Redistribution of magnetite during multi-stage serpentinization: Evidence from the Taishir Massif, Khantaishir ophiolite, western Mongolia

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Magnetite veins are commonly observed in serpentinized peridotite, but the mobility of iron during serpentinization is poorly understood. The completely serpentinized ultramafic rocks (originally dunite) in the Taishir Massif in the Khantaishir ophiolite, western Mongolia, contain abundant antigorite + magnetite (Atg + Mag) veins, which show an unusual distribution of Mag. The serpentinite records multi-stage serpentinization in the order: (1) Atg + lizardite (Lz) with a hourglass texture (Atg–Lz); (2) thin vein networks and thick veins of Atg; (3) chrysotile (CtI) that cuts all earlier textures. Mg# values of the Atg–Lz (0.94–0.96) are lower than those of the Atg (~ 0.99) and chrysotile (~ 0.98). In the Atg–Lz regions, magnetite occurs as arrays of fine grains (<50 µm) around the hourglass texture, and magnetite is absent in the thin Atg vein networks replacing Atg–Lz. Magnetite occurs as coarse grains (100–250 µm) in the center of some thick Atg veins. As the volume ratio of thin Atg veins to Atg–Lz increases, both the modal abundance of Mag and the bulk iron content decrease. These features indicate that hydrogen generation occurred mainly during Atg–Lz formation, and that the Mag distribution was largely modified by dissolution and precipitation in response to the infiltration of the higher temperature fluids associated with the Atg veins. The transport of iron during redistribution of Mag in the late-stage of serpentinization is potentially important for ore deposit formation and modifying the magnetic properties of ultramafic bodies.

Keywords: Serpentinization, Magnetite, Antigorite, Iron mobility, Khantaishir ophiolite, Taishir Massif

INTRODUCTION

Serpentinization of mantle peridotites in the oceanic lithosphere and subduction mantle wedges has an important role in various processes, including global water circulation, seismic activity in subduction zones, and hydrogen and hydrocarbon generation that sustains microbial activity on the seafloor. During serpentinization, the iron component in olivine is oxidized to magnetite, which results in hydrogen production (Klein et al., 2014), with the typical reaction being Olivine + H2O = Serpentine + Brucite + Magnetite + Hydrogen. Therefore, progressive serpentinization of mantle peridotite in the oceanic lithosphere results in an increase of magnetic susceptibility as well as a decrease in rock density (Ou 2002; Klein et al., 2014). However, the distribution of magnetite is not always uniform in serpentinites, and serpentinites without magnetite have been reported in many localities. Magnetite formation and the behavior of iron during serpentinization are potentially controlled by temperature (Evans 2008, 2010; Klein et al., 2014), silica activity (Frost and Beard 2007; Ogasawara et al., 2013; Oyanagi et al., 2018) and the presence of Fe(III)-serpentine and/or Fe-rich brucite (Bach et al., 2006). For example, magnetite is absent in bastite after orthopyroxene, due to the high silica activity in the orthopyroxene region (Ogasawara et al., 2013; Oyanagi et al., 2018). Evans (2008, 2010) suggested that magnetite is not formed during high-temperature serpentinization associated with antigorite, because the Fe²⁺Mg¹ potential of olivine is high. In outcrops of serpentinite, magnetite is often observed as distinct veins, and magnetite ores can be formed (Hodel et al., 2017), suggesting that iron is mobile.

In this paper, we describe a novel microtexture of magnetite in serpentinite, which consists mainly of a mixture of antigorite + lizardite and antigorite veins, in the Taishir Massif of the Khantaishir Ophiolite, western...
Mongolia. Based on detailed petrographic observations and mineralogical analyses of the serpentinite and veins, we demonstrate that magnetite was redistributed in response to fluid infiltration during multi-stage serpentinization.

GEOLGICAL BACKGROUND AND SAMPLE

The Khantaishir ophiolite is located in western Mongolia and is part of the Central Asian Orogenic Belt (Fig. 1a). The ophiolite comprises ultramafic rocks, gabbros, sheeted dikes, pillow lavas, and pelagic sediments, and previously published geochemical data for the igneous rocks have indicated an origin in a suprasubduction zone (Gianola et al., 2017). The ophiolite is divided into two massifs: the Taishir and Naran Massifs (Fig. 1b). The Naran Massif comprises a thick ultramafic body that consists of meta–harzburgite and dunite and a thin section of crustal rocks (Gianola et al., 2017; Dandar et al., 2019). In contrast, the Taishir Massif contains a thin body (2 km) of ultramafic rocks and thick section of crustal rocks (gabbros = 1.8 km; volcanic rocks = 2.5 km). The meta–harzburgite in the Naran Massif contains both primary and secondary olivine, and the latter formed after orthopyroxene during antigorite formation (Dandar et al., 2019). In contrast to the Naran Massif, the ultramafic rocks in the Taishir Massif are completely serpentinized and experienced intense shear deformation.

ANALYTICAL METHODS

The identification of serpentine was conducted with a Raman spectrometer (Horiba XploRa) coupled to an Olympus BX51 microscope at Tohoku University, Japan. A microscope with a 100× objective lens was used to focus an incident laser beam (532 nm green laser with 1800 grooves/mm grating) into a 1 µm spot size and collect the Raman spectra from the sample. The serpentine minerals were determined based on Schwartz et al., (2013).

The chemical compositions of minerals in a thin section were determined by wavelength-dispersive X-ray spectrometry and an electron probe microanalyzer (EPMA; JEOL JXA8200) at Tohoku University. The accelerating voltage was 15 kV, the beam current was 12 nA for quantitative analyses and 120 nA for element mapping, and the beam diameter was 1 µm. Based on the elemental maps, a mineral map was created with XMaptools software (Lanari et al., 2014). Given that chrysotile cannot be distinguished from other serpentine minerals solely based on elemental maps, we traced the outline of chrysotile using photomicrographs.

MINERALOGY AND MICROSTRUCTURE

The analyzed sample (14080901A) consists of serpentine minerals, magnetite, Cr–spinel, and a minor amount of heazlewoodite (Fig. 2a). Olivine and pyroxenes do not occur in the sample. Based on the Raman spectra, three types of serpentine minerals were identified: a mixture of antigorite and lizardite (Atg–Lz), antigorite (Atg), and chrysotile (Ctl).

The Atg–Lz occurs in the matrix with a hourglass texture, and is pale green in color (Figs. 2b and 2c). Each hourglass texture exhibits relatively uniform extinction under cross-polarized light and is outlined by magnetite grains. The Atg is colorless and occurs as thick veins.
cutting the hourglass texture (Fig. 2a) or as thin vein net-works that propagate from the thick veins (Figs. 2b and 2c). The thick Atg veins are formed as filling of open

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OCCURRENCES OF MAGNETITE

Magnetite occurs mainly as arrays of fine grains (<50 µm) along the outlines of the hourglass texture of Atg–Lz (Figs. 2b and 4a). In contrast, magnetite tends to be absent within the network of thin Atg veins, but some does occur as coarse grains (100–250 µm) in the center of the thick Atg veins (Figs. 2a and 4a). Magnetite also occurs in the chrysotile veins and as rims on spinel grains (<50 µm; Fig. 4a).

In the mineral map of a 20 × 4 mm area (pixel size of 4 µm; Fig. 4a), there are several thick, parallel, Atg veins at x = 6, 13, 14, and 16–18 mm, and networks of thin Atg veins extend into the Atg–Lz. Based on the mineral map and representative mineral compositions, we determined the modal abundance of minerals across the thick antigorite veins (Fig. 4b) and the bulk Fe content of the analyzed area. \(X_{Fe,bulk} = \frac{Fe}{(Fe + Mg)}\) as molar ratio of total Fe and Mg (Fig. 4c). The modal abundances of Atg–Lz and magnetite decrease when that of Atg increases (Figs. 4a and 4b). The bulk Fe content of the analyzed area also decreases from 0.1–0.4 in the region of the Atg–Lz hourglass texture to almost zero in the thick Atg veins (Fig. 4c). We also quantified the extent of the replacement of the Atg–Lz by the thin Atg network veins as the areal ratio \(Y_{Atg.net} = A_{Atg.net}/(A_{Atg.net} + A_{Atg-Lz})\) along the vertical lines shown in Figure 4a, where \(A_{Atg.net}\) and \(A_{Atg-Lz}\) are the areas of the thin Atg vein networks (i.e., excluding the areas of the thick Atg veins, coarse magnetite, and chrysotile) and Atg–Lz, respectively. In the matrix excluding thick Atg veins, the modal abundance of magnetite \(A_{Mag}\) decreases with increasing \(Y_{Atg.net}\) (Fig. 4d).

Figure 4. Relationship between Mag and Srp. (a) Mineral map obtained using Xmaptools software (Lanari et al., 2014). Gray arrows mark the Atg–reaction zone used for mass balance calculation. (b) Modal mineralogy. (c) \(X_{Fe,bulk} = \frac{Fe}{(Fe + Mg)}\) as a molar ratio and area of magnetite vs. distance (mm). Red indicates moving-average in 1mm of the \(X_{Fe,bulk}\). Blue indicates \(A_{Mag}\) which is equal to area of magnetite. (d) \(A_{Mag} \text{ versus } Y_{Atg.net} = \frac{A_{Atg.net}}{A_{Atg.net} + A_{Atg-Lz}}\) plot. \(A_{Atg.net}\) is equal to the area of the thin Atg network. Abbreviations are the same in Figure 2. Color version is available online from https://doi.org/10.2465/jmps.201130a.
DISCUSSION

As there is no evidence of pyroxene and bastite in the sample, the protolith was likely dunite. This sample did not form brucite in the Atg–Lz and Atg stages. The lack of brucite is consistent with the lower Mg/Si ratios of serpentinites in the Taishir Massif (Dandar et al., 2019) and suggests serpentinization was associated with input of silica. One key characteristic is the presence of hourglass Atg–Lz with magnetite. Based on the serpentine minerals present and temperature estimates from surrounding metamorphic rocks, Schwartz et al. (2013) reported that a mixture of Atg–Lz formed at higher temperatures (340–380 °C) than lizardite (<340 °C), but lower temperatures than typical antigorite. The Raman spectra of the Atg–Lz in the Taishir Massif (Fig. 3a) are similar to those presented in Schwartz et al. (2013). Evans (2010) also suggested that high-temperature serpentinization (i.e., 400–600 °C) tends to proceed without magnetite formation as Fe³⁺Mg⁻⁻ diffusion of olivine can proceed faster at higher temperatures. Therefore, we consider that initial serpentinization (Atg–Lz + Mag) occurred at a higher temperature than the stability field of lizardite + brucite and at a lower temperature than that where olivine compositions can be modified by diffusion (i.e., ~ 340–400 °C).

During Atg–Lz formation, magnetite crystallized uniformly along the outlines of the hourglass texture, meaning that pervasive fluid infiltration occurred (Figs. 2b and 4a). At this stage, olivine in the dunite was completely serpentinized to produce a large amount of hydrogen. The thick Atg veins and thin Atg vein networks have Raman spectra typical of antigorite, indicating the infiltration of higher temperature fluids than in the Atg–Lz stage. Thermodynamic calculations suggest that ferric iron is incorporated in Fe(III)–serpentine rather than magnetite at higher silica activity or lower oxygen fugacity (Frost and Beard 2007; Oyanagi et al., 2018). However, given that the iron content of the Atg–Lz (Mg# = 0.94–0.97) is higher than that of the Atg (Mg# ~ 0.99; Fig. 2b), the absence of magnetite in the thin Atg vein networks cannot be explained by the iron content of the serpentine although we are unable to determine the ferric/ferrous iron ratio of the Atg–Lz and Atg. In contrast, we performed a simple mass-balance calculation on iron assuming a constant volume during replacement of the Atg–Lz by the thin Atg veins. For the calculation, we assumed (1) the Atg–reaction zone (Atg 38%, Atg–Lz 55%, Mag 8%; gray arrows in Fig. 4a) was formed by the replacement of the Atg–Lz with the hourglass texture (Atg–Lz 84%, Mag 16%) by the thin Atg vein networks, and (2) at least a part of iron from the Atg–reaction zone precipitated in the thick Atg veins. In Figure 4a, the area of the Atg–reaction zone (indicated by gray arrows) is 0.43 mm², and the area of magnetite in thick antigorite is 0.02 mm². Based on mass balance calculation with assuming the thickness of 0.01 mm of the thin section, iron loss (~5.3 × 10⁻⁵ g) from the Atg–reaction zone is estimated to be ~2 times larger than the iron content (2.4 × 10⁻⁵ g) of magnetite which precipitated in the thick Atg veins (Figs. 4a and 4c). This implies that the half of iron loss was precipitated as coarse magnetite whereas the half was transported at least in thin section scale. The textures (Figs. 2a and 2b and 4a), spatial distribution (Figs. 4b–4d), and mass-balance relationships indicate that magnetite surrounding the hourglass serpentine was dissolved during fluid infiltration along the thin Atg vein networks, and that iron was re-precipitated in the thick antigorite veins (Figs. 2d and 2e). Such dissolution and precipitation of magnetite could be due to local differences in oxygen fugacity and silica activity (Schwarzenbach et al., 2016) between the matrix (i.e., the hourglass serpentine) and open cracks (i.e., the thick Atg veins). As some thick Atg veins has high Al

Table 1. Representative electron microprobe data (in wt%) and calculated structural formula (in a.p.f.u)

| Samples | Serpentine | Spinel |
|---------|------------|--------|
|         | Atg-Lz     | Atg    | Ctl   |
| SiO₂    | 41.97      | 43.38  | bdl   |
| TiO₂    | bdl        | bdl    | bdl   |
| Al₂O₃   | 0.68       | 0.43   | 0.55  |
| Cr₂O₃   | 0.08       | 0.09   | 0.16  |
| FeO     | 3.22       | 0.65   | 1.21  |
| MnO     | 0.04       | 0.10   | 0.03  |
| CaO     | 0.04       | 0.01   | 0.01  |
| MgO     | 40.00      | 40.53  | 30.34 |
| NiO     | 0.04       | 0.80   | 0.10  |
| Na₂O    | 0.02       | 0.04   | 0.06  |
| Total   | 86.10      | 85.31  | 85.69 |

Cations of serpentines are calculated for 7 oxygen for comparison of different serpentine species. Mg# = Mg/(Mg + Fetot). Cr# = Cr/(Cr + Al + Fe³⁺). bdl, below detection limit; n.a, below <0.01; Atg-Lz, antigorite and lizardite; Ctl, chrysotile; Atg, antigorite.

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contents (Fig. 3b), aluminum also was transported from the Atg–reaction zone of Atg–Lz to the thick Atg veins.

Our study indicates that magnetite-rich veins (Fig. 1c) did not always form at the stage of olivine serpentinization which accompanied with hydrogen generation, but reflect redistribution of magnetite that formed during multi-stage serpentinization. Such redistribution of magnetite is a potential indicator of hydrothermal fluid activity in serpentinized mantle rocks (e.g., Hodel et al., 2017). Hodel et al. (2017) suggested that late chlorine-rich hydrothermal fluids enhance the mobility of transient metals and are associated with formation of large magnetite veins. Our results show that hot hydrothermal fluids were infiltrated during the late stages of serpentinization of the Taishir Massif. This fluid activity may have been associated with antigorite formation in the Naran Massif, and a response to the infiltration of fluids derived from the subducting slab during the evolution of the Khantaishir ophiolite (Dandar et al., 2019). Further studies are necessary to determine the nature of the fluids associated with magnetite redistribution and their link to tectonic processes.

ACKNOWLEDGMENTS

We thank O. Gerel, B. Munkhtsengel, and B. Batkhishig for introducing us to this field of study and providing advice. U. Burenjargal, B. Undarmaa, and D. Tsendbazar are thanked for assistance in the field. This research was supported by JSPS KAKENHI Grant Numbers 16H06347, 17H02981, and 18KK0376 to A.O. and JP25000009 to N.T.

SUPPLEMENTARY MATERIALS

Color version of Figures 1–4 is available online from https://doi.org/10.2465/jmps.201130a.

REFERENCES

Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., et al. (2006) Unraveling the sequence of serpentinization reactions: Petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). Geophysical Research Letters, 33. https://doi.org/10.1029/2006GL025681

Dandar, O., Okamoto, A., Uno, M., Oyanagi, R., et al. (2019) Formation of secondary olivine after orthopyroxene during hydration of mantle wedge: evidence from the Khantaishir Ophiolite, western Mongolia. Contribution to Mineralogy and Petrology, 174. https://doi.org/10.1007/s00410-019-1623-1

Evans, B.W. (2008) Control of the products of serpentinization by the Fe2+-Mg–I exchange potential of olivine and orthopyroxene. Journal of Petrology, 49, 1873–1887.

Evans, B.W. (2010) Lizardite versus antigorite serpentinite: Magnetite, hydrogen, and life? Geology, 38, 879–882.

Frost, R.B. and Beard, J.S. (2007) On silica activity and serpentinization. Journal of Petrology, 48, 1351–1368.

Gianola, O., Schmidt, M.W., Jagoutz, O. and Sambu, O. (2017) Incipient boninitic arc crust built on denudated mantle: the Khantaishir ophiolite (western Mongolia). Contribution to Mineralogy and Petrology, 172, 1–18.

Hodel, F., Macouin, M., Triantafyllou, A., Carludt, J., et al. (2017) Unusual massive magnetite veins and highly altered Cr-spinels as relics of a Cl-rich acidic hydrothermal event in Neo-protorozoic serpentinites (Bou Azzer ophiolite, Anti-Atlas, Morocco). Precambrian Research, 300, 151–167.

Ishii, T., Robinson, P.T., Mackawa, H. and Fiske, R. (1992) Petrological studies of peridotites from diapiric serpentinite sea-mounts in the Izu-Ogasawara-Mariana Forearc, Leg 125. In Proceedings of the Ocean Drilling Programs, Scientific Results 125 (Fryer, P., Pearce, J.A., Stokking, L.B., et al. Eds.). Ocean Drilling Program, College Station, Texas, 445–486.

Jahn, B., Wu, F. and Chen, B. (2000) Granitoids of the Central Asian Orogenic Belt and continental growth in the Phanerozoic. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 91, 181–193.

Klein, F., Bach, W., Humphris, S.E., Kahl, W.-A. and Jöns, N. (2014) Magnetite in seafloor serpentinite—Some like it hot. Geology, 42, 135–138.

Lanari, P., Vidal, O., De Andrade, V., Dubacqdef, B., et al. (2014) XMapTools: A MATLAB®-based program for electron microprobe X-ray image processing and geothermobarometry. Computers & Geosciences, 62, 227–240.

Ogasawara, Y., Okamoto, A., Hirano, N. and Tsuchiya, N. (2013) Coupled reactions and silica diffusion during serpentinization. Geochimica et Cosmochimica Acta, 119, 212–230.

Outi, O. (2002) Magnetic properties of variably serpentinized abyssal peridotites. Journal of Geophysical Research, 107. https://doi.org/10.1029/2001jb000549

Oyanagi, R., Okamoto, A., Harigane, Y. and Tsuchiya, N. (2018) Al-zoning of serpentine aggregates in mesh texture induced by metasomatic replacement reactions. Journal of Petrology, 59, 613–634.

Schwartz, S., Guillot, S., Reynard, B., Lafaya, R., et al. (2013) Pressure-temperature estimates of the lizardite/antigorite transition in high pressure serpentinites. Lithos, 178, 197–210.

Schwarzenbach, E.M., Caddick, M.J., Beard, J.S. and Bodnar, R.J. (2016) Serpentinization, element transfer, and the progressive development of zoning in veins: evidence from a partially serpentinized harzburgite. Contribution to Mineralogy and Petrology, 171, 1–22.

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