A new occurrence of okhotskite in the Kurosegawa belt, Kyushu, Japan: the okhotskite + Mn-lawsonite assemblage as a potential high-pressure indicator

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We present the first report of okhotskite in a lawsonite–blueschist–subfacies metachert of the Hakoishi subunit, Kurosegawa Belt, Kyushu, Japan, which was metamorphosed at peak temperatures and pressures of 200–300 °C and 0.6–0.8 GPa. This okhotskite–bearing assemblage is particularly notable because it formed at higher pressures than that of previously documented okhotskite with available pressure estimations. Textural relationships indicate that okhotskite formed during peak metamorphism in equilibrium with piemontite, Na pyroxene, magnesiowüstite, braunite, and hematite. Okhotskite shows a significant variation in Fe:Mn ratio (\(\text{Fe}^{tot}/\text{Mn}^{tot} = 0.13–0.56\)) and a following average empirical formula; \((\text{Ca}_{7.62}\text{Mn}_{2+0.16})^{\Sigma}7.78(\text{Mn}_{2+2.71}\text{Mg}_{1.29})^{\Sigma}4.00(\text{Mn}_{3+4.13}\text{Fe}_{3+2.26}\text{Al}_{1.36}\text{V}_{3+0.23}\text{Ti}_{0.02}\text{Si}_{11.86}\text{O}_{44.02}(\text{OH})_{16.98}\). Raman spectra of okhotskite are reported for the first time and show characteristic peaks at 362, 480, and 563 cm\(^{-1}\). The stability relationships between okhotskite and other Mn-bearing minerals, such as piemontite, sursassite, spessartine, braunite, and Mn-bearing lawsonite, are examined using a revised Schreinemakers’ analysis. The obtained petrogenetic grid provides tight constraints on the \(P-T\) relationship of natural mineral assemblages observed in Mn-bearing cherts within epidote–blueschist-grade and lawsonite–blueschist-grade. Furthermore, this petrogenetic grid predicts that the assemblage of okhotskite and Mn-bearing lawsonite should be stable at higher pressures. The higher-pressure stability suggests that highly oxidized Mn-bearing metacherts can transport water and buffer oxygen in the deeper parts of subduction zones, given that okhotskite and Mn-bearing lawsonite contain high water contents (6.9 and 11.3 wt% \(\text{H}_2\text{O}\), respectively) and trivalent manganese.

Keywords: Okhotskite, Lawsonite–blueschist subfacies, Metachert, Kurosegawa Belt, Schreinemakers’ analysis, Raman spectra

INTRODUCTION

Pumpellyite group of minerals have a general chemical formula of \([\text{W}_{8}\text{X}_{4}\text{Y}_{8}\text{Z}_{12}\text{O}_{56-n}(\text{OH})_{n}]\) (Passaglia and Gottardi, 1973) and are common hydrous minerals in low-grade metamorphic rocks. Root-names of the group have been defined based on the dominant cation in the Y-site: pumpellyite with \(\text{Al}^{3+}\) (Palache and Vassar, 1925), julgoldite with \(\text{Fe}^{3+}\) (Moore, 1971), shuiskite with \(\text{Cr}^{3+}\) (Ivanov et al., 1981), okhotskite with \(\text{Mn}^{3+}\) (Togari and Akasaka, 1987), and poppiite with \(\text{V}^{3+}\) (Brigatti et al., 2006). Okhotskite, the \(\text{Mn}^{3+}\)-dominant member, was first reported from the Kokuriki mine, in the Tokoro Belt, Hokkaido, Japan (Togari and Akasaka, 1987). Okhotskite has also been reported from metamorphosed manganese deposits in the Sanbagawa (Minakawa, 1992) and Chichibu (Minakawa et al., 2008) belts in Shimoku, Japan; metamorphosed manganese oxide ores of the Precambrian Sausar Group, India (Dasgupta et al., 1991); and manganese deposits in the Askiz ore district, Khakassia, Russia (Kassandrov and Mazurov, 2009). These reports include the coexistence okhotskite with braunite (\(\text{Mn}^{2+}\text{Mn}^{3+}\text{SiO}_{12}\)) and/or bixbyite (\(\text{Mn}_2\text{O}_3\)), and the presence of trivalent Mn suggests that the mineral records a strongly oxidizing environment. Furthermore, okhotskite is expected to provide a considerable part of the water budget of impure metacherts in the subduction zone, because of its high \(\text{H}_2\text{O}\) content (6.89 wt% \(\text{H}_2\text{O}\); Togari and Akasaka, 1987).
In considering phase relations among such highly oxidized Mn minerals, oxygen fugacity ($f_O^2$) has been considered as a critical factor in addition to pressure ($P$) and temperature ($T$) (e.g., Mottana, 1986). Numerous synthetic experiments have been conducted at various $f_O^2$ values controlled by buffers of certain mineral assemblages (e.g., Abs–Wurmbach and Peters, 1999). Akasaka et al. (2003) conducted a series of hydrothermal experiments at 400–500 °C and 300 MPa to constrain the stability of Mn-rich pumpellyite. Those authors confirmed Mn-bearing pumpellyite as the precursor to piemontite and that it is stable at lower temperatures and higher oxygen fugacity, as proposed by Akasaka et al. (1988). Reinecke (1986) investigated phase relations in Mn–Al–rich quartzites of the upper–blueschist facies from Evvia and Andros islands, Greece, to schematically show the low–$T$ stability of sulfasite–bearing assemblages from Evvia when compared to spessartine–bearing assemblages from Andros.

These previous studies were based on the premise that oxygen is a perfectly mobile component (Korzinskii, 1959) and therefore that cations (e.g., Fe and Mn) can be freely oxidized or reduced in metamorphic rocks. However, some recent studies have found that oxygen behaves as an inert element in natural systems (Tumiati et al., 2015; Li et al., 2016). In such cases, the oxidation states of cations are instead fixed, and $f_O^2$ is lowered as a dependent variable that describes bulk cation oxidation states. Thus the phase relations among Mn–rich minerals need to be reconsidered in terms of oxygen mobility. Furthermore, during geochemical interaction in subduction zones, oxygen is bound to highly oxidized rocks and is thus transported deep into the Earth by subduction. Refining the relevant phase relations should provide a clear view of the oxidation process in the ‘oxidized’ upper mantle (Thomson et al., 2016).

In this paper, okhotskite-bearing rocks from a new locality from the Hakoishi sub-unit of the Kurosegawa belt in Kyushu are described, including the chemical composition and Raman spectra of the okhotskite. A provisional petrogenetic grid is developed for Mn-bearing minerals under a quartz–excess environment. We also discuss the behavior of oxygen and the significance of highly oxidized minerals, including okhotskite, in subduction zones.

**GEOLOGICAL BACKGROUND AND MINERALOGY**

The Usuki–Yatsushiro Tectonic Line (UYTL) trends NE–SW across Kyushu Island, Japan (Fig. 1). In the Yatsushiro area, the Kurosegawa Belt lies to the south of the UYTL. The studied sample was collected from the western part of the Hakoishi sub-unit, which occupies the western half of the Otao unit. Localities of other Mn-bearing samples, i.e., OT19, KY1811, and OD70, are also shown.

Figure 1. (a) Distribution of the Kurosegawa belt in SW Japan and study area. (b) Geotectonic map of the Kurosegawa Belt in the Yatsushiro area, Kyushu, Japan (modified after Saito et al., 2010; Sato et al., 2016). The okhotskite-bearing sample was collected from outcrop OT10 in the western part of the Hakoishi sub-unit, which occupies the western half of the Otao unit. Localities of other Mn-bearing samples, i.e., OT19, KY1811, and OD70, are also shown.

mélange that is exposed over an area of $2 \times 10$ km$^2$, occupying the western half of the Otao unit (Saito et al., 2010; Sato et al., 2014; Fig. 1). The Hakoishi subunit consists mainly of serpentinites, lawsonite–bearing blueschists (LBSs), metasiliceous rocks, and minor metagranulite and is separated from adjacent units by serpentinites (Saito et al., 2010). Saito et al. (2010) mapped areas of metabasaltic rocks and metasiliceous rocks, but in the present study area the two lithological types are intercalated with each other and form a coherent block (Ibuki et al., 2008). Sato et al. (2016) reported that lawsonite + Na pyroxene + pumpellyite is the predominant mineral assemblage in LBS of the eastern part of the study area and that lawsonite + Na amphibole + Na pyroxene forms the predominant one in LBS of the western part. Such a systematic distribution of low–variance assemblages shows that the pumpellyite + Na pyroxene + chlorite + H$_2$O = lawsonite + Na amphibole reaction is recorded in the study area, and an increase in grade to the west is associated with hydration. The peak metamorphic conditions have been estimated to be 200–300 °C and 0.60–0.80 GPa (Sato et al., 2016). Notably, the Hakoishi LBS (i.e., metabasalt) lacks epidote (Fujimoto et al., 2010; Kami-mura et al., 2012; Sato et al., 2014; Sato et al., 2016).

Metasiliceous rocks in the study area are rich in manganese and rare–earth elements (REEs), and are
found in the abandoned Taneyama mine (Yoshimura, 1969; Yabuta and Hirajima, 2018). The Mn-rich rocks have been interpreted as impure metacherts that formed from siliceous oozes mixed with oceanic sediments, given that manganese and REEs are common in abyssal sediments (Yoshimura, 1969; Togari et al., 1988; Kato et al., 2011). A variety of Mn-bearing minerals have been reported from metasiliceous rocks related to the abandoned Taneyama mine (e.g., taneyamalite: Aoki et al., 1981; howieite: Ibuki et al., 2008; Mn$^{3+}$-bearing lawsonite: Ibuki et al., 2010).

The okhotskite-bearing sample (OT10J) is a banded rock composed of centimeter-thick intercalated quartz-rich and Fe-Mn-rich layers composed of fine-grained (<30 µm) minerals. Boundary layers (<100 µm thick) composed of Na pyroxene and amphibole (with minor hematite, piemontite and okhotskite) occur at the contacts between the quartz-rich and Fe-Mn-rich layers (Figs. 2a and 2d). The Fe-Mn-rich layers are fractured and include quartz-dominated veins that contain okhotskite (Figs. 2a–2c). The different parts of the sample consist of different mineral assemblages reflecting the local ‘bulk-rock’ composition (Table 1). The quartz-rich layers consist of quartz + Na pyroxene + piemontite + braunite + albite + apatite. The Fe-Mn-rich layers are composed of hematite + braunite + quartz ± albite ± apatite ± titanite. The quartz veins are composed predominantly of quartz along with Na amphibole + okhotskite ± braunite ± albite ± apatite, and notably developed within Fe-Mn-rich layers.

METHODS

The chemical composition of okhotskite was determined using a Hitachi S3500H scanning electron microscope equipped with an energy-dispersive X-ray analyzer.
OPERATING CONDITIONS included an accelerating voltage of 20 kV, a beam current of 500 pA, and a spot size of 5 µm. Following materials were used as standards; albite for Na, synthetic periclase for Mg, synthetic corundum for Al, synthetic quartz for Si, orthoclase for K, synthetic wolastonite for Ca, synthetic rutile for Ti, vanadium metal for V, manganese metal for Mn, and hematite for Fe. A ZAF correction scheme was used to process the X-ray intensity data.

Raman spectra of okhotskite were acquired using an NRS-3100 JASCO spectrometer at the Department of Geology and Mineralogy, Kyoto University, using a diode-pumped solid-state (DPSS) 532 nm laser. The wave number was calibrated using the 520.7 cm$^{-1}$ line produced by a Si-wafer, and the spectrum of Ne.

We also conducted thermodynamic calculations to estimate phase relations among Mn-bearing minerals. Thermodynamic parameters of mineral phases followed those in the standard state of Holland and Powell (1998) or were calculated by the summation method of Fyfe et al. (1958) based on the database of Robie and Hemingway (1995). Parameters of fluid species were calculated after Woolley (1953) and Burnham et al. (1969). Scheinemanke's nets were generated with Calnet ver. 2.1 developed by Yoshida and Hirajima (1999).

Mineral abbreviations follow Whitney and Evans (2010), except for okhotskite (Okh), braunite (Br), and sursassite (Sus).

**CHEMICAL ANALYSES AND RAMAN SPECTROSCOPY**

Okhotskite shows characteristic orange to dark-orange pleochroism, commonly occurs within the quartz veins as fine-grained (<30 µm long) crystals, and is uncommon in the boundary layers (Figs. 2b and 2c). The average chemical formula is (Ca$_{7.62}$Mn$_{2.71}$Mg$_{1.29}$)$^{12+}$Si$_{3.02}$O$_{10.02}$ (after Kato et al., 1981; Togari and Akasaka, 1987). Although H$_2$O content in the Hakoishi okhotskite was not measured in the present study, it is calculated as 7.15 wt% H$_2$O by difference of the average chemical composition, which is similar to the values (6.89 wt% H$_2$O) of the Tokoro okhotskite determined by Togari and Akasaka (1987). From the given formula for the average composition of the Hakoishi okhotskite and the nomenclature scheme after Passaglia and Gottardi (1973), this mineral should be called okhotskite-(Mn$_{7.5}$). Piemontite is present as a major Mn-bearing mineral in the quartz-rich layers and boundary layers, and shows characteristic striking pinkish-red to yellow pleochroism (Fig. 2d). Some grains show oscillatory zoning, which is attributed to variable REE contents (e.g., La and Nd). The chemical composition of the REE-poor zones is close to that of ideal piemontite: Ca$_2$Al$_2$Mn$_{3+}$Si$_3$O$_{12}$(OH) (Table 2). Na pyroxene occurs as acicular grains with a low molar fraction of diopside (Di < 15 mol%) (Table 2). The proportions of aegirine (Aeg) and jadeite (Jd) are variable and reflect the local bulk-rock composition, with Aeg$_{45}$Jd$_{50}$Di$_{5}$ in the quartz-rich layers and Aeg$_{70}$Jd$_{30}$Di$_{10}$ in the boundary layers (Yabuta and Hirajima, 2018). The Na amphibole is Mg-rich, consistent with a high ratio of ferric to ferrous iron, and is classified as magnesiobickeite according to the scheme of Leake et al. (1997) (Table 2). Na amphibole grains in boundary layers and quartz veins show nearly identical compositions. Hematite and braunite occur in the Fe-Mn-rich layers, reflecting the highly oxidized Si-rich composition (Abs-Wurmbach, 1980). Braunite also occurs as tiny grains of ~20 µm diameter in the quartz-rich layers.

Figure 4 compares the Raman spectrum of an okhotskite grain with those of related minerals. This is the first report of Raman spectrum of okhotskite, so the characteristic peaks are described. Peaks are observed consistently close to 362, 480, 537, 563, 593, 684, and 921 cm$^{-1}$. Even though the Raman spectra of julgoldite–Fe and Mg-pumpeylite also show a peak near 550 cm$^{-1}$, the spectrum of okhotskite show few similarities to those of other pumpeylite group minerals. The peaks close to 362, 480, and 563 cm$^{-1}$ are considered to be diagnostic of okhotskite.
Reinecke (1986) performed thermodynamic calculations among Mn-bearing minerals, such as piemontite, Mn-pumpellyite, surssassite, spessartine, and chlorite, in a pseudo-quaternary system of Mg–Mn*(= Mn²⁺ + Mn³⁺)–Ca–Al, with excess Qz, H₂O, and O₂. This is applicable to the Hakoishi metacherts, as quartz is saturated in the whole sample and relevant minerals except in the presence of garnet.

However, the Schreinemakers’ net proposed by Reinecke (1986) has a fundamental shortcoming. The net has the invariant point \([Pₘ, Pₚ]\) (= \([Pₘᵗ, Pₘᵖ]\)), representing reactions where the two Ca-bearing phases are absent. As Reinecke’s analyses do not deal with other Ca-phases, when one occurs as a reactant in a reaction, the other is always present as a product. Consequently, either of the two is present on the same side as the invariant point \([Pₘ, Pₚ]\) across a reaction curve, contravening the method proposed by Akasaka et al. (1997).

For piemontite, braunite, and Na-Amp, Mn²⁺ and Mn³⁺ were calculated based on the charge balance. Pmt, piemontite; Na-Px, Na pyroxene; Na-Amp, Na amphibole.

### Table 2. Mineral compositions for sample OT10

| Mineral | Okhotskite (Σ cation = 32) | Pmt (O = 12.5) | Na-Px (O = 6) | Braune (O = 12) | Na-Amp (O = 23) |
|---------|-----------------|----------------|--------------|----------------|----------------|
| Sample  | OT10J | OT10I | Mean | OT10J | |
| SiO₂    | 33.77 | 33.85 | 32.69 | 32.63 | 33.35 | 33.26 | 36.63 | 55.84 | 11.44 | 57.60 |
| TiO₂    | bdl   | bdl   | 0.07  | bdl   | 0.31  | 0.10  | bdl   | 0.32  | 0.10  | 0.48  |
| Al₂O₃   | 3.58  | 2.17  | 3.93  | 3.82  | 2.72  | 3.24  | 19.85 | 11.69 | 0.33  | 1.39  |
| V₂O₅    | 0.35  | 0.82  | 1.10  | 1.11  | 0.63  | 0.80  | n.d.  | n.d.  | n.d.  | n.d.  |
| Fe₂O₃   | 4.03  | 10.45 | 9.84  | 9.10  | 8.69  | 8.42  | 2.42  | 14.81 | 5.23  | 12.78 |
| MnO₂*   | 18.93 | 14.74 | 12.36 | 13.02 | 15.27 | 14.98 | 14.10 | 0.45  | 66.88 | 0.01  |
| MnO**   | 10.59 | 8.91  | 8.70  | 9.48  | 11.24 | 9.68  | 0.53  | bdl   | 10.14 | 1.20  |
| MgO     | 1.31  | 3.02  | 3.41  | 2.90  | 1.52  | 2.43  | 0.20  | 1.80  | 0.24  | 15.52 |
| CaO     | 19.75 | 19.59 | 20.53 | 20.05 | 19.79 | 19.94 | 22.17 | 1.51  | 1.73  | 1.48  |
| CuO     | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | 0.95  | n.d.  | 7.29  |
| Na₂O    | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | 0.15  |
| K₂O     | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | 0.15  |
| Total   | 92.31 | 93.55 | 92.63 | 92.11 | 93.52 | 92.85 | 95.90 | 100.08 | 97.04 | 97.90 |

* Total Fe as Fe₂O₃.
** Recalculated values. For okhotskite, Mn in the X- and Y-sites was assumed to be Mn²⁺ and Mn³⁺, respectively, and the Y-site was filled with Al³⁺, Mn³⁺, and Fe³⁺ in this order, following the method proposed by Akasaka et al. (1997).

For piemontite, braunite, and Na-Amp, Mn²⁺ and Mn³⁺ were calculated based on the charge balance. Pmt, piemontite; Na-Px, Na pyroxene; Na-Amp, Na amphibole.

### Figure 3. Y-site occupancy in okhotskite. Sources: (1) Tokoro Mn-Fe ore deposits (Togari et al., 1988). (2) Bichhua Formation, Süssar Group, India (Dasgupta et al., 1991). (3) Mn ore deposits, Sanbagawa belt (Minakawa, 1992).
In addition, the petrogenetic grid contains viridine, Mn–bearing andalusite. Viridine has been reported from many Mn–rich metamorphic rocks of relatively lower metamorphic pressure but has not been identified on Evvia or Andros islands (Greece) or in Hakoishi. Therefore, it is questionable to consider phase relations in blueschist facies (kyanite stability) with viridine. Therefore, in place of viridine, we used Mn–bearing lawsonite (Ibuki et al., 2010). The Mn–bearing lawsonite is ubiquitously identified in the Hakoishi metacherts (Yabuta and Hirajima, 2019), making it suitable for estimating phase relations in the metamorphic rocks of interest. In addition, compositions of garnet, braunite, and sursassite were revised to contain Ca, reflecting natural occurrences in Greece and Kyushu (Table 3). The detail petrography and mineralogy of these Mn–bearing minerals in the Hakoishi sub-unit will be shown elsewhere.

The Calnet program yields two possible bundles of reactions, corresponding to the invariant points of [Pmt] and [Okh]. We selected the latter to account for the mineral assemblages of Evvia–Andros (Reinecke, 1986).

In the provisional petrogenetic grid (Fig. 5), the representative mineral assemblages of Evvia (Pmt + Sus + Br + Chl) and Andros (Pmt + Sps + Br + Chl) are stable around the invariant point [Lws]. The two assemblages are separated by the following reaction:

\[
\text{Sus} + \text{Br} = \text{Pmt} + \text{Sps} + \text{Chl} + \text{Qz} + \text{H}_2\text{O} + \text{O}_2
\]

\(1\)

corresponding to the reaction (8) of Reinecke (1986).

In contrast, mineral assemblages in the Hakoishi metacherts (Sus + Chl + Pmt, Lws + Sus + Chl, and Lws + Br + Chl; W. Yabuta, unpublished data, 2020) are stable around the invariant point [Okh]. This does not contradict the occurrence of okhotskite, which can stably coexist with Br and Pmt on the low–P side of the reaction curve:

\[
\text{Lws} + \text{Okh} + \text{O}_2 = \text{Pmt} + \text{Br} + \text{Chl} + \text{Qz} + \text{H}_2\text{O}
\]

\(2\)

On the whole, the petrogenetic grid indicates that the Evvia–Andros assemblages are stable at higher pressure and temperature compared with the Hakoishi metacherts. This is consistent with estimated \(P-T\) conditions of the two areas: 350–450 °C and 1.0–1.2 GPa for south-

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**Figure 4.** (a) Raman spectra of okhotskite. (b) and (c) Related minerals. Julgoldite-Fe (ID R070725) and pumpellyite-Mg (R120172) are from the RRUFF database.

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**Table 3.** Thermodynamic parameters of Schreinemakers’ analyses

| Mineral | Chemical composition | Volume [J/bar mol] | Entropy [J/K mol] |
|---------|----------------------|--------------------|-------------------|
| Lawsonite (Lws) | Ca(Al$_3$Mn$_{0.5}$Si$_3$O$_{10}$(OH)$_2$H$_2$O | 10.21 | 239.0 |
| Sursasite (Sus) | (Ca$_3$Mn$_{0.5}$)$_3$[(Al$_3$Mn$_{0.5}$)$_3$Si$_2$O$_{10}$(OH)$_2$] | 28.30 | 72.7 |
| Piemontite (Pmt) | Ca$_2$Al$_2$Mn$_{0.5}$Si$_2$O$_{12}$(OH) | 70.26 | 307.7 |
| Braunithe (Br) | (Al$_3$Mn$_{0.5}$)$_3$Si$_2$O$_{12}$(OH) | 12.51 | 415.8 |
| Spessartine (Sps) | Mn$_{2}$Al$_2$Si$_2$O$_{12}$ | 11.89 | 314.1 |
| Okhotskite (Okh) | Ca$_2$(Mn$_{0.5}$Mg$_{0.5}$)(Al$_3$Si$_3$O$_{10}$(OH)$_2$) | 30.70 | 753.7 |
| Chlorite (Chl) | Mg$_3$Al$_2$Si$_3$O$_{10}$(OH)$_6$ | 21.09 | 410.5 |
| Quartz (Qz) | SiO$_2$ | 2.269 | 41.5 |

Sources: (1) Ibuki et al. (2010). (2) calculated in this study (see the text). (3) Nagashima et al. (2009). (4) Anthony et al. (1995) and references therein. (5) Holland and Powell (1998). (6) Togari and Akasaka (1987).
ern Evvia (Shaked et al., 2000) and 200–300 °C and 0.60–0.80 GPa for Hakoishi (Sato et al., 2016). With reference to the study of Akasaka et al. (2003), who suggested that Mn–pumpellyite is stable below 500 °C at 300 MPa, although schematic, the petrogenetic grid in Figure 5 describes the phase relations below that temperature.

**DISCUSSION**

In the studied sample, okhotskite occurrence is limited to an environment closely associated with braunite and hematite, where Mn$^{3+}$ is abundant. In contrast, quartz–rich layers contain piemontite as the Ca–bearing mineral, and Al is relatively concentrated in the presence of albite. These observations suggest that local chemical compositions strongly control the mineral assemblage, supporting the finding of Akasaka et al. (1988) and Togari et al. (1988) on the compositional variations in Mn–rich pumpellyite and piemontite.

It is also important to note that no Mn–rich pumpellyite (with a high occupancy of Al in the Y-site) is observed in the Hakoishi metacherts, although pumpellyite–(Mn$^{2+}$) commonly coexist with okhotskite (Togari et al., 1988; Dasgupta et al., 1991). This can be explained in terms of the higher metamorphic pressure that affected the Hakoishi subunit; i.e., 200–300 °C and 0.60–0.80 GPa as estimated for Zone 2 at Hakoishi (Sato et al., 2016), and 200–230 °C and 0.25–0.35 GPa as estimated for rock units in the Kokuriki mine (Sakakibara, 1991). Instead of pumpellyite–(Mn$^{2+}$), sursassite and Mn–lawsonite occur as major minerals in the Hakoishi metacherts.

Figure 3 compares the compositions of the okhotskite described in this study with those of previous studies. A wide range in Mn:Al ratio but a narrow range in Fe:Mn ratio in okhotskite from the Tokoro Belt and Sassar Group have been documented by Togari et al. (1988) and Dasgupta et al. (1991), respectively. In contrast, the okhotskite described in the present study shows a narrow range in Mn:Al ratio and a wide range in Fe:Mn ratio (Fig. 3). Minakawa (1992) and Kassandrov and Mazurov (2009) reported similarly uniform Mn:Al ratios and consistently low $\text{Fe}_2\text{O}_3$ contents in okhotskite from the Sanbagawa belt and Askiz ore district.

These patterns of Y-site occupancy may be related to the presence or absence of bixbyite in host rocks, whereby Al$^{3+}$–Mn$^{3+}$ substitution is dominant in the former case and Fe$^{3+}$–Mn$^{3+}$ substitution is dominant in the latter case. As most bixbyite–free rocks contain quartz, assemblages of braunite + quartz and braunite + bixbyite may translate into Si saturation in highly oxidized systems (Abs–Wurmbach, 1980). However, further investigation is required, as some previous studies have reported okhotskite as mono-mineralic veins traversing the Mn–pumpellyite veinlets with/without piemontite (Togari et al., 1988); for such cases, equilibria within host rocks are not assured.

The provisional Schreinemakers’ net presented here (Fig. 5) predicts that okhotskite and Mn$^{3+}$–bearing lawsonite are characteristically stable at higher pressure compared with the P–T conditions determined for Hakoishi and Evvia–Andros. These minerals contain abundant Mn$^{3+}$ and host substantial contents of $\text{H}_2\text{O}$ (Okh: 6.89 wt%, Togari and Akasaka, 1987 and 7.15 wt% in this study; Lws: 11.3 wt%, calculated from data of Ibuki et al., 2010). This clearly shows that siliceous sediments can contain high contents of water in the deep Earth when impurities such as Mn–rich oceanic sediments are present, although such sediments have generally been thought to be water poor (Hacke, 2008).

In terms of oxygen transport, the Schreinemakers’ net in Reinecke (1986) assumes perfect mobility of oxygen (Korzhinskii, 1959), whereby oxygen is released as a fluid from oxidized solid phases. Under reduced mobility in a subduction zone, oxygen fluid is transported into the
mantle wedge along with highly oxidized minerals (as noted by Tumiati et al., 2015). Indeed, oxygen fluid is highly complicated when considering phase relations, as its high entropy sometimes leads to the prediction of contradictory phase relations.

For instance, phase relations between pumpellyite and epidote groups are discussed as simplified oxidation reactions (e.g., Fe–Pmp + O2 = Ep + H2O; Schiffman and Liou, 1983; Mn–Pmp + O2 = Pmt + H2O; Akasaka et al., 1988, 2003). These reactions, however, would have negative slope (ΔS < 0 and ΔV > 0, owing to high entropy of O2-fluid) with pumpellyite group stable at higher P–T side, even when some other solid phases are present. Needless to say, such reaction curves on P–T field would not explain the high-temperature stability of the epidote group against pumpellyite group in metabasites (e.g., Nakajima et al., 1977).

Such a simple case is sufficient to demonstrate problems in oxygen-mobile models. The effect of oxygen fluid on phase relations will be discussed in detail elsewhere. In the present study, it is noted that highly oxidized minerals (e.g., Okh and Br) are stable at high P–T even if oxygen is released freely from the system as a perfectly mobile element. This indicates that okhotskite serves as a component of the oxygen budget in deep subduction zones, in addition to its role as a water reservoir (Togari and Akasaka, 1987; Togari et al., 1988). However, further investigation is required regarding the fate of highly oxidized Mn-bearing minerals, including okhotskite, in subduction environments, where their oxidizing capacity may oxidize the mantle hanging wall.

ACKNOWLEDGMENTS

We sincerely thank Dr. M. Akasaka, Professor Emeritus of Shimane University, and Dr. S. Endo for their sincere and constructive comments, which guided the revision of an earlier draft of the manuscript. We also thank Professor M. Satish Kumar for his efficient editorial handling of the manuscript. We are grateful for the technical advice and the high-quality thin-section samples prepared by Mr. M. Takaya and the revision of the Calnet program by Mr. R. Kato. We acknowledge students of Matsubase High School, Kumamoto, for their contribution to the first report of piemontite in the study area. This work was supported by JSPS KAKENHI Grant No. JP19H19991 to T.H.

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Manuscript received August 31, 2019 Manuscript accepted August 5, 2020 Manuscript handled by M. Satish-Kumar