Compositional variation of olivine related to high-temperature serpentinization of peridotites: Evidence from the Oeyama ophiolite

Toshio NOZAKA

Department of Earth Sciences, Okayama University, Okayama 700-8530, Japan

Compositional variation of olivine in serpentinized peridotites provides a significant constraint on modeling the redox conditions of serpentinization and the tectonothermal history of ophiolites. Here I report the variations of Fe, Mg, Mn, and Ni contents of olivine from the Oeyama ophiolite, SW Japan and show textural and chemical evidence for compositional modification of olivine related to high-temperature (T) serpentinization. The Fe-enrichment of olivine adjacent to antigorite without significant magnetite formation indicates a reducing condition for high-T serpentinization. Systematic variations of forsterite (Fo) component with distance from antigorite suggest Mg-Fe volume diffusion took place in olivine porphyroclasts under the conditions of high-T serpentinization. In addition, a similar diffusion pattern of Mn to Fe results in a retrograde trend in MnO-Fo diagram, which could be a useful indicator of high-T serpentinization. Retrograde antigorite is different from prograde antigorite in having a shape of elongated blade, lacking a significant amount of magnetite inclusion, and being more ferrous than lizardite. The existence of retrograde antigorite provides another piece of evidence for high-T serpentinization even if olivine has been decomposed by intense low-T serpentinization. Approximate estimation of time required for the observed Mg-Fe diffusion profiles of olivine porphyroclasts reveals that a cooling duration under the conditions of high-T serpentinization was much longer than that of amphibolite-facies metasomatism previously reported. This suggests a long residence time of the forearc peridotites within the serpentinized mantle wedge following rapid exhumation immediately after the amphibolite-facies metasomatism.

Keywords: High-temperature serpentinization, Olivine composition, Retrograde antigorite, Retrograde olivine, Volume diffusion

INTRODUCTION

Because of the possible relation to the origin of life and the development of biosphere, molecular hydrogen produced by serpentinization of peridotites have attracted significant interests (e.g., Kelley et al., 2001; Früh-Green et al., 2003; Sleep et al., 2004; Takai et al., 2004; Kelley et al., 2005; Schulte et al., 2006; Russell et al., 2010). The hydrogen production is mainly caused by the oxidation of Fe in olivine and associated with the formation of magnetite (e.g., Frost, 1985; McColom and Bach, 2009; Klein et al., 2013, 2015). In this context, it is important to understand the formation conditions of magnetite and the effect of its presence or absence on serpentinization processes. Magnetite is commonly associated with lizardite and/or brucite in serpentinites. Recent studies have shown the uneven distribution of magnetite in serpentinites, suggesting a local variation in oxygen fugacity, silica activity and/or water-rock ratio (e.g., Bach et al., 2006; Beard et al., 2009; Katayama et al., 2010; Frost et al., 2013; Miyoshi et al., 2014; Schwarzenbach et al., 2016). In contrast, Evans (2010) has proposed that magnetite is absent at relatively high-temperature (T) antigorite-forming serpentinization, because Fe is distributed in olivine with a considerable Mg-Fe interdiffusion rate, instead of forming magnetite. Such a behavior of Fe during high-T serpentinization could be a constraint on hydrogen production at a mantle wedge of supra-subduction zone, at a deep level of oceanic lithosphere, or at the ancient Earth’s surface. However, observations of the Fe-enrichment of olivine caused by high-T serpentinization have not been reported.

doi:10.2465/jmps.180420
T. Nozaka, nozaka@cc.okayama-u.ac.jp Corresponding author
except for some examples (Murata et al., 2009a, 2009b; Plümper et al., 2012), probably because of the effect of intense low-T serpentinization or overprinting metamorphism.

In addition to reporting new occurrence of the retrograde ferroan olivine in the Oeyama ophiolite, SW Japan, I show here evidence for the volume diffusion of elements in olivine grains under the conditions of high-T serpentinization. This compositional modification of olivine could be a useful indicator of tectonothermal history of serpentinized forearc peridotites.

GEOLOGICAL SETTING

The Oeyama ophiolite is a collective name of ultramafic complexes exposed in the Renge high-P/T metamorphic belt of SW Japan (Ishiwatari, 1989, 1990; Nishimura, 1998; Takeuchi, 2002; Isozaki et al., 2010). In the present article, the Happo complex is included in the Oeyama ophiolite despite its long distance from the other complexes, because they are similar in geological and geochemical characteristics (Takeuchi, 2002; Nozaka, 2005; Khedr and Arai, 2010; Nozaka, 2014a).

The peridotites of the Oeyama ophiolite are considered to be residual mantle peridotites and cumulates from basaltic melt originated at a Paleozoic supra-subduction zone or forearc mantle wedge (Ishiwatari, 1989; Arai and Yurimoto, 1995; Ishiwatari and Tsujimori, 2003; Khedr and Arai, 2010; Nozaka, 2014a). They were subjected to two stages of mylonitization, which could be associated with metasomatic hydration at 700–800 °C and later high-T serpentinization at 400–600 °C (Nozaka, 2005; Nozaka and Ito, 2011; Nozaka, 2014a). Many of the serpentinized peridotite bodies of the Oeyama ophiolite were intruded by Cretaceous or Paleogene granitic rocks and consequently thermally metamorphosed (Arai, 1975; Nozaka, 2003, 2005; Khedr and Arai, 2012). The temporal sequence of these geologic events was summarized by Nozaka (2014a).

ANALYTICAL PROCEDURES

Polished thin sections of serpentinized peridotites from the Oeyama ophiolite were prepared for microscopic observations and chemical analyses of minerals. Several samples from the Ryumon ultramafic body in the Sanbagawa metamorphic belt exposed in the Kii Peninsula were analyzed for comparison. Quantitative microprobe analyses were carried out using an electron probe microanalyzer, JEOL JXA-8230 at Okayama University with an accelerating voltage of 15 kV and a probe current of 20 nA. Counting time was 30 s for major elements (Si, Fe, and Mg), 60 s for minor elements (Mn, Ni, and Ca) of olivine, and 10 s for the all element of serpentine; background counting time was 5 s for all the cases. Standards used were natural or synthetic oxides and silicates. The applied matrix corrections followed the procedures of Bence and Albee (1968), using alpha factors of Nakamura and Kushiro (1970). Identification of serpentine minerals of representative samples was confirmed with Raman shift spectra, using a micro-Raman spectrometer, JASCO NRS-3100 at Okayama University, with 488 nm laser excitation, a 100 × microscope objective lens, and a diffraction grating with 1800 grooves/mm.

RESULTS

As I have previously reported the petrographic observations of the serpentinized peridotites from the Oeyama ophiolite (Nozaka, 2005; Nozaka and Ito, 2011; Nozaka, 2014a), I just briefly describe here an outline of the characteristics of olivine and serpentine. Primary olivine of
the peridotites shows modes of occurrence with variable effects of plastic deformation: relatively coarse, equant grains with subgrain boundaries; ‘cleavable olivine’ with prominent parting planes; and elongated elliptic porphyroclasts distributed in a matrix of fine-grained recrystallized olivine and lepidoblastic antigorite. The primary olivine grains are serpentinized more or less from rims and along parting planes or fractures. Antigorite blades penetrate the porphyroclastic or cleavable olivine and are associated with chlorite, diopside and/or brucite in the lepidoblastic matrix of mylonites. These antigorite blades have been interpreted to be a product of high–T serpentinization (Nozaka, 2005). Lizardite, which is a product of low–T serpentinization, statically replaces olivine to form mesh texture with tiny grains of opaque minerals (mostly magnetite) and submicroscopic brucite. The mesh-forming lizardite is replaced by metamorphic olivine in contact aureoles around granitic intrusions. The contact metamorphic olivine occurs as discrete small grains or epitaxially grown rims over primary olivine grains, coexisting with antigorite at a low grade zone (Zone II) and with talc, anthophyllite and orthopyroxene at higher grade zones (Nozaka, 2003, 2005, 2011; Nozaka and Ito, 2011; Nozaka, 2014b).

Reflecting the metamorphic history of the Oeyama ophiolite, at least two generations of antigorite can be observed: i.e., retrograde antigorite formed by high–T serpentinization and prograde antigorite formed by metamorphism after low–T serpentinization. Similarly, I will refer to the olivine coexisting with the former antigorite or affected by the high–T serpentinization as ‘retrograde olivine’ and that coexisting with the latter antigorite as ‘prograde olivine’.

The retrograde olivine is common in serpentinite mylonites from the Happo and Wakasa complexes and locally found outside the contact aureole of the Ohsayama complex. This olivine does not form discrete grains but occurs as a part of chemically modified primary olivine in contact with retrograde antigorite blades. It cannot be distinguished from primary olivine under the optical microscope but is visible by a high electron back-scattered intensity resulting from an Fe-rich composition (Figs. 2a–2f, 3, and Table 1). Such an enrichment of Fe is lacking in olivine at any portions in contact with lizardite (Figs. 2c and 2f). Back-scattered electron images show bright halos around some small antigorite blades that are seemingly inclusions in olivine but possibly fracture-fillings cut by the thin-section surface (Fig. 2c) and locally show a small amount of bright streaks ~ 1 μm wide (not shown) within olivine grains.

Figure 3 shows a systematic decrease of Fo [= 100 × Mg/(Mg + Fe)] and increase of Mn contents in olivine porphyroclasts with decreasing distance from antigorite in serpentinites from the Happo complex. Such a compositional variation is unclear in other ultramafic complexes probably because of intense low–T serpentinization and/or contact metamorphism. The plots of olivine composition were obtained avoiding the bright halos and streaks in back-scattered electron images mentioned above but could be affected by modification along invisible fractures or subgrain boundaries to some extent as discussed later. Nickel contents show no systematic variation with distance unlike Fo and Mn (Fig. 3).

In the diagrams of NiO versus Fo and MnO versus Fo contents, a cluster of plots from each sample exhibits a trend of compositional variation from the magnesian primary olivine to the most ferroan retrograde olivine (Fig. 4). The NiO–Fo plots are similar, though more scattered, to the ‘mantle olivine array’ defined by Takahashi et al. (1987). The trend is much evident in MnO–Fo diagram and designated here as ‘retrograde trend’ (Fig. 4b).

Prograde olivine occurs in the contact aureoles of most of the ultramafic complexes of the Oeyama ophiolite. In a low–grade zone (Zone II), the prograde olivine commonly has highly magnesian compositions (Arai, 1975; Nozaka, 2005; Nozaka and Ito, 2011; Khedr and Arai, 2012), and in some cases there is another group of prograde olivine with relatively ferroan compositions (Nozaka, 2003). The ferroan prograde olivine is similar in Fo content to the retrograde olivine, but is different in highly variable contents of NiO and MnO (Fig. 4; Nozaka, 2003, 2010). Relatively ferroan olivine formed by regional metamorphism has been reported from the Sanbagawa metamorphic belt, and it is also different in NiO and MnO contents from the retrograde olivine (Kunugiza, 1980, 1982; Nozaka, unpublished data).

Retrograde antigorite coexisting with retrograde olivine occurs as elongated blades surrounding or penetrating primary olivine (Figs. 2e–2i). The antigorite blades commonly lack magnetite inclusions unlike lizardite (Figs. 2d, 2g, and 2h) and locally has the intercalation of elongated magnetite, chlorite or brucite. A small amount of awaruite in contact with the antigorite blades was observed in one sample (HP21). Retrograde antigorite has aluminous compositions indicative of the incorporation of chlorite components, and lacks evidence for mixing with brucite unlike the case of lizardite (Figs. 5a and 5c), which shows a brucite–mixing trend as reported from many localities (e.g., Beard et al., 2009). However, the Al-enrichment is less significant in antigorite apart from matrix chlorite as the case of fracture-filling antigorite in olivine porphyroclasts (Fig. 2d). Lizardite is commonly less aluminous than retrograde antigorite, excepting bastite-forming Al-rich lizardite (not shown in the figures).
Prograde antigorite occurs in contact metamorphic zones where prograde olivine occurs. This type of antigorite is characteristically smaller in size and in aspect ratio (length/width) than retrograde antigorite, and typically...

Figure 2. Mode of occurrence of olivine and antigorite. Abbreviations for minerals: Atg, antigorite; Chl, chlorite; Liz, lizardite; Mgt, magnetite; Ol, olivine; P-OI, prograde olivine. (a) Photomicrograph of an olivine porphyroclast in a serpentine mylonite from Happo (crossed polars, sample HP40). (b) Back-scattered electron image of the same olivine porphyroclast as shown in (a). (c) Back-scattered electron image of a part of (b). (d) Back-scattered electron image of a part of (c). (e) Photomicrograph of olivine porphyroclasts surrounded by dynamically recrystallized olivine neoblasts and lepidoblastic antigorite of a serpentine mylonite from Happo (crossed polars, sample HP11). (f) Back-scattered electron image of a part of (e). Color version is available online from https://doi.org/10.2465/jmps.180420.
Figure 2 (Continued). Mode of occurrence of olivine and antigorite. Abbreviations for minerals: Atg, antigorite; Chl, chlorite; Liz, lizardite; Mgt, magnetite; Ol, olivine; P-Ol, prograde olivine. (g) Photomicrograph of retrograde antigorite and lizardite replacing olivine in a gently deformed serpentinite from Wakasa (plane-polarized light, sample# WS0301). (h) Back-scattered electron image of a part of (g). (i) Photomicrograph of ‘cleavable olivine’ surrounded and penetrated by antigorite from a low-grade contact aureole (Zone II) in the Wakasa complex (crossed polars, sample# WS0615). (j) Back-scattered electron image of a part of (i). (k) Photomicrograph of prograde antigorite from a low-grade contact aureole (Zone II) in the Oeyama complex (crossed polars, sample# OE0817). (l) Back-scattered electron image of a part of (k). Color version is available online from https://doi.org/10.2465/jmps.180420.
forms fine-grained aggregate with subordinate amounts of magnetite (Figs. 2k and 2l). Antigorite of regional metamorphic origin from the Ryumon ultramafic body in the Sanbagawa belt is also smaller in grain size than the retrograde antigorite of the Oeyama ophiolite and shows granoblastic texture with metamorphic olivine (Kunugiza, 1980, 1982), suggesting their contemporaneous formation. The prograde antigorite, including that of the Ryumon body, typically has more magnesian compositions ($X_{Mg} > 0.96$) than the retrograde antigorite ($X_{Mg} = 0.94–0.96$) (Fig. 5d). The antigorite blades that have a typical shape, size, and mode of occurrence of retrograde antigorite occur in low-grade contact aureoles as well (Figs. 2i and 2j) and have compositions scattering in both the fields of typical retrograde and prograde antigorite (Fig. 5d).

**DISCUSSION**

**Compositional modification of olivine**

The textural relationship strongly suggests the contemporaneous formation of the retrograde olivine and retrograde antigorite in the peridotites of the Oeyama ophiolite. Further evidence is that plots of $X_{Fe}$ of the most ferroan olivine–antigorite pair in each sample are consistent with those of coexisting pairs from other localities (Fig. 6). The enrichment of Fe in olivine porphyroclasts and the deficiency of magnetite associated with retrograde antigorite indicate a reducing condition and support the hypothesis that Mg–Fe interdiffusion in olivine is effective under the conditions of high-$T$ serpentinization proposed by Evans (2010). Although a small amount of elongated magnetite is intercalated in some antigorite blades, they are not necessarily formed contemporaneously. Because brucite showing a similar mode of occurrence to magnetite was observed in some serpentinite mylonites, the possibility that the magnetite replaced brucite, as suggested by Bach et al. (2006) and Beard et al. (2009), cannot be ruled out.

The variations of Fo content with distance from antigorite (Fig. 3) suggest that Mg–Fe interdiffusion took place within the olivine porphyroclasts, i.e., between the cores keeping primary compositions and the rims of retrograde olivine coexisting with the retrograde antigor-
ite. Relatively low Fo values distributed below the diffusion profile curves (Fig. 3) could be the effects of hidden (not appeared on the thin-section surface) irregular small fractures filled with antigorite as shown in Figure 2c. Stripes of Fe-enriched olivine have been reported and interpreted as a result of Mg-Fe interdiffusion along subgrain boundaries, or pipe diffusion along dislocations, within deformed olivine crystals (Kitamura et al., 1986; Ando et al., 2001; Murata et al., 2009a, 2009b; Plümper et al., 2012). Although the bright streaks visible in back-scattered electron images suggest that an Fe-enrichment along linear defects within olivine crystals took place in the Oeyama ophiolite as well, their amount and frequency are just minor and volume diffusion, which forms a systematic compositional variation depending on the distance from antigorite, is probably the dominant mechanism. Since volume diffusion is a process more sluggish than grain/subgrain boundary diffusion or pipe diffusion, the serpentinization of the Oeyama ophiolite could proceed at a higher-T or over a longer period than the serpentinization accompanied by the ferroan olivine stripes. Because Mg-Fe volume diffusion in olivine looks unrealistic below 400 °C as discussed later, it probably took place under the conditions of high-T serpentinization.

Figure 3 indicates that Mn is enriched in retrograde olivine as well as Fe. As pointed out by Evans (2010) and Plümper et al. (2012), this enrichment can be explained by the average distribution coefficient of Mn established by Trommsdorff and Evans (1974). For example, the $X_{Mg} = \frac{Mn}{(Mg + Fe + Mn + Ni)}$ of the most ferroan olivine in two samples (HP11 and HP40) are 0.0019–0.0026, and applying the Mn distribution coefficient $K_D$ (antigorite/}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Sample & HP40 & HP40 & HP40 & HP11 & HP11 & HP11 & WS0615 & WS0615 & WS0615 & WS0615 & OE0817 \\
\hline
Mineral & Ol & Ol & Atg & Ol & Ol & Ol & Atg & Ol & Ol & Ol & Atg & Liz & Atg \\
\hline
Type & Pri & R & R & Pri & R & R-P & Pri & R & P & P-P & P \\
\hline
SiO$_2$ & 40.51 & 40.60 & 42.66 & 42.36 & 40.06 & 39.89 & 43.02 & 40.21 & 40.06 & 40.82 & 43.24 & 39.76 & 44.94 \\
TiO$_2$ & nd & nd & 0.02 & 0.03 & nd & nd & 0.01 & nd & nd & nd & 0.01 & 0.00 & 0.00 \\
Al$_2$O$_3$ & nd & nd & 2.22 & 0.26 & nd & nd & 2.54 & nd & nd & nd & 1.16 & 0.01 & 0.08 \\
Cr$_2$O$_3$ & nd & nd & 0.20 & 0.00 & nd & nd & 0.24 & nd & nd & nd & 0.33 & 0.00 & 0.00 \\
FeO$^*$ & 10.22 & 13.06 & 3.90 & 2.10 & 9.79 & 11.62 & 3.59 & 9.50 & 10.48 & 5.81 & 2.49 & 1.96 & 1.53 \\
MnO & 0.15 & 0.25 & 0.05 & 0.10 & 0.14 & 0.22 & 0.04 & 0.13 & 0.18 & 0.04 & 0.05 & 0.05 & 0.00 \\
NiO & 0.39 & 0.35 & 0.22 & 0.07 & 0.38 & 0.37 & 0.16 & 0.39 & 0.40 & 0.22 & 0.06 & 0.25 & 0.05 \\
MgO & 49.16 & 46.33 & 36.65 & 38.80 & 50.03 & 47.63 & 36.76 & 49.98 & 48.69 & 53.12 & 37.61 & 39.25 & 39.57 \\
CaO & 0.00 & 0.01 & 0.00 & 0.11 & 0.00 & 0.00 & 0.01 & 0.00 & 0.01 & 0.00 & 0.01 & 0.04 & 0.00 \\
Na$_2$O & nd & nd & 0.00 & 0.01 & nd & nd & 0.04 & nd & nd & nd & 0.00 & 0.01 & 0.01 \\
K$_2$O & nd & nd & 0.01 & 0.02 & nd & nd & 0.00 & nd & nd & nd & 0.00 & 0.01 & 0.00 \\
Total & 100.45 & 100.59 & 85.94 & 83.86 & 100.40 & 99.73 & 86.41 & 100.21 & 99.81 & 100.00 & 84.96 & 81.33 & 86.18 \\
\hline
O= & 4.000 & 4.000 & 7.000 & 7.000 & 4.000 & 4.000 & 7.000 & 4.000 & 4.000 & 4.000 & 7.000 & 7.000 & 7.000 \\
Si & 0.992 & 1.004 & 2.023 & 2.043 & 0.981 & 0.991 & 2.023 & 0.985 & 0.989 & 0.984 & 2.056 & 1.988 & 2.093 \\
Ti & nd & nd & 0.001 & 0.001 & nd & nd & 0.000 & nd & nd & nd & 0.000 & 0.000 & 0.000 \\
Al & nd & nd & 0.124 & 0.015 & nd & nd & 0.141 & nd & nd & nd & 0.065 & 0.000 & 0.004 \\
Cr & nd & nd & 0.007 & 0.000 & nd & nd & 0.009 & nd & nd & nd & 0.013 & 0.000 & 0.000 \\
Fe & 0.209 & 0.270 & 0.154 & 0.085 & 0.201 & 0.241 & 0.141 & 0.195 & 0.217 & 0.117 & 0.099 & 0.082 & 0.060 \\
Mn & 0.003 & 0.005 & 0.002 & 0.004 & 0.003 & 0.005 & 0.002 & 0.003 & 0.004 & 0.001 & 0.001 & 0.002 & 0.000 \\
Ni & 0.008 & 0.007 & 0.009 & 0.003 & 0.007 & 0.007 & 0.006 & 0.008 & 0.008 & 0.004 & 0.002 & 0.010 & 0.002 \\
Mg & 1.795 & 1.709 & 2.591 & 2.790 & 1.827 & 1.764 & 2.578 & 1.825 & 1.793 & 1.909 & 2.666 & 2.926 & 2.747 \\
Ca & 0.000 & 0.000 & 0.000 & 0.006 & 0.002 & 0.000 & 0.001 & 0.000 & 0.000 & 0.000 & 0.001 & 0.002 & 0.000 \\
Na & nd & nd & 0.000 & 0.001 & nd & nd & 0.004 & nd & nd & nd & 0.000 & 0.000 & 0.001 \\
K & nd & nd & 0.001 & 0.001 & nd & nd & 0.000 & nd & nd & nd & 0.000 & 0.000 & 0.000 \\
Total & 3.008 & 2.996 & 4.911 & 4.949 & 3.019 & 3.009 & 4.904 & 3.015 & 3.011 & 3.016 & 4.905 & 5.012 & 4.906 \\
$X_{Mg}$ & 0.896 & 0.863 & 0.944 & 0.971 & 0.901 & 0.880 & 0.948 & 0.904 & 0.892 & 0.942 & 0.964 & 0.973 & 0.979 \\
\hline
\end{tabular}
\caption{Representative microprobe analyses of olivine and serpentine}
\end{table}

* Total iron as FeO; nd, not determined; $X_{Mg} = \frac{Mn}{(Mg + Fe + Mn + Ni)}$ molar ratio.

Mineral abbreviations: Atg, antigorite; Liz, lizardite; Ol, olivine.

Type: P, prograde; Pri, primary; R, retrograde; R-P, retrograde type in prograde contact aureoles. Samples were collected from Happo (HP), Wakasa (WS) and Oeyama (OE).
olivine) = 0.18 (Trommsdorff and Evans, 1974) to these olivine, the calculated XMn of antigorite are 0.0003–0.0005. These values are consistent with the XMn of analyzed antigorite: 0.0002–0.0008 with an average of 0.0005 (24 analyses).

The Ni contents of olivine porphyroclasts do not show such a systematic variation as Fo and Mn (Fig. 3). In the same manner as Mn, using the KD = 0.65 (Trommsdorff and Evans, 1974), XNi was calculated for antigorite coexisting ferroan olivine to be 0.0021–0.0027. These values are not inconsistent with the analyzed values of antigorite: 0.0015–0.0034, and therefore retrograde olivine and retrograde antigorite probably tend to keep their equilibrium for Ni as well. However, such a diffusion profile as the case of Mn cannot be defined for Ni in the olivine porphyroclasts (Fig. 3). Olivine, which has enrichments of Fe and Mn showing deviation from the diffusion profiles at a significant distance from antigorite probably due to fluid infiltration along fractures or dislocations, shows an increase and decrease of Ni from the primary composition (e.g., the three data on the extreme right of Fig. 3a). This opposite behavior of Ni suggests a variation of Ni content of fluid during high-T serpentinization. The increase of Ni probably results from its distribution between olivine and antigorite (KD = 0.65 according to Trommsdorff and Evans, 1974), whereas the decrease of Ni could be explained by the formation of Ni-rich phase, e.g., awaruite, as pointed out by Plümper et al. (2012). In fact, the coexistence of awaruite with antigorite, though a small amount, was observed in at least one sample from the Oeyama ophiolite.

It is in no doubt that the successive zonal arrangements of olivine compositions in NiO–Fo and MnO–Fo diagrams (Fig. 4) are the results of intracrystalline element diffusion during high-T serpentinization and intracrystalline element diffusion. Compositional fields of olivine from the literature are shown for comparison: MOA, mantle olivine array (Takahashi et al., 1987); PFO, prograde metamorphic ferroan olivine from Zone II of contact aureoles, SW Japan (Nozaka, 2003, 2010). Iron-rich prograde metamorphic olivine from the Ryannon peridotites plot within PFO or significantly out of the retrograde trends, or outside the scale ranges (Kunugiza, 1980, 1982; Nozaka, unpublished data). Color version is available online from https://doi.org/10.2465/jmps.180420.

Figure 4. (a) NiO versus Fo contents and (b) MnO versus Fo contents of olivine in contact with antigorite in serpentinite mylonites (sample# HP40, HP11, and WS0615). Arrows, which are regression lines of olivine data from individual samples, indicate ‘retrograde trends’ caused by high-T serpentinization and intracrystalline element diffusion. Compositional fields of olivine from the literature are shown for comparison: MOA, mantle olivine array (Takahashi et al., 1987); PFO, prograde metamorphic ferroan olivine from Zone II of contact aureoles, SW Japan (Nozaka, 2003, 2010). Iron-rich prograde metamorphic olivine from the Ryannon peridotites plot within PFO or significantly out of the retrograde trends, or outside the scale ranges (Kunugiza, 1980, 1982; Nozaka, unpublished data). Color version is available online from https://doi.org/10.2465/jmps.180420.
pentinitized peridotites of ophiolites: i.e., crystallization differentiation of basaltic magma, deformation-induced pipe diffusion, metasomatic fluid infiltration, and prograde metamorphism. In these cases, a set of NiO–Fo and MnO–Fo diagrams (Fig. 4) could be useful to distinguish the ferroan olivine of different origin. In a given sample from the mantle section of ophiolites, compositions of olivine produced or affected by high-\(T\) serpentinization are expected to be plotted around the retrograde trends of Fo–MnO without no significant deviation of NiO from the mantle olivine array (Fig. 4). From this type of olivine, ferroan olivine produced by other processes could be different in some points: a progressive depletion of NiO and a gentle enrichment of MnO with decreasing Fo contents by magmatic differentiation (Takahashi et al., 1987); no significant change of NiO and MnO contents by high-\(T\) pipe diffusion in anhydrous, not serpentinized peridotite (Ando et al., 2001); much less extent of Fo, NiO, and MnO variations by amphibolite-facies metasomatism (Nozaka, 2014a); and highly variable NiO and MnO contents with a large deviation from the retrograde trend and the mantle olivine array by prograde contact/regional metamorphism (Kunugiza, 1980, 1982; Nozaka, 2003, 2010).

**Retrograde vs. prograde antigorite**

Retrograde antigorite would be easily found if it shows textural and chemical equilibration with retrograde olivine, but retrograde olivine grains might disappear because of intense low-\(T\) serpentinization. The question is whether it is possible to discriminate between retrograde and prograde antigorite in the latter case.

The two types of antigorite have differences in some microscopic features. Retrograde antigorite commonly occurs as relatively large blades with high aspect ratios and without magnetite inclusions (Figs. 2d, 2g, and 2h). Prograde antigorite typically forms fine-grained aggregates with minor amounts of magnetite in contact aureoles (Figs. 2k and 2l) or occurs as relatively small blades forming an equilibration texture; e.g., granoblastic texture with prograde metamorphic olivine (e.g., Kunugiza, 1980). However, retrograde antigorite also occurs as a small blade (Fig. 2d), and the shape or size may not be concluding evidence for identification.

A constraint on the spatial distribution of minerals is given by metamorphic zonal mapping. In the contact aureoles of SW Japan, prograde antigorite occurs in Zone II, which is defined by the first appearance of prograde metamorphic olivine (e.g., Nozaka, 2003, 2011). However, this is not a condition for excluding the occurrence of retrograde antigorite, because it also occurs in Zone II (Figs. 2i and 2j).

Chemical composition is an effective constraint if equilibration compositions are maintained. Retrograde antigorite is relatively rich in Fe resulting in low \(X_{\text{Mg}}\) (Figs. 5b and 5d). The contrasting high \(X_{\text{Mg}}\) of prograde antigorite is likely inherited from lizardite, a reactant from which the prograde antigorite has formed. During low-\(T\) serpentinization, Fe in olivine is mainly incorporated into magnetite (e.g., Nozaka, 2003; Evans, 2010), some of which could form after Fe-bearing brucite (e.g., Bach et al., 2006; Beard et al., 2009), resulting in the highly magnesian compositions of lizardite. Although the \(X_{\text{Mg}}\) of lizardite and antigorite varies depending on primary olivine or bulk rock compositions, the retrograde antigorite directly formed after primary olivine should be richer in Fe than prograde antigorite after lizardite in any samples. However, some relict blades of retrograde antigorite in contact aureoles have a slightly magnesian compositions probably resulting from a reequilibration process during prograde metamorphism (Fig. 5d). An additional signature of retrograde antigorite of the Oeyama ophiolite is an Al-enrichment (Figs. 5c and 5d). This could be an indication of increasing chlorite component in antigorite under high-\(T\) conditions (Padrón-Navarta et al., 2013). Before discussion about \(T\) conditions, however, a caution is needed for whether or not the antigorite coexists with chlorite; in fact, antigorite in olivine fractures apart from matrix chlorite, tends to be deficient in Al.

In summary, the identification of retrograde antigorite requires the diagnostic characteristics: a shape of elongated blade, the absence of a significant amount of magnetite inclusion, and a composition richer in Fe than that of lizardite. These characteristics would provide empirical evidence for high-\(T\) serpentinization even in intensely serpentinized peridotites from ophiolites. However, the possibility of chemical disturbance in prograde metamorphic rocks should be carefully investigated.

**Tectonic implication**

The diffusion profiles of olivine porphyroclasts (Fig. 3) provide a constraint for tectonic model of the forearc mantle wedge (Fig. 7; Schmidt and Poli, 1998; Peacock and Wang, 1999; Stern, 2002; Hacker et al., 2003; Reynard et al., 2011; Nozaka, 2014a). The illustrated diffusion profiles differ between the two samples (Fig. 3) in a reflection of primary olivine composition, and possibly in addition, crystallographic orientation, degree of crystal deformation and \(T\) condition. Nevertheless, similar diffusion distances are determined: \(\sim 35 \ \mu m\) for sample HP40 and \(\sim 45 \ \mu m\) for sample HP11, which allow us to estimate the time necessary for the diffusion.
The diffusion time was calculated on the basis of the equation: 

\[ x \sim \sqrt{Dt} \]

where \( x \), \( D \) and \( t \) is diffusion distance, diffusion coefficient and time, respectively, using a diffusion distance of 40 \( \mu m \) (Fig. 3) and the diffusion coefficient based on the global equation of Dohmen and Chakraborty (2007a, 2007b). The diffusion coefficient for the direction of [001] of olivine is obtained by the global equation, and it is necessary to subtract \( \log 6 \), i.e., \( \sim 0.78 \) order of magnitude for [100] and [010] according to the global equation of Dohmen and Chakraborty (2007a, 2007b).
to Dohmen and Chakraborty (2007a, 2007b). However, the difference of $D$ below 700 °C is less than 0.3 order of magnitude (Dohmen et al., 2007). Actually, the difference is considered to be much less because the interference colors under the microscope indicate that the directions of the observed diffusion are not [100] nor [010]. To obtain the minimum duration of cooling during or after high-$T$ serpentinization, $T$ conditions were supposed to be close to the maximum estimation for high-$T$ serpentinization of the Oeyama ophiolite (Nozaka, 2014a). The results are $\sim 7.6 \times 10^6$ years at 550 °C and 1 GPa, and $\sim 4.0 \times 10^7$ years at 500 °C and 0.5 GPa. An unreasonably long time ($> 4.5 \times 10^9$ years) was estimated at 400 °C, suggesting the observed intracrystalline element diffusion of olivine mainly took place under the conditions of high-$T$ serpentinization.

In contrast, much shorter diffusion time of tens to hundreds of years has been estimated for the diffusion profile caused by the fluid injection that formed olivine–phlogopite veins in the Oeyama ophiolite and interpreted as a result of rapid exhumation after amphibolite-facies metasomatism of the forearc mantle wedge (Nozaka, 2014a). That short time was obtained using $D$ of Jaoul et al. (1995), which is one or two orders of magnitude larger than that of Dohmen and Chakraborty (2007a, 2007b). Using the latter $D$ in this study, the time was recalculated to be $\sim 5.0 \times 10^2$ to $8.0 \times 10^3$ years at 750-800 °C, which is still an extremely short period in the geologic time frame. Although exact time required for the observed diffusion profiles is difficult to be estimated because of the uncertainties of $D$, $T$, and pressure conditions, the approximate estimation suggests that the cooling duration under the conditions of high-$T$ serpentinization was at least three to four orders of magnitude longer than that of the amphibolite-facies metasomatism in the Oeyama ophiolite. It is concluded that the peridotites of the Oeyama ophiolite retained for a considerably long period in the region of serpentinized mantle wedge following the rapid exhumation immediately after the amphibolite-facies metasomatism (Fig. 7).

**CONCLUDING REMARKS**

Iron–enriched retrograde olivine instead of magnetite was formed along with retrograde antigorite by high-$T$ serpentinization in the Oeyama ophiolite. Intracrystalline volume diffusion of Mg, Fe, and Mn between the most ferroan retrograde olivine, which coexists with retrograde antigorite, and primary olivine took place under the conditions of high-$T$ serpentinization. The diffusion produced a characteristic zonal arrangement of olivine compositions in MnO–Fo and NiO–Fo diagrams, which could be useful to distinguish retrograde or retrogressively modified olivine from ferroan olivine of different origin, even if intense low-$T$ serpentinization has obscured the early record of the diffusion process. Retrograde antigorite is different from prograde antigorite in having a shape of elongated blade, lacking a significant amount of magnetite inclusion, and having a composition richer in Fe than that of lizardite. These characteristics are expected to provide empirical evidence for high-$T$ serpentinization even in intensely serpentinized peridotites from ophiolites. Approximate estimation of time required for the observed diffusion profiles of olivine porphyroclasts suggests a long residence time of the forearc peridotites within the serpentinized mantle wedge following rapid exhumation immediately after the amphibolite-facies metasomatism.

**ACKNOWLEDGMENTS**

I thank Dr. Masaki Mifune for permission to use a Raman spectrometer in his laboratory at Okayama University. Comments from reviewers, J. Ando and E. Takazawa have improved the manuscript. This study was financially supported by JSPS KAKENHI Grant Number JP16K05611.

**SUPPLEMENTARY MATERIALS**

Color versions of Figures 1–7 are available online from https://doi.org/10.2465/jmps.180420.

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Manuscript received April 20, 2018
Manuscript accepted July 23, 2018
Published online October 6, 2018
Manuscript handled by M. Satish-Kumar