicating the development of a simple generic model for redox evolution of the subducted oceanic crust. For example, Tumiati and Malaspina (2019) and Cannaò and Malaspina (2018) highlighted the complicated and inhomogeneous  $fO_2$  patterns in subducted rocks:  $fO_2$  in orogenic (U)HP mafic and ultramafic rocks range from FMQ – 6 in the Ugelvik peridotite, Norway, to FMQ + 4.5 in epidote-bearing eclogites. These variations partially arise due to differences in the *P*–*T* path and bulk composition (and therefore RB) inherited from the heterogenous alteration of the seafloor prior to subduction. However, as we have shown, RB may also be affected by the open system transfer of redox-sensitive elements during subduction.

In a rock-buffered system, a reduced fluid can be produced in a rock with a low RB, such as the UHP-CH<sub>4</sub> eclogite studied here (Fig. 11b, c, Table 2). At the instant of fluid production, the  $fO_2$  of the fluid and rock are equal, but the redox budget is not equal when considering the fluid and solid assemblage separately. Fe<sup>2+</sup> was oxidized to Fe3+ in the silicate assemblage to produce fluid enriched in CH<sub>4</sub>, producing garnet and omphacite cores enriched in Fe<sup>3+</sup>. In this case, the RB of the fluid decreased, whereas the RB of the solid assemblage increased. The CH<sub>4</sub>-bearing fluid was lost from the rock during prograde to peak metamorphism, whereas Fe<sup>3+</sup> remained. As a result, the remaining rock is more oxidized once a new equilibrium is reached. Progressive oxidation of the residuum through CH4 removal may partly explain the higher  $fO_2$  of the garnet and omphacite rims, in addition to the lower-P higher-T conditions of early-retrograde metamorphism which are predicted to stabilize higher  $fO_2$  even in a closed system (Fig. 10a and EA7). Because the ratio of oxidized to reduced components in the bulk rock increases, the chemical potential of O<sub>2</sub>, and therefore  $fO_2$ , must also increase. The systematic change in the RB during fluid loss, as well as oxidation during late retrograde metamorphism (e.g., pyrite-chalcopyrite by magnetite and rutile by ilmenite), contributed to higher predicted  $fO_2$  when considering the measured bulk composition only for the UHP-CH<sub>4</sub> eclogite. This scenario highlights the need to consider the *P*-*T*-*X* evolution of the rock system when interpreting  $fO_2$ : Small changes in the RB of a rock during open system processes may lead to large changes in  $fO_2$  (see Fig. EA4), particularly when a buffering assemblage is consumed or changed.

As a complementary example, the reaction of carbonate to graphite results in the loss of electrons from  $Fe^{2+}$  and the gain of electrons by  $C^{4+}$  in the HP-CO<sub>2</sub> eclogite (Fig. 3e, d and g). In this case, the overall redox budget of the rock remains unchanged, as the reactions occurred in a closed system. Even though the RB of the bulk rock is fixed, the redox reaction would change the  $fO_2$  to that of the graphite-CO<sub>2</sub> buffer.

Combining our observations, we propose: Carbon in the AOC is mainly initially subducted as carbonate ( $C^{4+}$ ), at slab-top depths beneath the forearc carbonate dissolution driven by dehydration reactions enables the transport of carbonate and bicarbonate ions (Ague and Nicolescu, 2014; Frezzotti et al., 2011; Facq et al.,

2014; Kelemen and Manning, 2015; Vitale et al., 2018) from the slab. Thus, oxidizing fluids may be possible at forearc depths. Loss of oxidized species (e.g.,  $CO_2$  (a),  $CO_3^{2-}$ ,  $HCO_3^{-}$ ) with depth may result in a reduction of the slab residuum, possibly aiding the stabilization of CH<sub>4</sub> at greater depths. Similarly, Gerrits et al. (2019) and Walters et al. (2020) demonstrated that the loss of oxidized sulfur species in mafic slab fluids across the blueschist-toeclogite facies drives decreasing  $fO_2$  in the slab residue. Similarly, the deceased  $fO_2$  of the subducting ultra-mafic slab is also consistent with recently petrological and geochemical studies on HP serpentinites (Debret et al., 2014, Debret et al., 2015, Debret et al., 2016, Debret and Sverjensky, 2017). Depending on the degree to which the redox budget decreases, prograde redox reactions may stabilize CH<sub>4</sub> in the C–H–O fluid at deeper levels. Similarly, once CH<sub>4</sub> is produced, its extraction leaves an increasingly oxidized slab residuum. This effect, as well as that of late-retrograde oxidation. contributed to a redox budget of the UHP-CH<sub>4</sub> that is inconsistent with the  $fO_2$  conditions needed to stabilize CH<sub>4</sub> during peak metamorphism. In addition, our data suggest that pre-subduction alteration of the seafloor is also important, while a shallow loss of oxidizing species could produce deeper more reducing conditions. these open system processes may not be sufficient to produce CH<sub>4</sub> under (U)HP conditions. The comparison between the UHP-CH<sub>4</sub> and HP-CO<sub>2</sub> eclogites demonstrates that the initial redox budget inherited by the protolith, as well as the *P*-*T* path, are also important controls on carbon speciation in slab fluids.

The feedback between open system behavior and  $fO_2$  evolution, which may drive both increases and decreases in the redox budget of the slab as different species are stabilized, combined with the influences of *P*, *T*, and initial bulk composition, may result in complex redox histories, even in internally rock-buffered systems. More research is required to quantify how these variables may stabilize redox-sensitive species in deep C–O–H–N–S fluids, particularly regarding the degree that devolatilization drives the redox evolution of the slab at different depths.

# 5.4. $CH_4$ production in eclogites: Dual formation and preservation challenges

To date, there have been few observations of  $CH_4$ -bearing fluid inclusions in mafic (U)HP metamorphic rocks in the literature. One possible explanation for this is that such inclusions are rarely preserved. Retrograde metamorphism commonly produces more oxidized mineral assemblages relative to the metamorphic peak (see Section 5.3.1 and Fig. 10a). The UHP-CH<sub>4</sub> eclogite examined in this study exhibited only very limited retrogression, and the peak assemblage (mineral + fluid; Table 2) was well-preserved (see Section 5.1), which is a rare case for many (U)HP rocks. In addition to issues with preservation, not all P-T paths or bulk compositions are conducive to producing low enough  $fO_2$  to stabilize CH<sub>4</sub>-rich fluids.

First, our models show that  $CH_4$  is stable under relatively cold (U)HP conditions, whereas P-T paths along "hot" subduction geothermal gradients would intersect elevated  $fO_2$  fields (Fig. 10a). Thermodynamic predictions by other studies similarly demonstrated that abiogenesis production of  $CH_4$  is favorable under low-temperature conditions (Kenney et al., 2002; Connolly and Galvez, 2018). Lower temperatures favor  $CO_2$  dissociation and carbon polymerization (Sverjensky et al., 2014). Moreover, high-*P* conditions in subduction zones seem to overcome kinetic barriers at low temperatures (300–550 °C), such that multicomponent reactions abiotically convert dissolved carbon into  $CH_4$  (Chen et al., 2008; McCollom and Donaldson, 2016; Huang et al., 2017; Sverjensky et al., 2020; Vitale et al., 2020b).

Second, methane generation is less likely in strongly seaflooraltered rocks with high RB (i.e., the HP-CO<sub>2</sub> eclogite sample; Table 2). The oxidation state of the slab is likely buffered by  $Fe^{2+}$ -Fe<sup>3+</sup> equilibria because Fe is the most abundant redox modifier in most subducted mafic rocks (Cannaò and Malaspina, 2018; Tumiati and Malaspina, 2019). Therefore, Fe-bearing minerals are likely to control C speciation in fluids formed during devolatilization. However, C exhibits a much larger range of valence states than Fe. For every 1 mol of  $C^{4+}$  reduced to  $C^{4-}$ , 8 mol of  $Fe^{2+}$  must be oxidized to Fe<sup>3+</sup> (e.g., reaction A). Therefore, carbonate reduction strongly depends on the FeO/CO<sub>2</sub> ratio of the protolith. Furthermore, seafloor alteration processes that introduce carbonates into the oceanic crust may also increase the  $Fe^{3+}/\Sigma Fe$  ratio (Bach and Edwards, 2003). If the alteration is too extensive or oxidizing and the FeO/CO<sub>2</sub> ratio in the protolith is too high, CO<sub>2</sub> may be produced instead of CH<sub>4</sub>. We suggest that these differences drove the CO<sub>2</sub> vs CH<sub>4</sub> stability in the HP-CO<sub>2</sub> eclogites compared to the UHP-CH<sub>4</sub> eclogite (Fig. 11b and d). The effect of seafloor alteration on slab fO<sub>2</sub> conditions has also been observed in subducted serpentinites. Evans et al. (2017) reported that the dehydration of incompletely serpentinized ultramafic rocks (usually those beneath the oceanic crust) in which awaruite is present can be buffered to lower  $fO_2$  conditions and will produce  $H_2$ -bearing fluids, whereas completely serpentinized rocks (usually those more directly exposed to seawater) in which magnetite is present will produce more oxidizing fluids during subduction.

In addition, disequilibrium/heterogeneous  $fO_2$  may occur to a certain extent in rock-buffered systems where O<sub>2</sub> is not perfectly mobile (Korzhinskii, 1936). Oxygen is unlikely to be perfectly mobile in rock-buffered systems at high-P, as no free O<sub>2</sub> does exist and O<sub>2</sub> is mostly bound in silicate, oxide, and other solid phases (e.g., Tumiati and Malaspina, 2019). Disequilibrium may be further enhanced when there are insufficient internal fluids or if chemical reactions are inhibited at low T due to slow reaction rates. Therefore, careful mineralogical studies are necessary to link the observed reaction history of the rock with the combined effects of P-T and RB on  $fO_2$ . For example, we observed carbonates and methane in garnet cores, but our garnet-clinopyroxene oxybarometry and thermodynamic modeling results suggest that carbonates should not be stable (Figs. 5 and 7). It may be that the reactions that trapped the carbonate phases and changes in P-T outpaced the reactions that were predicted to fully convert carbonate to  $C^0$  +  $CH_4$ . Disequilibrium, in addition to open system modification of the bulk rock composition, may also lead to the discrepancy between measured  $fO_2$ , the observation of CH<sub>4</sub> inclusions in garnet and omphacite, and the fO<sub>2</sub> predicted using the whole-rock composition, which is too high to stabilize CH<sub>4</sub>. As a result, (immiscible) CO<sub>2</sub>-rich and CH<sub>4</sub>-rich fluid (Huang et al., 2017) may be trapped in fluid inclusions under the same *P*–*T* but heterogeneous  $fO_2$  conditions. For example, calcite crystals within the CH<sub>4</sub>-rich fluid inclusions in the UHP-CH<sub>4</sub> eclogite measured at atmospheric P-T were clearly step-daughter minerals (Fig. EA1d). Compared with other carbonates (magnesite and siderite), the extremely high solubility of aragonite and dolomite under high P-T makes the aqueous fluid rich in Ca<sup>2+</sup> (Pan et al., 2013; Kelemen and Manning, 2015), thus accounting for the possible crystallization of daughter minerals directly from the trapped fluid ( $Ca^{2+} + CO_3^{2-} \rightarrow$ CaCO<sub>3</sub>) during the exhumation progress (cooling-decompression), leaving only CH<sub>4</sub> bubbles. The results from complicated thermodynamic models, which rely on bulk rock equilibrium, should be interpreted as a guide to examine potential trends in the  $fO_2$  evolution of rocks. In contrast, there are fewer assumptions in the calculation of  $fO_2$  sensitive equilibria that may require equilibrium between only a few phases over short distances. However, these methods rely on the precise and accurate determination of  $Fe^{3+}$  $\Sigma$ Fe ratios in garnet, clinopyroxene, glaucophane, epidote, and other phases, which are not commonly measured.

## 6. Conclusions

In this study, we identified both CH<sub>4</sub>- and CO<sub>2</sub>-bearing fluid inclusions in carbonate-bearing eclogites from the SW Tianshan HP-UHP metamorphic belt in China. The coesite-bearing UHP-CH<sub>4</sub> eclogite formed at peak P-T conditions of 2.8 GPa and 525 °C, whereas the CO2-rich (~10 wt% CO2) HP-CO2 eclogite formed at 2.6 GPa and 500 °C. Combined with fluid inclusion measurements,  $P-T-fO_2$  models for the UHP-CH<sub>4</sub> eclogite revealed that  $fO_2$  was as low as FMQ – 3 at UHP conditions, as well as the cold subduction P-T paths, may have intersected the CO<sub>2</sub>-CH<sub>4</sub> fO<sub>2</sub> transition at "max  $\alpha$ H<sub>2</sub>O" and thus stabilized CH<sub>4</sub>. In addition to the P–T dependency, pre-subduction alteration of the oceanic crust was found to be a first-order control of C speciation in slab fluids. The elevated  $CO_2$  concentration and  $Fe^{3+}/\Sigma Fe$  ratio of the HP-CO<sub>2</sub> eclogite bulk composition inherited from the pre-subduction alteration prohibited sufficiently low  $fO_2$  to produce CH<sub>4</sub> but stabilized C<sup>0</sup>. These data show that the release of oxidized or reduced slab fluids depends on both the thermal structure of the subduction zone and the composition of the slab, therefore redox reactions and how the total redox budget evolves should be considered simultaneously. Depending on the degree to which the redox budget decreases, prograde redox reactions may stabilize different carbon species in the C-H-O fluid at variable depth levels during subduction. Open system modification of the bulk rock composition, through the loss of oxidized or reduced fluids, as well as disequilibrium, may hinder the reconstruction of the redox evolution of metamorphic rocks from thermodynamic modeling alone. Importantly, we show that subduction metamorphism of partially altered oceanic crust in ultra-cold subduction zones (e.g., the SW Tianshan subduction zone) can produce favorable conditions for CH<sub>4</sub> forming reactions.

#### **Declaration of Competing Interest**

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

#### Data availability

Data will be made available on request.

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#### **Appendix A. Supplementary material**

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