

Retrograde pumpellyite in the Yunotani garnet blueschist of the Omi area, Japan: An update on the cooling path

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Retrograde pumpellyite was newly found in garnet blueschist that is Mg-rich equivalent of late Paleozoic retrograde eclogite of the Yunotani Valley in the Omi area, Hida-Gaien Belt. The pumpellyite with high Al/(Al + Mg + Fe) occurs in pressure shadows around garnets; it is associated with secondary glaucophane, epidote, chlorite, titanite, phengite, albite, and quartz, which all characterize a retrograde blueschist-facies mineral assemblage after peak eclogite-facies mineral assemblage. This feature is comparable with retrograde pumpellyite in late Paleozoic garnet blueschist (with relict eclogite-facies mineral assemblage) in the Osayama area of the Chugoku Mountains. Equilibrium phase calculation confirmed that the pumpellyite is stable at a low temperature and pressure portion of the lawsonite-blueschist-facies. *T*-bulk-composition (Mg) pseudosection suggests that pumpellyite appears preferentially in high Mg/(Mg + Fe) bulk composition. The limited occurrence of retrograde pumpellyite in the Yunotani garnet blueschist and retrograde eclogite would be explained by Mg-rich bulk compositions. Also, the limited occurrence in pressure shadows around garnets suggests that the fluid trapped in the pressure shadows might have enhanced growth (or precipitation) of pumpellyite. This finding provides a strong evidence that the deeply subducted (eclogite-facies) metabasaltic rocks both in the Hida-Gaien Belt and the Chugoku Mountains were subjected to a very similar blueschist-facies overprinting locally reached the pumpellyite stability field. The ‘Franciscan-type’ cooling path suggests a ‘steady-state’ underflow of the paleo-Pacific oceanic plate in late Paleozoic at a convergent margin of the South China Craton.

Keywords: Pumpellyite, Retrograde *P*-*T* path, Retrograde eclogite, Omi, Hida-Gaien Belt

INTRODUCTION

When tectonic slices of subducting oceanic crust are exhumed from the depth of eclogite-facies condition, the ascending slices are subjected to various degrees of retrograde metamorphism. If the underflow of an oceanic plate is in ‘steady-state’, the ascending slices follow a decompression path with significant cooling due to subduction-induced refrigeration (Ernst, 1988; Ernst and Peacock, 1996). Ernst (1988) defined ‘Franciscan type’ pressure-temperature (*P*-*T*) trajectory as a ‘hairpin like’ loop from burial to exhumation with significant cooling in *P*-*T* space. In the ultrahigh-pressure (UHP) terranes of continent-continent collision zones, *P*-*T* slopes of cooling path of retrograde eclogites are simply related to size of UHP slice (Kylander-Clark et al., 2012). In contrast,

there might be no systematic correlation between size and cooling *P*-*T* path of retrograde eclogite in HP terranes of oceanic subduction zones. Probably the differences would be more sensitively controlled by exhumation mechanism and retention duration at depth in the slab-mantle wedge interface rather than the size.

A typical ‘Franciscan-type’ *P*-*T* trajectory was reported in retrograde eclogites and garnet blueschists associated with metasedimentary rocks in the Yunotani Valley of the Omi area, the Hida-Gaien Belt, Japan (Tsuji-mori et al., 2000; Tsujimori, 2002; Tsujimori and Matsumoto, 2006). Previous studies have demonstrated that the Yunotani eclogites and garnet blueschists are severely subjected to blueschist-facies recrystallization and deformation whereas unaltered prograde-zoned garnets preserve a transition from blueschist to eclogite (Tsuji-mori, 2002; Tsujimori and Matsumoto, 2006). During reappraisal of prograde mineral assemblage in garnets, we confirmed that the prograde blueschist condition occurred in the epi-

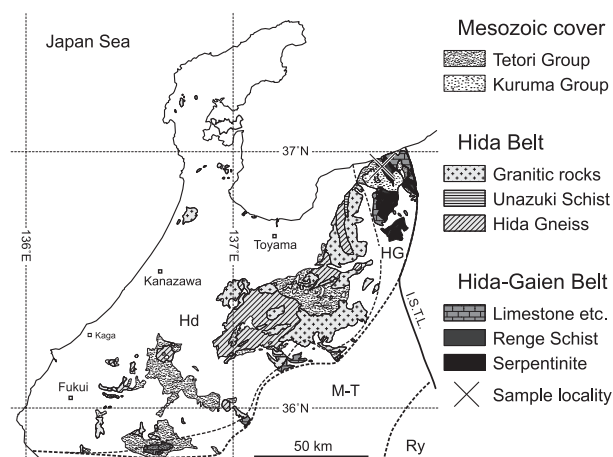


Figure 1. Simplified geological map of the Hokuriku Region, showing location of the Omi area (modified after Tsujimori, 2002). HG, Hida-Gaien Belt; Hd, Hida Belt; M-T, Mino-Tamba Belt; Ry, Ryoke Belt.

dote stability field; in other words, we found neither prograde lawsonite nor pseudomorphs of lawsonite. However, we newly found retrograde pumpellyite as the blueschist-facies retrograde mineral assemblage in garnet blueschists. This finding provides a new insight into the cooling path of the rocks and regional correlation among the late Paleozoic Renge metamorphic rocks in southwestern Japan. In this paper, we present the first report of retrograde pumpellyite in the garnet blueschist and discuss the geological significance. Mineral abbreviations throughout this paper are after Whitney and Evans (2010).

GEOLOGICAL OUTLINE

The Hida-Gaien Belt is a composite geotectonic unit that tectonically lies between the Hida Belt and a Jurassic accretionary complex of the Mino-Tamba Belt (Fig. 1). The Hida-Gaien Belt consists mainly of fragments of various pre-Jurassic rocks that are more widely developed in the Chugoku Mountains, southwestern Japan. Late Paleozoic schists associated with serpentinite (including serpentinitized peridotite and meta-serpentinite) and Paleozoic to lower Mesozoic (Middle Ordovician to Upper Triassic) non-metamorphic clastic rocks are the most characteristic components. The HP schists of the Hida-Gaien Belt have been named the ‘Renge Schists’; they record mainly greenschist- to amphibolite-facies metamorphism, and locally preserve blueschist- to eclogite-facies metamorphism. In the Omi area, the Renge Schists are subdivided into two distinct groups: a non-eclogitic unit and an eclogitic unit (Tsujimori, 2002; Kunugiza et al., 2004). Medium- to coarse-grained garnet-amphibolites occur as layers and lens within garnet- and biotite-bearing meta-

sedimentary rocks of the non-eclogitic unit (Matsumoto et al., 2011); they are characterized by the amphibolite-facies mineral assemblage $\text{Grt} + \text{Hbl} + \text{Pl} \pm \text{Czo} \pm \text{Bt} \pm \text{Ilm} + \text{Rt} + \text{Qz}$. Prograde-zoned garnet porphyroblasts of the amphibolite contain rare paragonite (Tsujimori and Matsumoto, 2006). On the other hand, medium to coarse-grained glaucophane-bearing eclogite and garnet blueschist occur as mafic layers within paragonite-bearing metasedimentary rocks of the eclogitic unit; the assemblage $\text{Grt} + \text{Omp} + \text{Gln} + \text{Czo/Ep} + \text{Rt} + \text{Ph} + \text{Qz}$ characterizes the eclogite-facies metamorphism. The host metasedimentary rock is characterized by the $\text{Grt} + \text{Pg} \pm \text{Gln} + \text{Czo} + \text{Rt} + \text{Ph} + \text{Qz}$.

The Omi area has been known as classic ‘glaucophanitic’ metamorphic region where Banno (1958) and Miyashiro and Banno (1958) defined mineral isograds based on mineral assemblages of metasedimentary rocks; it was the world’s first mineral isograd defined in the ‘glaucophanitic’ metamorphic region. Retrograde eclogite was first found in the Yunotani Valley (Tsujimori et al., 2000). Exposures of coarse-grained garnet-bearing metasedimentary rocks (host rock of eclogite) and metabasaltic rocks with blueschist-facies mineral assemblages can be tracked at least ~ 6 km in the mountainous area (Tsujimori et al., 2001; Tsujimori and Matsumoto, 2006); Banno (1958) described them as the ‘garnetiferous schist’ in his chlorite zone (biotite-free zone) as a continuous key lithology to map the Omi Schists. Recently, more eclogite occurrences have been confirmed (e.g., Takeuchi et al., 2017; Satish-Kumar et al., 2018). In the Yunotani Valley, garnet blueschist is Mg-rich and Ca-poor variation of eclogite-facies metabasaltic rocks (Tsujimori, 2002); the lack of omphacite is simply due to bulk composition rather than the degree of retrogression. Both eclogite and garnet blueschist show rare earth element (REE) patterns with an N-MORB affinity (Tsujimori, 2002); the peak eclogite-facies condition was estimated as ~ 2.0 – 2.2 GPa and 550 – 600 °C (Tsujimori, 2002; Tsujimori and Matsumoto, 2006).

Occurrence of jadeitite has been well known in the Omi area (e.g., Miyajima, 2017; Kunugiza et al., 2017). However, the Renge Schist (~ 300 – 360 Ma) is significantly younger than jadeitite (~ 520 Ma), suggesting different tectonic origin (cf. Tsujimori, 2010, 2017; Tsujimori and Harlow, 2017).

SAMPLE DESCRIPTION AND PUMPELTYITE TEXTURE

Retrograde pumpellyite was found in garnet blueschist that was described by Tsujimori (2002). The sample was collected from a boulder from the Yunotani Valley; note that rare outcrops of garnet blueschist and retrograde eco-

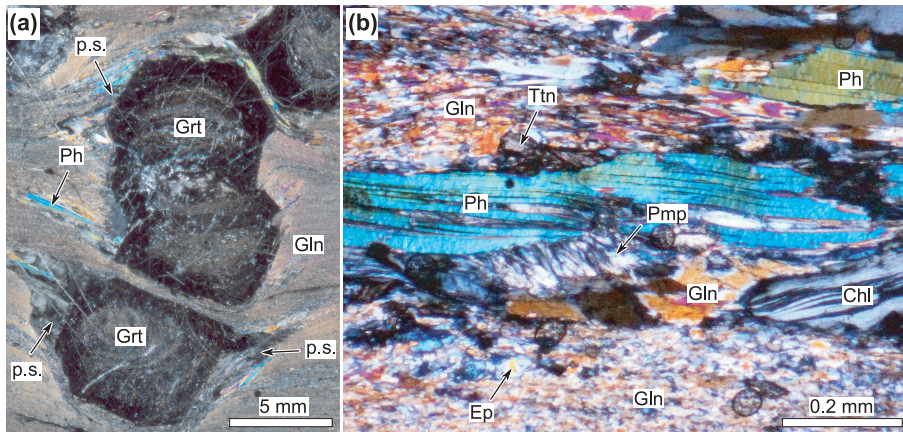


Figure 2. (a) Crossed-polarized light photomicrograph showing pressure shadows (p.s.) around porphyroblastic garnets. Note that the minerals in the pressure shadows are coarser than matrix-forming minerals. (b) Crossed-polarized light photomicrograph of retrograde pumpellyite.

gite were observed in some steep slopes of the valley (e.g., Takeuchi et al., 2017). The studied samples are well deformed and composed of fine-grained matrix and garnet porphyroblasts. Rare undeformed coarse-grained glaucophanes remain without recrystallization during a post-eclogite-facies deformation. The preferred orientation of fine-grained, nematoblastic glaucophane and coarse-grained phengite define a schistosity (Fig. 2). The matrix contains small amount of epidote, phengite, and rutile partially (or completely) replaced by titanite. Porphyroblastic garnet with pressure shadow reaches up to ~ 1 cm in diameter (Fig. 2). Internal fabric (inclusion trail) in garnet is discontinuous with the matrix foliation. The pressure shadows around garnets are composed of phengite, chlorite, pumpellyite, glaucophane, titanite, quartz, albite, and rare calcite. Size of minerals in the pressure shadows is larger than that of well-deformed matrix. Both albite and calcite contain fluid inclusions. Retrograde pumpellyite forms fine-grained aggregates (~ 0.2–0.5 mm in size) in the pressure shadows (Fig. 2). The pumpellyite is colorless exhibiting weak abnormal interference color under crossed-polarized light.

CHEMICAL COMPOSITIONS OF PUMPELLYITE

Pumpellyite

Chemical compositions of pumpellyite are shown in Table 1. The retrograde pumpellyite is pumpellyite-(Al) that is characterized by high Al/(Al + Mg + Fe) (0.75–0.84; mean 0.82 [$n = 51$]) and moderate Mg/(Mg + Fe) (0.44–0.68; mean 0.61) (Fig. 3). It contains 0.1–0.3 wt% MnO and up to 0.17 wt% Na₂O. The compositional range is comparable with blueschist-facies pumpellyite (cf. Ward Creek blueschist of the Franciscan Complex: Maruyama and Liou, 1988) rather than prehnite-pumpellyite-facies pumpellyite (cf. metabasaltic rocks of the East Taiwan ophiolite: Liou, 1979). In the late Paleozoic blueschist

Table 1. Representative electron microprobe analyses data of retrograde pumpellyite

	Pumpellyite			Mean, $N = 51$ ($\pm 1\sigma$)
wt%				
SiO ₂	36.84	36.46	37.09	36.99 (0.45)
TiO ₂	0.11	0.05	0.03	0.08 (0.06)
Al ₂ O ₃	26.70	25.53	26.63	26.30 (0.51)
Cr ₂ O ₃	0.02	–	0.10	0.04 (0.03)
FeO*	2.68	3.76	2.64	3.20 (0.67)
MnO	0.36	0.19	0.27	0.28 (0.07)
MgO	2.69	2.58	2.84	2.74 (0.19)
CaO	22.48	23.68	23.60	23.45 (0.27)
Na ₂ O	0.14	0.08	0.12	0.10 (0.03)
K ₂ O	0.02	0.01	0.01	0.01 (0.01)
Total	92.05	92.33	93.33	93.17 (0.56)
O=	24.5	24.5	24.5	24.5
Si	5.942	5.926	5.921	5.929 (0.041)
Ti	0.013	0.006	0.004	0.010 (0.007)
Al	5.077	4.891	5.009	4.969 (0.075)
Cr	0.003	–	0.012	0.003 (0.004)
Fe ²⁺	0.362	0.511	0.352	0.429 (0.094)
Mn	0.050	0.026	0.037	0.038 (0.010)
Mg	0.646	0.626	0.675	0.655 (0.043)
Ca	3.886	4.124	4.035	4.027 (0.051)
Na	0.043	0.026	0.038	0.032 (0.010)
K	0.005	0.001	0.003	0.002 (0.002)
Total	16.028	16.136	16.085	16.092 (0.032)

FeO* = total Fe as Fe²⁺

localities in the Hida-Gaien Belt and the Chugoku Mountains, pumpellyite occurs in lawsonite- and/or pumpellyite-bearing low-grade blueschist as well as retrograde eclogite (Tsujimori, 1998; Tsujimori and Itaya, 1999; Tsujimori and Liou, 2005, 2007). In comparison with pumpellyites from the late Paleozoic Renge metamorphic rocks in the literatures and author's (T. Tsujimori's) unpublished data, the pumpellyite in the studied sample resembles that from garnet blueschist (retrograde eclogite) of the Osayama (Tsujimori and Liou, 2005) (Fig. 3).

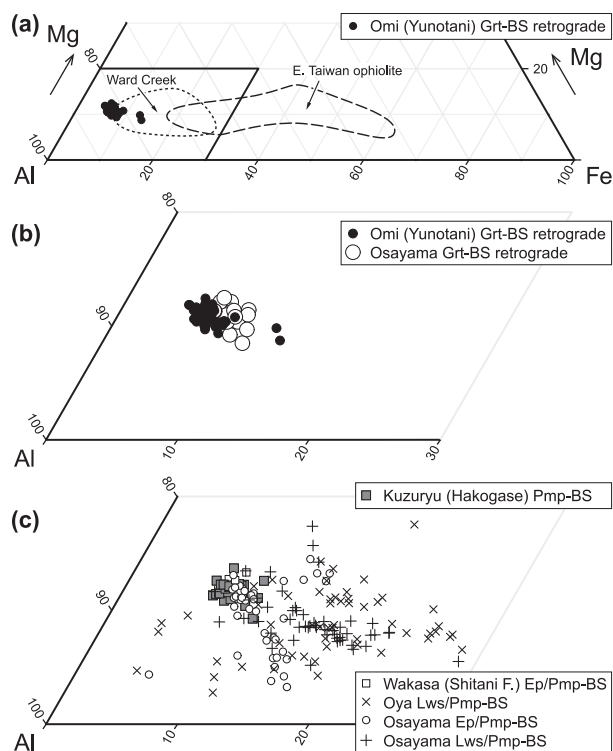


Figure 3. Compositional plots of pumpellyite in the Al-Fe-Mg ternary diagram. (a) Compositional trend of retrograde pumpellyite in the Yunotani garnet blueschist. For comparison, compositional fields of pumpellyite from the Ward Creek (Franciscan Complex) blueschist (Maruyama and Liou, 1988) and the East Taiwan ophiolite (Liou, 1979) are also shown. (b) Comparison of retrograde pumpellyite between the Omi (Yunotani) (this study) and the Osayama garnet blueschist (Tsujimori and Liou, 2005). (c) Compositional variation of pumpellyite from low-grade blueschists in the Renge metamorphic rocks from the Hida-Gaien Belt (Hakogase area) and the Chugoku Mountains (Wakasa, Oya, and Osayama) (Tsujimori, 1998; Tsujimori and Liou, 2007; T. Tsujimori, unpublished data).

Other minerals

Fine-grained amphibole near pumpellyite has a glaucophane composition, with $Mg\# [= Mg/(Mg + Fe^{2+})] = 0.66\text{--}0.72$ and $Fe^{3+}/(Fe^{3+} + Al) < 0.13$. Note that the Fe^{2+}/Fe^{3+} ratios of amphiboles were estimated assuming total cations = 13 (O = 23) excluding Ca, Na, and K. Phengite associated with pumpellyite is Si-rich (6.7–6.9 a.p.f.u., O = 22) with $Mg\# = 0.71\text{--}0.76$. Chlorite has a composition of $Mg\# = 0.51\text{--}0.59$. Titanite replacing rutile in matrix contains 1.1–1.7 wt% Al_2O_3 .

DISCUSSION

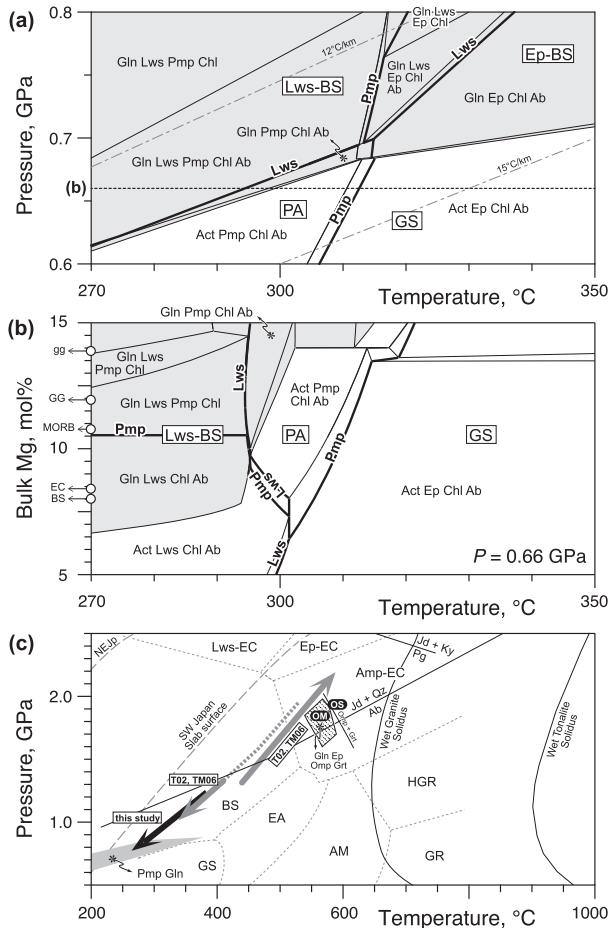
Stability field of pumpellyite in blueschist-facies

In order to evaluate the semi-quantitative P – T stability

field of the pumpellyite-bearing retrograde mineral assemblage found in the Yunotani garnet blueschist, pressure–temperature–bulk-composition (P – T – X) pseudosections were calculated using the bulk composition of the garnet glaucophane schist (GG) shown in Tsujimori (2002). Phase equilibrium modelling was performed using the Theriak/Domino software (de Capitani and Petrakakis, 2010) and the internally-consistent thermodynamic dataset of Holland and Powell (1998). For the calculation, the model system Na_2O – CaO – FeO^* – MgO – Al_2O_3 – SiO_2 – H_2O (NCFMASH) was assumed and TiO_2 , MnO , and K_2O were neglected. H_2O and SiO_2 were treated as excess phases. Quartz–fayalite–magnetite (QFM) buffer was considered for the oxidation state. We adopted the solid-solution models of minerals that used in Tsujimori and Ernst (2014). Although modelling with a fixed effective bulk composition, fluid activity, oxidation state, etc. as well as uncertainty of thermodynamic data and solid-solution models for low-temperature minerals can bring large uncertainty in the results, the chemographic relations in P – T – X space are still helpful in order to understand natural metamorphic parageneses.

The calculated phase diagram suggests that the $Pmp + Gln + Chl + Ab$ assemblage is stable at a low temperature and pressure portion of the lawsonite–glaucophane stability field, at $P = \sim 0.62\text{--}0.70$ GPa and $T = \sim 280\text{--}320$ °C (Fig. 4a). Similar chemographic relations among Pmp-, Lws- and Ep-bearing mineral equilibria with glaucophane in P – T space have been proposed in the Schreinemaker's net (e.g., Liou et al., 1985; Frey et al., 1991; Sato et al., 2016) and P – T pseudosections (e.g., Zhang et al., 2009; Willner et al., 2016; Tsujimori and Ernst, 2014). The retrograde pumpellyite in the $Pmp + Gln + Ep + Chl + Ab$ assemblage might have been formed by the univariant reaction $Gln + Zo + H_2O = Pmp + Chl + Ab$ in the NCMASH with excess chlorite, albite, quartz, and H_2O (Liou et al., 1985; Beiersdorfer and Day, 1995). In any case, our new finding suggests that a retrograde P – T path of the eclogitic unit reaches the $Pmp + Gln$ stability field. However, a question then arises: why is retrograde pumpellyite rarely found in the Yunotani Valley? Based on available petrological and geological interpretations, at least three scenarios should be considered.

First, incomplete infiltration of H_2O -rich fluid during retrogression may explain the limited occurrence of retrograde pumpellyite, if the pumpellyite was formed by the reaction $Gln + Zo + H_2O = Pmp + Chl + Ab$ (Liou et al., 1985). However, presence of abundant fluid inclusions in retrograde albite and calcite in pressure shadows around garnets suggests that H_2O was saturated during the retrogression.



Second, different bulk composition may also explain the limited occurrence of retrograde pumpellyite. As mentioned above, the garnet blueschist has a Mg-rich bulk composition. *T*-bulk-composition (Mg) pseudosection at *P* = 0.66 GPa is shown in Figure 4b. As shown in the diagram, pumpellyite appears preferentially in high Mg/(Mg + Fe) (or Mg-rich) bulk composition. Although effective bulk compositions of the retrograde mineral equilibration would be different from the real bulk composition, the inferred tendency that pumpellyite prefers Mg-rich bulk composition is consistent with observation. Note that the assumption of ideal Mg end-member pumpellyite-(Mg) for the calculation might also affect the stability of pumpellyite in the *T*-bulk-composition (Mg) pseudosection.

In the third, kinetics of crystal growth and nucleation cannot be ruled out. The rate of crystal growth in low-temperature blueschist is irregular (e.g., Carpenter, 1980). Furthermore, rock-wide chemical equilibria are not achieved during retrogression. In the blueschist-facies condition, mineral growth can be enhanced by fluid-infiltration; the typical examples are vein-filling HP minerals

Figure 4. Equilibrium phase diagrams of the Yunotani garnet blueschist for evaluating the stability field of pumpellyite in blueschist-facies. (a) *P*-*T* pseudosection in NCFMASH (+ Qz + H₂O) for the bulk composition of the garnet blueschist (sample 'GG' from Tsujimori, 2002), SiO₂:Al₂O₃:FeO:MgO:CaO:Na₂O = 48.47:15.79:9.95:12.02:7.25:6.52 (in mol%), showing the stability field of Gln + Pmp + Chl + Ab assemblage. The gray region represents the stability field of glaucophane. Lower pressure limit of lawsonite-bearing mineral assemblage and lower temperature limit of pumpellyite are highlighted bold lines with 'Lws' and 'Pmp'. Lws-BS, lawsonite-blueschist-facies; Ep-BS, epidote-blueschist-facies; GS, greenschist-facies; PA, pumpellyite-actinolite-facies. (b) *T*-bulk-composition (Mg) pseudosection at *P* = 0.66 GPa. Bulk Mg values (in mol%) of HP rocks of the Yunotani Valley (Tsujimori, 2002) are shown in the left axes: GG, garnet blueschist; EC, eclogite (average value); BS, epidote blueschist. For comparison, average MORB composition (MORB) (Gale et al., 2013) and the composition of the Osayama garnet blueschist (gg) (Tsujimori and Liou, 2005) are also shown. (c) *P*-*T* diagram showing new cooling path (heavy black arrow) of the eclogitic unit in this study. The gray area represents the stability field of Pmp + Gln assemblage of a petrogenetic grid proposed by Liou et al. (1985). The prograde and retrograde *P*-*T* paths of the eclogitic unit (T02, TM06: Tsujimori, 2002; Tsujimori and Matsumoto, 2006) are shown as gray arrows. Hatched area with 'OM' label represents a newly calculated stability field of peak eclogite-facies mineral assemblage of the Yunotani eclogites. The 'Omp + Grt' reaction line with 'OS' label represents low-*T* limit of the eclogitic mineral assemblage of the Osayama garnet blueschist based on *P*-*T* pseudosection. Inferred slab surface *P*-*T* trajectories of present-day Nankai (SW Japan) and Tohoku (NEJp) (Syracuse et al., 2010) are also shown. The metamorphic facies, their abbreviations and solidus curves are after Liou et al. (2004).

(e.g., Tsujimori, 1997; Takahashi et al., 2018). Considering the limited occurrence of pumpellyite in pressure shadows around garnets, the fluid trapped in the pressure shadows might have played a role to enhance growth (or precipitation) of pumpellyite. The pumpellyite was formed in the Pmp + Gln stability field (Fig. 4c).

Geologic significance

There are geological evidences that the late Paleozoic subduction metamorphism reached eclogite-facies from the epidote-blueschist-facies and retraced the same path as the prograde *P*-*T* path (Tsujimori, 2002). Glaucophane-bearing eclogite-facies mineral assemblage has been reported not only from the Omi area, but also the Osayama area (about 430 km west of the Omi area) of the Chugoku Mountains (Tsujimori, 1998; Tsujimori and Itaya, 1999; Tsujimori and Liou, 2005). Tsujimori and Liou (2005) argued similarities of the peak eclogite-facies mineral assemblage and the retrograde *P*-*T* path between the Omi and the Osayama area. The Osayama garnet blueschist with relict eclogite mineral assemblage is subjected to a

blueschist-facies overprinting locally reached the Pmp + Gln stability field. Our new finding of retrograde pumpellyite supports their idea. The very similar retrograde *P-T* path between the Omi and the Osayama area would not be coincidence. The 'Franciscan-type' blueschist-facies recrystallization after eclogite-facies in both the Omi (Yunotani) and the Osayama are indicative of significant cooling due to subduction-induced refrigeration during exhumation of the 'high-grade' *HP* rocks. Although the prograde subduction path from epidote-blueschist to eclogite is expected in a warm-slab environment like present-day Nankai subduction margin (e.g., Syracuse et al., 2010) (Fig. 4c), the 'Franciscan-type' retrograde *P-T* path suggests a 'steady-state' underflow of the paleo-Pacific oceanic plate in late Paleozoic at a convergent margin of the South China Craton.

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