Compositional variation of talc in metamorphosed serpentinites from Southwest Japan

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Compositional variations of talc in peridotites and serpentinites could have significant implications for modeling of geochemical cycles involving the upper mantle but have been scarcely studied. We analyzed chemical compositions of prograde and retrograde talc and associated minerals in thermally metamorphosed serpentinites from Southwest Japan. The analyzed talc has variations of Si, Al, Mg, Fe, and Na contents. Most of the Si, Al, Mg, and Fe variations indicate mechanical mixing with serpentine and chlorite at a submicroscopic scale. Spatial distribution of talc-chlorite mixtures suggests their prograde metamorphic origin. Talc-serpentine mixtures could be formed by retrograde decomposition of talc-olivine assemblage and orthopyroxene at conditions of higher temperature and/or higher Si activity than serpentine-brucite mixtures, which are the typical products of serpentinization of olivine. Talc itself, regardless of prograde or retrograde origin, has compositional variations with Na enrichment as a likely result of solid solution or Na-mica mixing. The Na enrichment suggests that talc could be the most capable reservoir of Na in metamorphosed peridotites and serpentinites.

Keywords: Talc, Prograde metamorphism, Retrograde metamorphism, Peridotite, Serpentinite

INTRODUCTION

Talc is a common mineral in metamorphosed peridotites and serpentinites. Its formation requires the addition of water and silica to original peridotites and results in a drastic change of the physical properties of the rocks (e.g., Moore and Rymer, 2007). Therefore, the chemical compositions and formation conditions of talc are essential for modeling geochemical cycles and tectonic processes involving the upper mantle. It is believed that talc in metaperidotites commonly has almost the ideal composition Mg₃Si₄O₁₀(OH)₂, and physicochemical conditions of its formation are usually inferred from phase equilibria in the simplified system MgO-SiO₂-H₂O (e.g., Evans and Guggenheim, 1988). However, our preliminary analyses of talc in metaperidotites have detected a considerable deviation from its ideal composition. To clarify the extent and cause of compositional variations, we analyzed talc and associated minerals in metaperidotites and serpentinites from the contact aureoles of the Oeyama ophiolite, Southwest Japan, where metamorphic zones and parageneses have been established.

GEOLOGICAL SETTING

The Oeyama ophiolite is the collective name of ultramafic complexes originated at a Paleozoic supra-subduction zone and exposed in the Renge high-P/T metamorphic belt (e.g., Ishiwatari, 1989; Nishimura, 1998; Khedr and Arai, 2010). The ophiolite was subjected to amphibolite-facies (700-800 °C) metasomatic hydration, high-to medium-T (300-600 °C) serpentinization with Fe-monticellite formation, and low-T (<300 °C) serpentinization (Nozaka, 2014, 2018, 2020). The serpentinitized peridotites were thermally metamorphosed by Cretaceous-Paleogene granitic intrusions, and their contact aureoles have been divided into four or five metamorphic zones: Zone I is almost unaffected by thermal metamorphism, and Zones II, III, IV, and V are characterized by the first appearance of metamorphic olivine, talc, anthophyllite, and orthopyroxene (Opx), respectively, indicating increasing temperatures of metamorphism from Zone I to V (Arai, 1975; Matsumoto et al. 1995; Nozaka, 2003, 2011; Nozaka and Ito, 2011; Khedr and Arai, 2012).

ANALYTICAL PROCEDURES

Polished thin sections of 5 samples of metaserpentinite
from Zone III (Talc Zone) and 4 samples from Zone V (Opx Zone) of the Ohsayama, Tari-Misaka, Oeyama and Happo complexes were selected for petrographic observations and microprobe analyses.

Microprobe analyses were carried out using an electron probe microanalyzer (EPMA, JEOL JXA-8230) at Okayama University with an accelerating voltage of 15 kV, a probe current of 20 nA, a beam diameter of 3 µm and a counting time of 6 s for each element. Standards used were natural or synthetic oxides and silicates. Matrix corrections followed the procedures of Bence and Albee (1968) with alpha factors of Nakamura and Kushiro (1970).

The identification of sheet silicates was confirmed by supplementing optical characteristics and chemical compositions with Raman shift spectra, using a Raman spectrometer (JASCO NRS-3100) at Okayama University, with 488 nm laser excitation.

**RESULTS**

All the minerals were initially identified on the basis of optical characteristics, among which birefringence is the most critical for the sheet silicates observed. However, especially in fine-grained aggregates, individual grains are too small to be optically identified and have chemical compositions indicative of the mixing of different kinds of minerals as described below. This means that the optical identification is erroneous; however, mineral names determined under the microscope are used hereafter for consistency.

In Zone III, talc typically occurs as fine-grained (<0.1 mm) aggregates with obscured grain boundaries to form the matrix of granoblastic olivine and tremolite (Figs. 1a and 1b). Metamorphic olivine characteristically contains minute grains of opaque minerals (mainly magnetite), which were produced during serpentinization before thermal metamorphism (e.g., Nozaka, 2003), and is cut by serpentine veins. Representative samples of the serpentine veins show Raman shift spectra of lizardite. Chlorite typically fringes relict grains of primary chromite or Cr-spinel, which has been compositionally modified by serpentinization and/or thermal metamorphism (e.g., Arai, 1975).

In Zone V, talc cuts or replaces metamorphic Opx (Figs. 1c and 1d), which contains inclusions of magnetite and metamorphic olivine. Talc typically forms fine-grained (<0.1 mm) aggregates and locally occurs as platy grains up to 0.5 mm long. Serpentine (lizardite) veins cut olivine and Opx. Serpentine and talc veins cutting Opx are similar in width and connected with each other to form composite vein networks (Fig. 1d).

Chemical compositions of sheet silicate minerals (Supplementary Table S1: available online from https://doi.org/10.2465/jmps.211112) show systematic variations indicative of mixing with other minerals as follows. Increases of Mg + Fe with decreasing Si indicate mixing trends of talc-serpentine and serpentine-brucite in both
Figure 2. Chemical compositions of talc and other sheet silicates. The amounts of cations were calculated on the basis of 11 oxygen atoms and total iron as Fe$^{2+}$. (a) Mg + Fe versus Si. The ideal composition of Chl is that of clinochlore. (b) Al versus Si. (c) Fe versus Si in Zone III. (d) Fe versus Si in Zone V. (e) Interlayer charge (IC) versus Si. IC was calculated assuming TOT-trioctahedral phyllosilicates with the tetrahedral site occupied by Si with or without Al and Cr. (f) $H_2O$ wt% versus Si. See text for $H_2O$ wt% estimation. (g) $H_2O$ wt% versus Na$_2$O wt%. (h) 100 × Na versus Si. (i) Al versus Si. (j) 100 × Na versus Al. (k) Al + Na versus Si + Mg + Fe. For (h)–(k), talc compositions with Si > 3.1 and Al < 0.25 were selected. Abbreviations: Br, brucite; His, hisingerite; Liz, lizardite; M, metamorphic; P, primary; Phl, phlogopite; Prg, paragonite; Pw, preiswerkite; Sap, saponite; SS, solid solution; others are the same as those of Figure 1.
Zones III and V (Fig. 2a). Some grains of Zone III talc show an Al-enrichment trend indicative of mixing with chlorite (Fig. 2b). Consistently, Raman shift analyses of representative samples showed peaks suggestive of mechanical mixing of these minerals at a submicroscopic scale.

The data points of Fe versus Si (Figs. 2c and 2d) for talc showing the effect of mixing with serpentine are distributed within an area between the lines connecting the compositions of talc and metamorphic olivine with Mg# [(= 100 × Mg/(Mg + Fe)] ranging from 85 to 98 in Zone III and from 85 to 96 in Zone V, displaying an average trend through talc (Mg# 99) and lizardite (Mg# 93), which corresponds to a trend toward the approximate composition of primary olivine with Mg# ~ 91 (for primary and metamorphic olivine compositions, see Nozaka, 2003, 2011). By contrast, serpentine veins cutting olivine show trends indicative of the mixing of lizardite (Mg# = 96) with brucite (Mg# = 75 in Zone III and 80 in Zone V). The distinct mixing trends of talc-serpentine and serpentine-brucite were observed even within the same samples. Compared with serpentine veins of Zone III, those of Zone V show more scattered Fe-Si plots, suggesting a mixing effect of Fe³⁺-lizardite, hisingerite or talc formed by Opx decomposition (Fig. 2d). Interlayer charges (IC) indicate that talc has little effect of saponite mixing (Fig. 2e; for calculation procedures of IC and saponite compositions, see Newman and Brown, 1987; Nozaka et al., 2008).

Evidence for the mixing of talc with serpentine or chlorite is also shown by the increasing amount of H₂O, which was estimated from microprobe analyses, i.e., residuals of the total amounts of analyzed oxides [= 100 × (SiO₂ + TiO₂ + Al₂O₃ + Cr₂O₃ + FeO* + MnO + NiO + MgO + CaO + Na₂O + K₂O) wt%]. Talc with H₂O higher than typical contents (4–5 wt%) shows a decreasing trend of Si, accompanied by increasing Mg + Fe or Al, as expected for the effects of serpentine or chlorite mixing (Fig. 2f). The mixing effects are also detected by slight enrichments of Cr₂O₃ (<1.91 wt%) and CaO (<1.24 wt%), which are concentrated in chlorite and Opx-cutting serpentine, respectively. Other minor components (Table S1) show no clear deviation from typical talc compositions, except for Na₂O, which tends to be higher in talc with little excess H₂O and lower with increasing H₂O (Fig. 2g).

**DISCUSSION**

The distribution and mode of occurrence of talc suggest its prograde and retrograde metamorphic origin in Zone III and Zone V, respectively. The Al enrichment with a gentle increase of Mg + Fe in Zone III talc (Figs. 2a and 2b) is an indication of chlorite mixing with some possible effects of retrograde serpentine mixing. Because chlorite was stable during prograde metamorphism (e.g., Nozaka, 2011) and its mixing effect on talc composition is not detectable in Zone V, the talc-chlorite mixture is probably a product of prograde metamorphism at T = 500–600 °C (for T estimation, see Nozaka, 2011). The compositional variation of talc without Al enrichment in Zone III (Figs. 2a, 2c, and 2e) can be explained as the result of mixing with serpentine produced by a retrograde reaction between talc and olivine at T < 500 °C with a silica activity (point ① in Fig. 3) higher than that for brucite formation (point ②). Although T condition for retrograde talc in Zone V is not well constrained, if talc and serpentine have formed contemporaneously as suggested by the composite vein networks cutting Opx, then its T could be somewhat higher (>500°C; point ③, Fig. 3) than that of the serpentinitization of the talc–olivine assemblage (point ①). The presence of two distinct mixing trends, i.e., talc-serpentine and serpentine-brucite trends (Figs. 2c and 2d), within the same samples suggests a difference of silica activity between talc- and brucite-bearing domains, i.e., a limited scale of Si diffusion during serpentinitization.

The enrichment of Na in talc without increasing H₂O (Fig. 2g) cannot be explained by mixing with chlorite, serpentine nor smectites containing large amounts of H₂O, and talc itself looks rich in Na. To eliminate the
mixing effects of serpentine and chlorite as much as possible, talc compositions with high Si (>3.1) and low Al (<0.25) were selected to plot, and those with low H2O (<6.0 wt%), close to the ideal composition of magnesian talc are highlighted in Figures 2h–2k. The compositional variations of talc with the least effects of serpentine and chlorite mixing can be explained by the formation of a solid solution, in which the exchange of Si with Al (tetrahedral site) + Na (interlayer site) is dominant; however, they show a slight deviation from 1:1 exchange trends (Figs. 2h–2j). To fit the compositional variations, considering the octahedral-site occupancy of the talc analyzed (~3.0 with almost no vacancy, i.e., O2 = (Al + Cr, not in tetrahedral site) + Mg + Fe + Ni + Mn > 3.0, Table S1) as well, a more likely exchange trend is expressed by 5Si + (Mg, Fe) = 4Na + 6Al (Figs. 2h–2k), which is the integration of Si4+ = Na+ + Al3+ and Si4+ + (Mg, Fe)2+ = 2Al3+ with approximately 80 and 20% contribution, respectively.

The observed compositional variation of talc can also be explained by the mixing of Na-phlogopite and preiswerkite (Figs. 2h–2k), as referred to by Schreyer et al. (1980). However, because of their small amounts, if any (<5% in most cases of our talc analyses), it seems difficult to detect the Na–micas, which have crystal structures similar to talc, using an ordinary XRD or Raman spectrometer. The most promising way to detect them may be TEM analysis (e.g., Veblen, 1983), which will be included in subsequent studies. Instead it is noted here that Na enrichment is observed exclusively in ‘talc’ and not in serpentine, chlorite, nor clay minerals (Figs. 2g and 2h). Even if the ‘talc’ is Na-rich talc–Na-mica mixture, the talc and Na-mica should have a close genetic link, e.g., exsolution from precursor Na-rich talc.

Because the Na enrichment occurs both in prograde and retrograde talc (Figs. 2h–2k), the compatibility of Na seems to be one of the common characteristics of this mineral. The Na contents of talc reported here are similar to or higher than those of Na–Al talc in metavolcanics from Vermont (Spear et al., 1981). Considering much Na-depleted rock compositions, talc is likely the most capable reservoir of Na in peridotites and serpentinites, although its Na content could be variable probably depending on the compositions of the original rocks and infiltrated fluids. Amphibole is another phase that may contain a considerable amount of Na in metaperidotites, and in fact, the occurrence of Na–enriched amphiboles in metasomatized or thermally metamorphosed peridotites has been reported; however, these amphiboles formed at higher T than talc, whereas tremolitic amphiboles coexisting with talc are deficient in Na (e.g., Nozaka, 2005; Khedr and Arai, 2010; Nozaka, 2011; Khedr and Arai, 2012; Nozaka, 2014). The compatibility of Na with talc has significant implications for geochemical cycling associated with Si metasomatism of peridotites in variable tectonic settings. It is encouraged to conduct further analyses of talc in peridotites and serpentinites from many localities with special caution to avoid the effects of mixing with other minerals.

**CONCLUDING REMARKS**

Compositions of talc in thermally metamorphosed serpentinites from Southwest Japan are apparently variable due to submicroscopic mixing with serpentine and chlorite. Talc–chlorite mixtures are likely a product of prograde metamorphism. Talc–serpentine mixtures could be formed by retrograde decomposition of prograde talc–olivine assemblages and Opx at conditions of higher T and/or higher Si activity (with a limited Si diffusion) than serpentine–brucite mixtures, which were formed by the serpentization of olivine. Talc itself, regardless of prograde or retrograde origin, has compositional variations with Na enrichment, suggesting that talc could be the most capable reservoir of Na in metamorphosed peridotites and serpentinites.

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**SUPPLEMENTARY MATERIAL**

Supplementary Table S1 is available online from https://doi.org/10.2465/jmps.211112.

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