Titanian andradite in the Nomo rodingite: Chemistry, crystallography, and reaction relations

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Titanian andradite and hydroandradite containing up to ~10 wt% TiO2 were identified in rodingite as well as the host serpentinite in a sample obtained from the Nomo unit, Nagasaki Metamorphic Rocks (western Kyushu, Japan), representing a Cretaceous subduction complex. The rodingite consists of garnet (solid solution among three end-member compositions: grossular, andradite, and titanian hydrogarnet), diopside and chlorite, along with minor amounts of perovskite, ilmenite, and titanite. This assemblage was formed by metasomatism under conditions of epidote-blueschist facies metamorphism at 0.6–0.8 GPa and ~400°C. X-ray single crystal diffraction and chemical analyses determined the formula Ca3.00(Fe3+0.64Ti4+0.24Mg0.03V0.02Sc0.01Al0.06)(Si0.90Al0.03□0.07)3O11.35(OH)0.65, in which Fe3+ preferentially occupies the Y-sites and Ti is solely in the tetravalent state. We propose a new type of coupled substitution, Fe3+ +H+ +□ = Ti4+ +□, in the titanian andradite, indicating that it does not belong to the solid solution in the andradite-morimotoite-schorlomite system of the International Mineralogical Association (IMA) classification scheme. The Fe ions are ferric (Fe2+ is estimated to be 3% or less), showing that the formation of the titanian andradite occurred under oxidizing conditions. In the reaction zone, the titanian andradite overgrowth on the ilmenite and the partial replacement of the perovskite by titanian andradite show the incorporation of TiO2 into the garnet via reaction with TiO2-bearing minerals under relatively oxidizing conditions. In addition, the presence of andradite coronas around the magnetite rim formed from the alteration of primary chromite provides evidence of Ti mobility in the serpentinite. These reaction relations highlight the titanian andradite formation process and allow us to propose associated reactions based on the singular value decomposition method.

Keywords: Rodingite, Serpentinite, Titanian andradite, Melanite, Ilmenite, Perovskite

INTRODUCTION

Andradite rich in TiO2 up to 27 wt% commonly occurs in alkaline igneous rocks (Deer et al., 2013). In addition, andradite with moderate amounts of TiO2 (~10 wt%) occurs in skarns (e.g., Kusachi et al., 1975; Huggins et al., 1977a, 1977b) and serpentinites (e.g., Onuki et al., 1981). Some had been formerly named as melanite, a variety of Ti-bearing andradite (in which Fe3+ > Ti at the octahedral sites), and schorlomite, (Fe3+ < Ti) as in the standard text of rock-forming minerals (Deer et al., 2013). However, this classification scheme and the former name were abandoned in the new IMA classification scheme of garnet (Grew et al., 2013). Morimotoite {Ca3}[Ti4+Fe2+](Si3)O12 was defined as a new end-member, and Ti-rich garnets are described in the system andradite-morimotoite-schorlomite {Ca3}[Ti3+](SiFe2+)O12. Thus, the solid solutions between andradite and morimotoite can be characterized by a substitution of 2Fe3+ = Ti4+Fe2+ and those between andradite and schorlomite by 2Fe3+2Si4+ = 2Ti4+3Fe2+ (Grew et al., 2013). During the course of our study on rodingites in the Nomo unit (Fig. 1) within the Nagasaki Metamorphic Rocks, western Kyushu, Japan (Nishiyama et al., 2017), we identified Ti-bearing andradite containing up to ~10 wt% TiO2, in purple-colored rodingite (Figs. 2a and 2b). We named it ‘titanian andradite’ because the composition of this garnet does not fit in the IMA classification scheme as discussed later. Regarding Ti-rich garnets in the literature,
we cite them as Ti-rich andradite or Ti-rich garnets because it is not clear if they have the same chemistry and crystal structure as those of the Nomo titanian andradite. This material coexists with other TiO$_2$-bearing minerals, notably perovskite and ilmenite. In the serpentinite part of the specimen, andradite occurs as magnetite rims. Magnetite is formed by the alteration of primary chromite, preserved in the core of the grain. Rodingite represents the product of low-grade epidote–blueschist facies metamorphism under conditions of approximately 0.6–0.8 GPa and 400 °C based on the occurrence of omphacite and magnesio-riebeckite in metabasites associated with the serpentinite containing the rodingite. Fukuyama et al. (2014) reported that zircon from the Nomo rodingite can be dated to 108–105 Ma. Although grossular containing up to 3 wt% TiO$_2$ is common in the Nomo rodingites (Nishiyama et al., 2017), titanian andradite occurs in a limited region near Kawara–Koba, Nagasaki City (Fig. 1). Onuki et al. (1981) identified Ti-rich hydroandradites, containing up to 18.2 wt% TiO$_2$, within serpentinite in the Sanbagawa Metamorphic Rocks. They also reported that this hydroandradite contained a small amount of Ti$^{3+}$ as reduced cations, based on electron–probe analysis. The crystal chemistry of Ti-rich andradite is complicated, particularly with respect to the site preference and oxidation state of the Ti cations, and thus it has been the subject of considerable study. As an example, Huggins et al. (1977a, 1977b) examined high temperature Ti-rich andradite from alkaline igneous rocks and proposed the following coupled substitution process to account for Ti substitution in the garnet structures: Ti$^{4+}$ $\rightleftharpoons$ Si$^{4+}$, M$^{2+}$ + Ti$^{4+}$ $\rightleftharpoons$ 2M$^{3+}$, and Ti$^{3+}$ $\rightleftharpoons$ M$^{4+}$. In addition, they determined that the Ti cations were essentially all in the Ti$^{4+}$ oxidation state at high temperatures. Based on this prior work, we examined the titanian andradite from the Nomo unit, a relatively low-temperature variety, to elucidate the substitution processes involving Ti cations in the garnet structures. It is also important to determine the Ti oxidation state to interpret the reaction relations with the associated Ti-minerals, perovskite and ilmenite. To date, the genesis of Ti-rich andradite in low grade metamorphic rocks has not been studied in detail, thus we examined the reaction textures between the titanian andradite and TiO$_2$-bearing minerals, as well as between the titanian andradite and partially altered chromite. Based on the results, we report the reaction relations among these minerals during rodingite formation.

**OCCURRENCES**

The rodingite occurs as a dike–like body several tens of centimeters thick with a reaction zone at the contact with the serpentinite host (Nishiyama et al., 2017) at Kawara–Koba, Nagasaki City. Samples for the present study were collected from a number of blocks (Fig. 2a) or pebbles (Fig. 2b) near the outcrop. In contrast to the platy reaction zones previously described by Nishiyama et al. (2017), these samples show a complicated distribution of rodingite and serpentinite zones. This distribution can also be observed in the pebbles, in which a thin serpentinite part is included within the rodingite. In cases such as this, the transitional zone between the original dike and the serpentinite represents a succession of several thin reaction zones. The mineral paragenesis of titanian-andradite-bearing rodingite comprises a garnet solid solution between grossular and titanian hydrogarnet (later discussed in detail), diopside, and chlorite, with lesser amounts of perovskite, ilmenite, titanite, and apatite. In the present specimen, the garnet solid solution, diopside, chlorite, and perovskite are the major constituents of the reaction zone (Figs. 2d and 2e) while ilmenite, magnetite, and titanite occur as accessory minerals. The garnet solid solution in this reaction zone shows a narrower compositional range than that in the rodingite. In the serpentinite near the reaction zone, only andradite–rich garnet occurs, together with diopside and serpentinite (aluminum–rich antigorite), while the minor minerals are magnetite, partially altered chromite, and pentlandite. The titanian andradite shows several occurrence types in the samples. The prin-
Principal occurrence is as aggregates of tiny crystals forming layers, mottled or connected, in chlorite (Figs. 2c and 2e) and concentrated at the boundary between the reaction zone and the rodingite but also sometimes occurring dispersed in the rodingite. Each crystal is typically less than 40 μm in size and has a fairly homogeneous deep red-brown color under plane polarized light. The titanian andradite for the single crystal X-ray diffraction analysis was extracted from this part of the specimen (Fig. 2d). In the serpentinite, the grains of titanian andradite are larger (approximately 100 μm) than those in the reaction zone and in the rodingite and have a deep red-brown color in the core but a transparent rim under plane polarized light (Fig. 2f). Other significant occurrences are re-

![Figure 2](image-url)
lated to reaction textures highlighted in back-scattered electron (BSE) images and are discussed in detail in the following section. Mineral abbreviations in the figures follow those provided in Whitney and Evans (2010).

**EXPERIMENTAL METHODS**

The chemical composition of the titanian andradite was determined using an energy-dispersive X-ray microanalyser [JEOL JSM-7001F field emission scanning electron microscope equipped with an Oxford AZtec energy-dispersive X-ray spectroscopy (EDS) system] at Kumamoto University operating at an accelerating voltage of 15 kV with a beam current of 1.02 nA and beam area of 2 × 2 µm². The EDS was equipped with a large caliber X-ray detector (20 mm²), a spectral separation, and X-ray absorption correction programs based on the X-ray pump-probe (XPP) method (Pouchou and Pichoir, 1988) with a high resolution for low-energy elemental lines. Standards used are CaSiO₃ for Si and Ca, Al₂O₃ for Al, TiO₂ for Ti, Fe₂O₃ for Fe, Mn for Mn, MgO for Mg, NaCl for Na, KBr for K, Cr₂O₃ for Cr, V for V, and Sc for Sc. The process time was set to optimize the conflicting relation between the X-ray counting rate and the spectral resolution. The TiKα₁, ScKα₂, VKα₁, and CrKα₁ lines were used for quantitative analyses of Ti, Sc, V, and Cr, respectively. The interference between the TiKβ₁ and VKα₁ lines was carefully checked.

Single crystal X-ray diffraction analysis of the titanian andradite garnet was performed using a SuperNova, single source at offset/far, HyPix3000 diffractometer in conjunction with monochromatic MoKα radiation generated at 50 kV and 0.8 mA. Systematic absence in the data was consistent with the Ia3d space group. A total of 3141 reflections were collected and the data were corrected for Lorentz and polarization factors based on a MoKα absorption coefficient, μ, of 4.907 mm⁻¹. Absorption correction was performed using the integration method on the basis of the observed arbitrary shape of each specimen. A total of 219 unique reflections were employed for refinement [with Fo > 2σ(Fo)] using the full matrix least square method.

Raman spectra of the titanian andradite (RZ in Table 1) were obtained using a LabRAM HR800 spectrometer (HORIBA Jobin Yvon, Edison, NJ, USA) combined with a Fandango 50 diode-pumped solid-state laser (Cobalt AB, Solana, Sweden, λ = 514.5 nm), a BX41 microscope (Olympus, Tokyo, Japan), and an LMPlanFL N 100 × objective (Olympus, Tokyo Japan, NA = 0.80) at Kumamoto University. A 50 mW laser power at the sample surface, a 1000-µm pinhole, a 100 µm slit, an 1800 lines/mm grating, a 30 s acquisition time, and a 3000–4000 cm⁻¹ spectral range were used for detection of the OH band.

**RESULTS**

**Chemistry**

In agreement with the typical characteristics reported for natural anhydrous TiO₂-bearing garnets (Huggins et al., 1977a, 1977b), these analyses also demonstrated that the number of divalent cations exceeds 3.0 apfu, the number of trivalent cations is less than 2.0 apfu, and the number of quadrivalent cations and (Si + Ti) exceeds 3.0 (even though Si is deficient at the tetrahedral sites). The titanian andradite characteristically contains Ti, Sc, and V (Table 1) and approximately one third of the octahedral Y sites are occupied by ions other than Fe. The empirical formula derived from the mean chemical composition of the titanian andradite from a specific garnet-rich layer from which the sample for the X-ray study was taken is Ca₂.₉₉(Fe²⁺₀.₈₇Ti⁴⁺₀.₅ₗMg₀.₀₂V₀.₀₇Sc₀.₀₂Al₀.₁₃)(Si₂.₆₉Al₀.₀₈□₀.₂₃)O₁₁.₃₅

| Zone | Ro  | Ro  | Ro  | Ro  | Srp | Srp | Srp |
|------|-----|-----|-----|-----|-----|-----|-----|
|      | n=4 | n=5 | n=4 | n=5 | n=1 | n=5 | n=1 |
| SiO₂ | 36.47 | 35.50 | 33.44 | 33.29 | 32.74 | 32.29 | 32.62 | 34.73 |
| TiO₂ | 1.00 | 4.15 | 5.45 | 6.60 | 8.50 | 10.28 | 8.21 | 0.31 |
| Al₂O₃ | 16.91 | 13.57 | 12.08 | 6.00 | 2.87 | 0.72 | 0.87 | 0.68 |
| Cr₂O₃ | 0.41 | - | 0.07 | - | 0.56 | 1.60 | 1.87 |
| Fe₂O₃ | 4.00 | 6.42 | 8.74 | 16.72 | 19.08 | 20.95 | 21.37 | 28.87 |
| MnO | - | - | 0.13 | - | - | - | - | - |
| MgO | 2.11 | 1.21 | 0.10 | - | 0.65 | 1.08 | 0.83 | - |
| CaO | 36.76 | 36.16 | 36.10 | 34.61 | 34.41 | 33.98 | 33.95 | 33.24 |
| V₂O₅ | 0.39 | 0.51 | 0.06 | 0.54 | - | 0.13 | - | - |
| Sc₂O₃ | 0.18 | 0.23 | 0.46 | - | 0.29 | 0.37 | - | - |
| Total | 97.25 | 98.07 | 96.75 | 97.49 | 99.36 | 99.86 | 100.04 | 99.07 |
| Si | 2.893 | 2.836 | 2.747 | 2.787 | 2.729 | 2.700 | 2.729 | 2.960 |
| Ti | 0.058 | 0.250 | 0.337 | 0.415 | 0.533 | 0.650 | 0.517 | 0.020 |
| Al | 1.578 | 1.278 | 1.170 | 0.592 | 0.282 | 0.070 | 0.086 | 0.070 |
| Cr | - | 0.026 | - | 0.004 | - | 0.040 | 0.106 | 0.060 |
| Fe⁺ | 0.235 | 0.386 | 0.540 | 1.054 | 1.197 | 1.320 | 1.345 | 1.850 |
| Mn | - | - | 0.009 | - | - | - | 0.010 | - |
| Mg | 0.250 | 0.144 | 0.013 | - | 0.081 | 0.130 | 0.104 | - |
| Ca | 3.120 | 3.096 | 3.178 | 3.105 | 3.074 | 3.040 | 3.044 | 3.030 |
| V⁶⁺ | 0.025 | 0.033 | 0.004 | 0.036 | - | 0.009 | - | - |
| Sc | - | 0.012 | 0.016 | - | 0.033 | - | 0.021 | 0.030 |
| Total | 8.133 | 8.051 | 8.035 | 7.971 | 7.964 | 7.970 | 7.971 | 8.020 |

Ro, RZ, and Srp are rodingite, reaction zone, and serpentinite, respectively. The number of oxygens is fixed at 12.
(OH)_{0.65}, where □ indicates vacancies (Table 2). This composition does not fit in the IMA classification of schorlomite in the diagram for andradite–morimotoite–schorlomite because Fe\textsuperscript{3+} occurs in the Y site instead of the Z site. Therefore, we developed a ternary Al–Ti–Fe\textsuperscript{3+} plot (Fig. 3) to describe the compositional range of the titanian andradite from the Nomo unit, although this diagram does not represent the proper substitution relation. The titanian andradite shows a wide compositional range by forming a solid solution with grossular. However, this compositional range depends on the lithology, that is to say, whether the grains are in the rodingite, reaction zone, or serpentinite. The titanian andradite from the serpentinite as well as some samples from the reaction zone showed total concentrations near 100 wt\% whereas the materials from the rodingite zone and some samples from the reaction zone were found to have totals of 97–98 wt\%, which are significantly less than 100 wt\% (Table 1). The Raman spectra of the latter showed characteristic OH bands (Fig. 4), indicating a variety of ‘hydrogarnet’ (i.e., titanian ‘hydroandradite’). As shown in Figure 3, the solid solution is formed not only between andradite Ca\textsubscript{3}Fe\textsubscript{2}Si\textsubscript{3}O\textsubscript{12} and grossular Ca\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{12} but also between hydrogrossular (katoite) Ca\textsubscript{3}Al\textsubscript{2}(□)\textsubscript{3}(OH)\textsubscript{12} and the hypothetical titanian hydrogarnet Ca\textsubscript{3}Ti\textsubscript{2}(□)\textsubscript{3}O\textsubscript{2}(OH)\textsubscript{10} as a Ti end member. The garnet in the serpentinite shows a small grossular (Ca) component because of the Al\textsubscript{2}O\textsubscript{3} paucity. In contrast, a wider compositional range containing up to 70 mol\% grossular is observed in the reaction zone. In the rodingite, the solid solution has the widest compositional range from Gr\textsubscript{s90}Ad\textsubscript{r10} to Gr\textsubscript{16}Ad\textsubscript{r51}Ti\textsuperscript{*33}, where Ti\textsuperscript{*} denotes the hypothetical Ti end member (titanian hydrogarnet). The compositional variation in the garnet occurs within one thin section, exhibiting a variation tendency to increase titanian andradite composition from rodingite to serpentinite through the reaction zone (Fig. 3). Variations in the

**Table 2.** Average chemical composition of titanian andradites

| Composition | Variance |
|-------------|----------|
| SiO\textsubscript{2} | 32.85 | 0.16 |
| TiO\textsubscript{2} | 7.57 | 1.87 |
| Al\textsubscript{2}O\textsubscript{3} | 2.22 | 2.43 |
| Cr\textsubscript{2}O\textsubscript{3} | 0.02 | 0.01 |
| Fe\textsubscript{2}O\textsubscript{3} | 21.01 | 8.32 |
| MnO | 0.00 | 0.00 |
| MgO | 0.47 | 0.17 |
| CaO | 34.08 | 0.25 |
| V\textsubscript{2}O\textsubscript{5} | 0.38 | 0.15 |
| Sc\textsubscript{2}O\textsubscript{3} | 0.21 | 0.07 |
| H\textsubscript{2}O* | 1.19 | |
| Total | 100.00 | 0.25 |

Wt\% as oxide, atomic unit when the oxygen number is 12 and each variance are indicated. H\textsubscript{2}O* is calculated as (100−total wt\% of other oxides).
TiO$_3$ content are apparent in each zone and even within individual grains. Grossular is the most abundant garnet in the fine-grained rodingite, except in the titanian-andradite-rich layers, but can be replaced by andradite at the rims. Moreover, even in some titanian-andradite-rich aggregates, small disseminated grossular grains occur. This can be clearly seen in the BSE image in Figure 5a based on the Fe content variations. Such changes reflect the significant lack of equilibrium in the rodingite formation, as previously discussed by Nishiyama et al. (2017), in conjunction with coexisting diopside and Fe-rich diopside. In the reaction zone, the andradite reaction textures with perovskite and ilmenite are conspicuous and the grossular content tends to decrease, along with the melanite, as the andradite content increases. These results suggest that the titanian andradite formed by consuming these TiO$_3$-bearing minerals. Finally, zoned garnets were identified in the serpentinite (Fig. 2f). The compositional range from nearly pure andradite to 35 mol% titanian hydrogarnet with a very low but constant grossular concentration (4–5% apfu) is shown in Figure 3. The compositional variation between the andradite and titanian hydrogarnet explains the color zoning observed under plane polarized light. In fact, these analyses confirm that Ti is richer in the deep red-brown core than in the rims. Thus, the deep red color of the mineral and the purple color of the samples (Figs. 2a and 2b) reflect the Ti content rather than the Fe concentration (Howie and Woolley, 1968). Moreover, the Fe is believed to solely exist in the Fe$^{3+}$ state at the octahedral sites. Thus, the previous suggestion that the deep red color is ascribed to Fe$^{2+}$ in octahedral or tetrahedral sites is believed to solely exist in the Fe$^{3+}$ state at the octahedral site.

**Crystallography**

Refinement was performed using the SHExL97 program (Sheldrick, 1997) via the least squares method applying a correction for isotropic extinction. The site occupancies were first analyzed based on a model in which octahedral Y sites were solely occupied by Fe and Ti and tetrahedral Z sites were only occupied by Si and Ti. The tetrahedral Z sites were occupied by elements with lower electron densities than that of Si. After several refinement cycles, the model Ca$_2$[Fe$_{0.64}$Ti$_{0.29}$Sc$_{0.05}$V$_{0.05}$Al$_{0.04}$]$_2$[Si$_{0.90}$Al$_{0.03}$]$_2$O$_{11.35}$Al$_{0.65}$ was obtained, in which the Fe Y site occupancy was fixed at 64%. The site occupancy was subsequently refined using a model in which the remaining 36% of the Y site was occupied by Ti and Mg. In the case of the tetrahedral Z sites, the Si occupancy was fixed at 90%, and the site occupancy was refined using a model in which the remaining 10% was occupied by Al and vacancies. The refined coordination, site occupancy, and equivalent isotropic displacement parameters are provided in Table 4. The final values obtained using the least square refinements are consistent with the chemical formula considering the ion size. Selected interatomic distances are provided in Table 5.

The Ti-garnet has the space group $Ia$

The formula obtained from the crystal structural analysis of $Ca_{3.00}[Fe_{0.64}Ti_{0.29}Sc_{0.05}V_{0.05}Al_{0.04}]_2[Si_{0.90}Al_{0.03}]_2O_{11.35}Al_{0.65}$ (Table 3) is therefore in good agreement with the estimated formula. According to the Shannon effective radius values (Shannon, 1976), the X-O, Y-O, and Z-O bond distances in the Ca$_3$[Fe$_{0.64}$Ti$_{0.29}$Sc$_{0.05}$V$_{0.05}$Al$_{0.04}$]$_2$Si$_{0.90}Al_{0.03}$O$_{11.35}$ (OH)$_{0.65}$ garnet can be estimated as 2.500, 2.012, and 1.664 Å, respectively. The ionic radius values are as follows: $IV^+$ = 1.38 Å, $VI^+$ = 0.645 Å, $V^+$ = 0.78 Å, $VI^+$ = 0.605 Å, $V^+$ = 0.72 Å, $V^+$ = 0.64 Å, $V^+$ = 0.745 Å, $VA^+$ = 0.535 Å, $VA^+$ = 0.39 Å, and $V^+$ = 0.26 Å, where the Roman numerals indicate the coordination numbers. The O-O distance between vacancies in the Z site and oxygen was estimated as 1.932 Å from the katoite results (Lager et al., 2005). Table 5 provides the cation-anion interatomic distances from the present work as well as those obtained from previous studies of andradite garnet for comparison (Novak and Gibbs, 1971, Hazen and Finger, 1989 and Quartieri et al. 2006). Although the lattice constant of the titanian andradite is obviously large, the two types of Ca-O bond, Ca-O short and Ca-O long, and average Ca-O distances agree well with the values for the andradite end-member. The Y-O and Z-O distances of 2.012 and 1.664 Å estimated from chemical analysis agree well with the observed values listed in Table 5. The Y-O distance in the titanian andradite is approximately 0.01 Å shorter and the Z-O approximately 0.02 Å longer than those in the andradite end-member (Table 5). Using a simple estimation based on the ionic radius values, the Y-O distance was...
Figure 5. BSE images of reaction texture forming titanian andradite. (a) Grossular-andradite transition in the rodingite part of sample 257-01R3. In this sample, a careful distinction was made with the titanite occurrence also in relation to grossular. (b) Ilmenite core altered to an andradite rim (258-1-1). (c) Perovskite altered to andradite at the periphery (258-1-1). (d) Remnant ilmenite in the titanian andradite aggregates of sample 258-2-3. (e) Close-up relation between titanian andradite and perovskite in an aggregate as (d); the red dot marks the limit between the two minerals (258-2-3). (f) Chromite first altered to magnetite then further altered to an andradite corona (258-1-1). Tiny dots on (c), (e), and (f) outline the phase change.
found to decrease by 0.012 Å when the Y site is occupied by 70% Fe\textsuperscript{3+} and 30% Ti\textsuperscript{4+}. In addition, the Z–O distance increases by 0.024 Å when the Z site is occupied by 90% Si, 3% Al, and 7% □. These values are also consistent with the results obtained from site occupancy refinement showing that Ti (having a smaller ionic radius) occupies the Y sites while the larger Al atoms occupy the Z sites. If all Fe in the Y site is Fe\textsuperscript{2+}, the estimated Y–O distance is 2.100 Å. From the interatomic distance of the Y site, Fe\textsuperscript{2+} can be determined to be 2% or less of the total iron. Based on a comparison of the interatomic distances listed in Table 5, it is clear that the site occupancy of the cations in the titanian andradite varies according to the ion size. As an optimal model, we propose the following chemical formula based on both the chemical composition and structure analysis: Ca\textsuperscript{1.00}(Fe\textsuperscript{3+}0.64Ti\textsuperscript{4+}0.25Sc\textsuperscript{3+}0.09V\textsuperscript{3+}0.08Mg\textsuperscript{2+}0.03Si\textsuperscript{4+}0.07Al\textsuperscript{3+}0.07□\textsuperscript{0.03})\textsuperscript{2+}(Si\textsuperscript{0.90}Al\textsuperscript{0.03}□\textsuperscript{0.07})\textsuperscript{2+}O\textsuperscript{11.26}(OH)\textsuperscript{0.65}.

Table 3. Crystallographic data, data collection parameters, and refinement parameters

| Chemical formula | Ca\textsuperscript{1.00}(Fe\textsuperscript{3+}0.64Ti\textsuperscript{4+}0.25Sc\textsuperscript{3+}0.09V\textsuperscript{3+}0.08Mg\textsuperscript{2+}0.03Si\textsuperscript{4+}0.07Al\textsuperscript{3+}0.07□\textsuperscript{0.03})\textsuperscript{2+}(Si\textsuperscript{0.90}Al\textsuperscript{0.03}□\textsuperscript{0.07})\textsuperscript{2+}O\textsuperscript{11.26}(OH)\textsuperscript{0.65} |
|------------------|-------------------------------------------------------------------------------------------------|
| \(a (\text{Å})\) | 12.0750(6)                                                                                     |
| \(V (\text{Å}^3)\) | 1760.6(3)                                                                                     |
| Space group     | \(\text{I}a\overline{3}d\)                                                                     |
| \(Z\)           | 8                                                                                             |
| Radiation type  | MoKα                                                                                           |
| Crystal size(mm) | 0.020 × 0.015 × 0.015                                                                         |
| \(\mu (\text{mm}^{-1})\) | 4.907                                                                            |
| Diffractometer  | Rigaku SuperNova                                                                               |
| \(2\theta\) range (°) | 8-60                                                                                  |
| Range of \(h, k, l\) | \(−16 ≤ h ≤ 15\) \(−9 ≤ k ≤ 16\) \(−16 ≤ l ≤ 7\) |
| No. of measured reflections | 3141                                                                  |
| Independent reflections | 219                                                                                     |
| \(R1 (I > 2.00 \sigma (I))\) (%) | 4.69                                                                               |
| \(wR2 (I > 2.00 \sigma (I))\) (%) | 6.16                                                                            |
| Goodness of fit, \(S\) | 1.092                                                                   |
| Largest diff. peak/void (e Å\(^{-3}\)) | 0.594/−0.566                                                          |

Table 4. Refined positional and occupancy parameters

| Sites | Atoms Occupancies | \(x\) | \(y\) | \(z\) | \(U_{eq} (\text{Å}^2)\) |
|-------|-------------------|------|------|------|-----------------|
| \(X\) Ca\textsuperscript{1.0} | 0.125 | 0.0 | 0.25 | 0.0079(6) |
| \(Y\) Fe\textsuperscript{0.64}/Ti\textsuperscript{0.25}(2)/Mg\textsuperscript{0.11}(2) | 0.0 | 0.0 | 0.0 | 0.0065(5) |
| \(Z\) Si\textsuperscript{0.90}/Al\textsuperscript{0.03}(2)/\textsuperscript{□0.07}(2) | 0.375 | 0.0 | 0.25 | 0.0044(9) |
| \(O\) O\textsuperscript{1.0} | 0.0385(3) | 0.0486(3) | 0.6548(3) | 0.0066(8) |

Occupancy of Fe in the Y site and Si in the Z-site were fixed as 0.65 and 0.90, respectively. Numbers in parentheses are errors.

Table 5. Lattice constants (Å) and cation–oxygen distances (Å) in andradite and titanian andradite (this study)

|                  | Novak and Gibbs (1971) | Hazen and Finger (1989) | Quartieri et al. (2006) | This study  |
|------------------|-------------------------|-------------------------|-----------------------|-------------|
| Lattice constant | \(a\) | 12.058(1) | 12.031(1) | 12.0578(2) | 12.0750(6) |
| Ca–O short       |                | 2.366(2) | 2.358(2) | 2.361(1) | 2.359(4) |
| Ca–O long        |                | 2.500(2) | 2.494(2) | 2.500(1) | 2.502(3) |
| Ca–O average     |                | 2.433 | 2.426 | 2.431 | 2.431 |
| Y–O              |                | 2.024(2) | 2.016(2) | 2.020(1) | 2.013(3) |
| Z–O              |                | 1.643(2) | 1.643(2) | 1.647(1) | 1.660(3) |

Numbers in parentheses are errors.
number of hydroxyl groups is 0.65 in the formula. The difference between 0.84 and 0.65 is 0.19. The amount of hydrogen is deficient and a substitution can be proposed as follows: $\text{Fe}^{3+} + \text{H}^+ + \Box = \text{Ti}^{4+} + \Box$. Here, two end members of hydroandradite can be defined as $\text{Ca}_3\text{Fe}_2(\Box)_3(\text{OH})_{12}$ and $\text{Ca}_3\text{Ti}_2(\Box)_3\text{O}_6(\text{OH})_{10}$. In this model, $Z$ sites are partially occupied by $\text{Al}^{3+}$. This agrees with the relative preference for substitution on the tetrahedral sites demonstrated by Huggins et al. (1977a). Our result is also consistent with the chemical formula determined using the method of Grew et al. (2013).

**FORMATION OF TITANIAN ANDRADITE**

As previously described, titanian andradite shows several occurrence types. In this section, we describe the reaction textures involving titanian andradite, compare these textures to those reported from other studies, and derive some andradite-forming reactions using the singular value decomposition (SVD) method (Fisher, 1989). Within the reaction zone, andradite can be observed together with both ilmenite and perovskite. The two latter minerals are related to one another by the following cation exchange reaction:

$$\text{FeTiO}_3 + \text{Ca}^{2+} = \text{CaTiO}_3 + \text{Fe}^{2+}$$

Low Si activity together with a substantial supply of Ca allows for the crystallization of perovskite after ilmenite, rather than titane crystallization, which in most cases are the principal characteristics of rodingite formation via metasomatism (Schandl et al., 1989; Frost and Beard, 2007; Bach and Klein, 2009). In the case of perovskite and andradite coexistence, Figure 5e shows that the replacement of perovskite by andradite progresses from the periphery to the interior of the perovskite aggregate. Within the reaction zone, because the dispersed perovskite aggregates account for the majority of the material, they can be considered the reactant mineral. This scenario is also found in the titanian-andradite-rich layers with less perovskite (Fig. 5e), in which perovskite is randomly distributed on the periphery of the andradite aggregates. We therefore propose that the following reaction occurs in the reaction zone:

$$0.460\text{Prv} + 0.788\text{Di} + 0.009\text{FeO} + 0.226\text{Fe}_2\text{O}_3 + 0.152\text{Al}_2\text{O}_3$$

$$\rightarrow 0.066\text{Chl} + 0.406\text{Adr} + 0.288\text{TiO}_2$$

with the conservation of $\text{CaO}$, $\text{MgO}$, and $\text{SiO}_2$.

This reaction was derived using the SVD method previously reported by Nishiyama et al. (2017). The replacement of perovskite by andradite from grain rims to interiors, occurring via grain-scale fluid-aided coupled dissolution–precipitation, has already been studied in rodingites and associated serpentinites in Slovakia (Putiš et al., 2012; and Li et al., 2014). Putiš et al. (2012) demonstrated that Ti-rich and/or Ti-poor andradite aggregates crystallize at the expense of perovskite and found evidence that Ti-rich andradite in both serpentinite and rodingite is closely related to perovskite. However, Li et al. (2014) also determined that perovskite can be initially replaced by pyrophanite. In the case of the present work, the primary ilmenite, which has an appreciable Mn content up to 0.30 apfu, can be initially replaced by perovskite as previously discussed. However, ilmenite can also be directly replaced by titanian andradite without the intermediate formation of perovskite. In fact, Figure 5b shows an obvious relation between ilmenite and andradite in these specimens such that they uniformly exhibit a core–rim reaction texture with an ilmenite core and an andradite rim. Thus, in this configuration, the reaction could be as follows:

$$0.501\text{Ilm} + 0.349\text{Chl} + 0.564\text{Fe}_2\text{O}_3 + 2.393\text{CaO}$$

$$\rightarrow 0.792\text{Adr} + 3.103\text{MgO} + 0.635\text{Al}_2\text{O}_3$$

$$+ 0.749\text{FeO}$$

with the conservation of $\text{TiO}_2$ and $\text{SiO}_2$.

Small remnants of ilmenite are even dispersed in the titanian-andradite–rich aggregates (Fig. 5d). Koutsovitis et al. (2013) also reported the formation of $\text{TiO}_2$–bearing garnets after ilmenite from rodingite. Moreover, our work shares other significant features with Koutsovitis’ study, such as the presence of a grossular–andradite solid solution and an advanced stage of rodingitization with no traces of the protolith, in which andradite formation occurs via Ca-rich hydrothermal fluid infiltrations under oxidizing conditions. Finally, the succession of the three minerals (ilmenite in the core surrounded by a perovskite rim that is subsequently replaced by andradite) can be observed in some larger grains with a complex symplectite–like texture. In these grains, both ilmenite and perovskite occur as intergrowths with andradite and diopside. Moreover, the existence of a few titanite zones suggests a later Si supply to the system. This is partly in agreement with Putiš et al. (2012) and Li et al. (2014), who concluded that increments in Ca and Si activities in rodingitization fluids allow for the replacement of perovskite by andradite during advanced rodingitization. However, these reports also required a second condition involving a decrease in oxygen fugacity according to Mün tener and Hermann (1994). In the former two studies (Putiš et al., 2012; Li et al., 2014), the replacement of perovskite by
Ti-rich andradite occurred in both rodingite and the associated serpentinite. However, in the present samples, titanian andradite formation in the serpentinite evident involved magnetite, formed from the alteration of primary chromite. Thus, whereas ilmenite and perovskite provide Ti for titanian andradite formation in the rodingite and reaction zone, titanian andradite formation in the serpentinite implies a Ti supply from the reaction zone. Therefore, this andradite occurrence provides evidence of Ti mobility. If the reaction texture shown in Figure 5f is carefully examined, it can be split into two stages. The primary chromite is first altered to magnetite, which is a common phenomenon often observed in the serpentinite part of these rocks. During this stage, a reaction texture consisting of a chromite core with a magnetite rim, along with an intermediate rim of Cr-rich magnetite in some grains, is produced. Subsequently, the magnetite rim is surrounded by an andradite corona. The andradite rim can be in direct contact with the surrounding diopside but, in most cases, aluminum-rich serpentine is formed at the boundary between the two phases. Therefore, we suggest the following reaction based on the SVD method:

\[
0.876\text{Di} + 0.298\text{Mag} + 0.183\text{Al}_2\text{O}_3 + 0.272\text{CaO} + 0.115\text{TiO}_2 + 1.426\text{H}_2\text{O} \rightarrow 0.023\text{Al}–\text{Srp} + 0.380\text{Adr}
\]

with the conservation of SiO2, FeO, Fe2O3, and MgO.

Similar reactions forming andradite, diopside, magnetite, and other phases such as brucite and awaruite have been established by Frost and Beard (2007). This study showed that the low silica activity in the serpentinites often observed in the serpentinite part of these rocks. During this stage, a reaction texture consisting of a chromite core with a magnetite rim, along with an intermediate rim of Cr-rich magnetite in some grains, is produced. Subsequently, the magnetite rim is surrounded by an andradite corona. The andradite rim can be in direct contact with the surrounding diopside but, in most cases, aluminum-rich serpentine is formed at the boundary between the two phases. Therefore, we suggest the following reaction based on the SVD method:

\[
0.876\text{Di} + 0.298\text{Mag} + 0.183\text{Al}_2\text{O}_3 + 0.272\text{CaO} + 0.115\text{TiO}_2 + 1.426\text{H}_2\text{O} \rightarrow 0.023\text{Al}–\text{Srp} + 0.380\text{Adr}
\]

with the conservation of SiO2, FeO, Fe2O3, and MgO.

CONCLUSION

The newly found purple rodingites described in this study are distinct from others previously identified in the field and show several characteristic features. First, the studied specimen exhibits solid solutions among three end-member compositions: grossular, andradite, and titanian hydrotogarnet. Within one thin section, compositional variation from grossular to titanian andradite is observed from rodingite to serpentinite through the reaction zone. However, all three zones (i.e., rodingite, reaction zone, and serpentinite) also show a wide range of compositions.

Second, these rocks show several titanian andradite occurrences. In the rodingite part, variations in Fe concentration are associated with a transition from a grossular to andradite component within the fine-grained garnets. This observation suggests that the rodingite is formed with a significant lack of equilibrium and also implies a Ti supply from the exterior of the rodingite. In the serpentinite, the titanian-andradite corona around the chromite initially altered to magnetite, providing new evidence for titanian andradite formation in serpentinite together with rodingitization. This process also requires an outside Ti supply. Within the reaction zone, andradite partly replaces the TiO2-bearing minerals, perovskite and ilmenite. Given that the Ti ion is only in the tetravalent state in the titanian andradite supports these replacements. According to the SVD method, TiO2 is conserved in the reaction forming titanian andradite from ilmenite, but is only partly consumed in the reaction involving perovskite. This Ti release could be a potential supply for titanian andradite formation in both the rodingite and serpentinite parts, especially perovskite is an abundant phase in the reaction zone. In addition, these results shed new light on Ti mobility. Remnants of perovskite and ilmenite in the titanian-andradite-rich layers also support the displacement of both oxides. However, the concentration of titanian andradite in these layers was not resolved and could involve metasomatic fluid action. Crystallographic studies have provided Ca(3.00(Fe0.64Ti0.24Mg0.01V0.02)Sc0.01Al0.06)2O2(OH)10(Si0.90Al0.03)2O2(H2O)10(Fe3+0.64Ti4+0.24Mg0.03)2O2(OH)10 as an optimal model for the chemical formula of titanian andradite extracted from a titanian-andradite-rich layer at the boundary between the rodingite and reaction zone. The data obtained in this study allowed us to conclude that Al is preferentially incorporated at the tetrahedral sites, while the octahedral sites contain primarily Fe3+ and Ti4+ with a smaller amount of Mg2+. This composition suggests that Fe3+ + H+ + □ = Ti4+ + □ is the principal substitution reaction and that the possible end-member of the titanian hydrogarnet is Ca3Ti2(□)2O12(OH)10. Finally, the Fe and Ti oxidation states in the titanian andradite indicate that its formation occurs under relatively oxidizing conditions.

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