Crystal chemistry of Sr-rich piemontite from manganese ore deposit of the Tone mine, Nishisonogi Peninsula, Nagasaki, southwest Japan

Mariko Nagashima*, Yuko Sano**, Takako Kochi**, Masahide Akasaka*** and Asami Sano-Furukawa†

*Division of Earth Science, Graduate School of Science and Technology for Innovation, Yamaguchi University, Yamaguchi 753-8512, Japan
**Department of Geosphere Science, Faculty of Science, Yamaguchi University, Yamaguchi 753–8512, Japan
***Department of Geoscience, Interdisciplinary Graduate School of Science and Engineering, Shimane University, Matsue 690-8504, Japan
†J-PARC Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki 319–1195, Japan

The crystal chemistry of Sr-rich piemontite from a layered manganese ore deposit of the Tone mine, Nishisonogi Peninsula, Japan, was studied using methods of electron microprobe analysis, single crystal X-ray structural refinement, ⁵⁷Fe Mössbauer spectroscopy, and X-ray and Time-of-Flight neutron Rietveld analyses to elucidate the intracrystalline distributions of Sr, Mn, and Fe and the general and individual features on the structural changes with Sr contents in piemontite and epidotes. Piemontite in the most piemontite-rich and Sr-coordinated sites, 9Sr containers in metamorphic rocks (e.g., Grapes and Watanabe, 1984; Mottana, 1986; Reinecke, 1986; Nagashima and Enami, 1998; Enami, 1999; Miyajima et al., 2006), metamorphosed manganese ore deposits (e.g., Kato and Matsubara, 1986; Bonazzi et al., 1990; Perseil, 1990; Minakawa, 1992; Nagashima et al., 2007; Minakawa et al., 2008; Nagashima et al., 2009). Epidote-group minerals of epidote–supergroup, such as clinozoisite, epidote and piemontite, are important Sr containers in metamorphic rocks (e.g., Grapes and Watanabe, 1984; Mottana, 1986; Reinecke, 1986; Nagashima and Enami, 1998; Enami, 1999; Miyajima et al., 2003; Nagashima et al., 2006), metamorphosed manganese ore deposits (e.g., Kato and Matsubara, 1986; Bonazzi et al., 1990; Perseil, 1990; Minakawa, 1992; Nagashima et al., 2007; Minakawa et al., 2008; Nagashima et al., 2009).

INTRODUCTION

Epidote–supergroup minerals are monoclinic in symmetry and have space group P2₁/m and the structural formula of A2[Al/Mg/Fe]₂M₃[T₁O₇][TO₄]O₆(F,OH)(OH), where A2 and A1 imply 10-coordinated and 9-coordinated sites, respectively, M₁, M₂, and M₃ represent octahedral sites; and T is tetrahedral sites (Armbruster et al. 2002; Mills et al., 2009). Epidote–group minerals of epidote–supergroup, such as clinozoisite, epidote and piemontite, are important Sr containers in metamorphic rocks (e.g., Grapes and Watanabe, 1984; Mottana, 1986; Reinecke, 1986; Nagashima and Enami, 1998; Enami, 1999; Miyajima et al., 2003; Nagashima et al., 2006), metamorphosed manganese ore deposits (e.g., Kato and Matsubara, 1986; Bonazzi et al., 1990; Perseil, 1990; Minakawa, 1992; Nagashima et al., 2007; Minakawa et al., 2008; Nagashima et al., 2009).

Keywords: Strontian Piemontite, Tone mine, X-ray diffraction, TOF neutron diffraction, Mössbauer analysis, Crystal structure
al., 2010), and metamorphosed manganiferous iron ore deposits (Akasaka et al., 1988; Togari et al., 1988). Thus, the occurrence and crystal chemical properties of Sr-bearing epidote-group minerals, such as solubility of Sr and its effect on the Mn and Fe contents and crystal structure, have been interested in.

The Sr contents of epidote-group minerals in the published studies cited above are less than 1 atom per formula unit (apfu). According to Akasaka et al. (2000), the synthetic piemontite in the join Ca$_2$Al$_2$Mn$^{3+}$Si$_3$O$_{12}$(OH)–Sr$_2$Al$_2$Mn$^{3+}$Si$_3$O$_{12}$(OH) also contained Sr up to 1 apfu. Such results are consistent with those clarified by the X-ray structural refinements that Sr$^{2+}$ ions occupy only the larger 10$<$A$>$ coordinated A2 site but not the smaller 9$<$A$>$ coordinated A1 site in the epidote structure (Bonazzi et al., 1990; Armbruster et al., 2002; Miyajima et al., 2003; Nagashima et al., 2010). Dörsam et al. (2007) indicated that the synthetic clinoloisite (Ca, Sr)$_2$Al$_2$Si$_3$O$_{12}$(OH) having Sr occupancy of >0.8 at the A2 site simultaneously contains Sr reaching up to 0.15(4) in occupancy at the A1 site. However, it is not the case of natural Sr-rich piemontite, as typically shown by strontiopiemontite in which the A2 site is occupied by 0.68 Sr (Bonazzi et al., 1990) and tweddillite with Sr occupying fully the A2 site (Armbruster et al., 2002). Whereas the smaller A1 site is occupied by Ca and additional Mn$^{3+}$, as clarified by the structural studies by Armbruster et al. (2002) and Nagashima et al. (2010).

In order to elucidate the general and individual features on the structural changes with Sr contents in epidotes, characterization of the epidote-group minerals containing various amounts of Sr has been required. With regard to Sr-rich piemontite, in addition to the maximum contents of Sr and transition metal ions and to the structural change due to the incorporation of Sr in the A2 site, the variation in intracrystalline partitioning of transition metal ions accompanying with the substitution of Sr for Ca have been particularly concerned (e.g., Ferraris et al., 1989; Bonazzi et al., 1990; Armbruster et al., 2002; Nagashima et al., 2010).

Piemontite occurring in the layered manganese deposit of the Tone mine, Nishisonogi Peninsula, Nagasaki, southwest Japan, contains significant amounts of Sr (Fukushima et al., 2003), as well as Sr-bearing piemontites from the various localities referred to above. However, the details of occurrence, chemical composition and structural properties of the Sr-bearing piemontite from the Tone ore deposit have not been studied systematically. In the present study, chemical compositions and crystal structure of the Tone Sr-bearing piemontite were studied by means of electron microprobe analysis (EMPA) and single crystal X-ray structural refinement to determine the distributions of Sr and Ca in the A2 and A1 sites and of transition metal ions in the octahedral sites. Since the occupancies of Fe and Mn in the octahedral sites are not determined using the single crystal X-ray diffraction method, they were complementary determined for the powder sample using the time-of-flight (TOF) neutron Rietveld analyses, where Al occupancy in the octahedral sites determined using X-ray Rietveld analysis was taken into the refinement. The oxidation state and coordination site of Fe cations were determined by the Mössbauer spectroscopic analysis. Based on the results, we examine the relationship between the Sr content in the A site and $M^{3+}$–cation distributions in the octahedral sites and clarify the effect of Sr and $M^{3+}$ cation distributions in the A and octahedral sites on the $A$–O bond lengths and the mean $M^{3+}$–O bond lengths. Finally, the effect of the Sr ↔ Ca substitution on overall structure of piemontite, which is characteristically represented by the change of the unit-cell parameters and Si(OH)–Si angle, are discussed.

GEOLOGICAL OUTLINE OF THE TONE ORE DEPOSIT

In Nishisonogi Peninsula, Nagasaki, southwest Japan, Nagasaki metamorphic complex consisting of schists subjected to epidote–glaucophane to epidote–amphibolite facies metamorphism is distributed (Nishiyama, 1990). In this district, some layered manganese ore deposits are intercalated in the Nagasaki metamorphic complex. The ore deposits were mined at the Tone, Muramatsu and Sakiyama mines (Yoshimura, 1952). Braunite and pyrolusite ores are considered to have been mined as manganese resource (Yoshimura, 1952), but the details are not known. Strontiopiemontite, hennomartinite and strontio-melane have been also reported from the ores (Fukushima et al., 2003).

EXPERIMENTAL METHODS

Piemontite sample preparation

The manganese sample preparation

The manganese ores were collected from dump of the Tone mine. The ores have layered structures. The layers showing reddish purple in color contain piemontite as one of major minerals. In this study, piemontite crystals were separated from the ore bearing piemontite as the most dominant phase. Selected piemontite crystals attain up to about 3 mm long and contain hematite inclusions or coexist with hematite. To analyze the chemical composition of piemontite, a thin section of the layer, from which piemontite crystals were separated, was prepared. For the single crystal X-ray diffraction analysis, a piemontite
crystal with 0.115 × 0.085 × 0.04 mm in dimension was picked up. The piemontite crystals used for the Mössbauer spectral analysis and powder X-ray and TOF neutron diffraction analyses were separated and ground under alcohol in an agate mortar and pestle to obtain a powder sample with fine grains less than 10 µm in size.

Electron microprobe analysis of minerals

The chemical compositions of minerals were determined using a JEOL JXA-8230 electron microprobe analyzer at Yamaguchi University, Japan. Operating conditions were as follows: accelerating voltage of 15 kV, a beam current of 20 nA and a beam diameter of 1–10 µm. Wave length-dispersive type X-ray detectors with LiF, PET, and TAP monochromator crystals were used for measurement of the X-ray spectra and X-ray intensities of Si, Ti, Al, Cr, V, Fe, Mn, Mg, Ca, Sr, Ba, Na, K, F, and Cl. The ZAF method was used for data correction. Elements below the detection limit are not shown in Table 1.

Single crystal X-ray diffraction analysis

The X-ray diffraction data of the piemontite single crystal were collected at room temperature with graphite-monochromated MoKα X-radiation (λ = 0.71073 Å) using a Bruker SMART APEX II CCD diffractometer installed at Shimane University, Japan. Preliminary unit-cell parameters and an orientation matrix were obtained from three sets of frames and refined during the integration process of the intensity data. Diffraction data were collected with ω scans with different φ settings (φ–ω scan) (Bruker, 1999). Data were processed using SAINT program (Bruker, 1999). An empirical absorption correction using SADABS program (Sheldrick, 1996) was applied. The systematic absences were consistent with space groups P21 and P21/m, and reflection statistics indicated that the observed structure is centrosymmetric. Thus, structural refinement was performed in the space group P21/m, using SHELXL–97 program (Sheldrick, 2015). Scattering factors for neutral atoms were employed. Since the preliminary refinement resulted in the full occupancy of Ca at the A1 site, Al at the M2 site, and Si at the Si1, Si2, and Si3 sites, the site occupancies were fixed to 1.0Ca for the A1 site, 1.0Al for the M2 site and 1.0Si for the Si1, Si2, and Si3 sites. The site occupancies at the A2, M1, and M3 sites were refined with Ca and Sr, Al and Mn, and Mn and Al, respectively. Position of the hydrogen atom was derived from difference-Fourier syntheses and was refined assuming full or half occupancy with fixed Uiso = 0.05 Å2. In addition, a bond-distance constraint of O–H = 0.98(2) Å after Franks (1973) was applied.

Collection of powder X-ray diffraction data and X-ray Rietveld analysis

The powdered piemontite sample was mounted in a sample holder made of glass, with a cavity measuring 20 × 15 × 0.2 mm. Following the method of Raudsepp et al. (1990), a straight edge was used to level the sample surface to that of the holder. The surface was then finely serrated several times with a razor blade to randomize the orientation of anisotropic crystals that are aligned during filling. The powder X-ray diffraction data were collected using Rigaku SmartLab X-ray powder diffractometer using CuKα radiation (λ = 1.5418 Å) and Dtex/Ultra detector with Bragg-Brentano geometry. The X-ray diffraction data was taken between 5.00 and 150.00° 2θ with a step interval of 0.01° 2θ. X-ray generator was operated at 40
kV and 200 mA. The crystal structures of the piemontite were refined using the RIETAN-FP program of Izumi and Momma (2007). The atomic coordinates and isotropic displacement parameters of a Sr-bearing piemontite analyzed by Dollase (1969) were used for the initial input. The isotropic displacement parameters for all atoms were fixed during the refinement. The unit-cell parameters determined using a Rigaku PDXL software were used as initial values of the Rietveld analysis. Peaks were defined using Modified split pseud-Voigt function for relaxed reflections (Izumi and Ikeda, 2000) in RIETAN-FP. Non-linear least-squares calculation using the Marquardt method was followed by the conjugate direction method to check convergence at local minima (Izumi, 1993). The March-Dollase function (Dollase, 1986) was applied to the correction of preferred orientation. Based on the result of the chemical analysis, the occupancies of Ca at the A1 site and Si at Si1, Si2, and Si3 sites were fixed at unity. The site occupancy at the A2 site was refined using the following constraint: $^{42}\text{Sr} = 1.0 - ^{42}\text{Ca}$. The occupancies of Al and Mn at the octahedral sites were refined using the following constraints: $^{M}\text{Mn} = 1.0 - M\text{Al}$ and $^{M}\text{Al} = 1.0 - ^{M}\text{Mn}$, where ‘Mn’ implies ‘Mn + Fe’. At the M2 site, Al was fixed at unity, because the preliminary refinement indicated that the M2 site is filled with Al.

**Collection of the TOF neutron data and Rietveld analysis**

TOF neutron powder-diffraction data of the piemontite powder sample was measured at room temperature using TOF neutron powder diffractometer at the BL11 beamline in MLF of Japan Proton Accelerator Research Complex (J-PARC) facility (Hattori et al., 2015). The sample of 0.04 g was mounted in a vanadium tube (ØD 3 mm and ID 2.8 mm). Diffraction was detected by a pair of $^3\text{He}$ PSD detector bank that covers 20 of 90 ± 11.3°, through the radial collimators with a gauge length of 3 mm. Data was collected for 8 h and 45 mm on accelerator power of approximately 500 kW. Intensity was corrected using the data of vanadium rod, empty vanadium holder and instrumental background which were measured separately. The Rietveld analysis of the neutron-diffraction data was performed using the Z-Rietveld software (ver. 1.0.2, Oishi et al., 2009; Oishi-Tomiyasu et al., 2012). Peaks were defined using a profile function 0 in Z-Rietveld. Based on the EMPA data and the results of the X-ray Rietveld refinement, Ca at the A1 site and Si at Si1, Si2, and Si3 sites were fixed at unity. Site occupancies of Sr and Ca in the A2 site were refined using the following constraint: $^{A}\text{Sr} = 1.0 - ^{A}\text{Ca}$. As mentioned by Ferraris et al. (1989), to obtain the occupancies of Al, Mn, and Fe at the M1 and M3 sites, Al content has to be fixed to the value given by the X-ray structural refinement. Thus, in the preliminary neutron Rietveld refinement, the occupancies of Al at the M1 and M3 sites were fixed to those determined by the X-ray Rietveld analysis, and the occupancies of Mn and Fe at these sites were refined. As a result of the refinement, it was found that the M1 site has Mn but no Fe, and that both Mn and Fe are present in the M3 site. Therefore, in the final refinement, the site occupancy at the M1 site was refined with Al and Mn; and that at the M3 site was refined with Mn and Fe using the fixed Al occupancy by the X-ray data. At the M2 site, Al was fixed at unity based on the result by the X-ray Rietveld analysis.

**$^{57}\text{Fe}$ Mössbauer spectroscopic analysis**

The $^{57}\text{Fe}$ Mössbauer spectrum of the powder sample of piemontite, with ~ 20 mg in weight, was measured at room temperature, using 370 MBq $^{57}\text{Co}$ in Pd as a source. Mössbauer data were obtained using a constant acceleration spectrometer fitted with a 1024 channel analyzer. The isomer shift was referred to a standard metallic iron foil, which was also used to calibrate the Doppler velocity. The spectrum was fitted to Lorentzians using the least squares method with line widths and intensities constrained to be equal for each doublet. The QBMOSS program written by Akasaka and Shinno (1992) was used for computer analysis. The quality of the fit was judged using the $\chi^2$ value and standard deviations of Mössbauer parameters.

**RESULTS**

**Chemical composition of the Tone piemontite**

Chemical composition of the Tone piemontite is shown in Table 1, where total Fe and Mn are shown as Fe$_2$O$_3$ and Mn$_2$O$_3$. The trivalent oxidation state of Fe was proved by the Mössbauer spectroscopic analysis, as shown later, and that of Mn ions was evaluated from stoichiometry of the chemical composition. The SrO content is 4.63 ± 2.66 wt% on average, but attains 8.48 wt% at maximum, corresponding to 0.41 apfu [O$_{12}$(OH)]. Rather large standard deviation of the average SrO content is due to the zonal structure with Sr-poorer core and Sr-richer overgrowths (Fig. 1). The chemical formula derived from the average composition by 23 point analytical data is [Ca$_{1.73(15)}$Sr$_{0.22(13)}$]$_{1.95}$[Al$_{1.99(9)}$Mn$_{0.48(8)}$Fe$_{0.13(7)}$]$_{3.05}$Si$_{2.99(1)}$O$_{12}$(OH) (Z = 2), which was applied to the powder piemontite sample used for the Mössbauer spectroscopic and the X-ray and neutron Rietveld analyses in this study.
Single crystal X-ray structural refinement

Crystallographic data and refined parameters in the single crystal X-ray structural refinement of the piemontite single crystal are summarized in Table 2. The refined site occupancies, atomic positions and anisotropic atomic displacement parameters are listed in Table 3. The interatomic distances, selected angles, volumes of the coordination polyhedra and site distortion parameters are listed in Table 4. The respective errors in all tables are shown by the standard deviation of 1σ.

The refinement was converged to $R_1 = 2.51\%$. The determined unit cell parameters are $a = 8.8942(1)$, $b = 5.6540(1)$, $c = 10.1928(2)$ Å, and $\beta = 115.100(1)\degree$. The site occupancies are Ca0.711(3)Sr0.289 at the $A_2$ site, Al0.898(4)Mn0.102 at the $M_1$ site, and Mn0.949(4)Al0.051 at the $M_3$ site, where the occupancy of Mn includes that of Fe. The $A_1$ site is only occupied by Ca and the smallest octahedral $M_2$ site is filled with aluminum. The Sr population in the $A_2$ site, 0.289 apfu, is more than the average composition, 0.23 apfu, by EMPA, whereas the (Mn + Fe) content, 1.051 apfu, agrees with the EMPA data, 1.05 apfu.

X-ray and TOF neutron Rietveld analyses

Details of data collection for the X-ray and TOF neutron Rietveld analyses, the refined unit cell parameters, $R$-factors, goodness-of-fit ($S = R_{wp}/R_e$) and the Durbin–Watson $d$ statistic are listed in Table 5. The refined powder patterns by the X-ray and TOF neutron diffractions are given in Figure 2a and b, respectively. The site occupancies and atomic positions are listed in Table 6. Figure 3 shows the crystal structure of the Tone piemontite.

The refinement of the powder X-ray diffraction data was reduced to $R_{wp} = 2.95$, $R_c = 2.13$ and $S = 1.38$. The refined unit cell parameters are $a = 8.8769(3)$, $b = 5.66844(7)$, $c = 10.1881(4)$ Å, and $\beta = 115.199(3)\degree$. The determined site occupancies at the $A_2$, $M_1$, and $M_3$ sites are Ca0.795(6)Sr0.205, Al0.909(7)Mn0.091, and Mn0.80(1)Al0.20, respectively, where the occupancy of Mn includes that of Fe.

The refinement of the TOF neutron data was reduced to $R_{wp} = 2.11$, $R_c = 0.88$ and $S = 2.39$ and resulted in the unit cell parameters of $a = 8.8879(2)$, $b = 5.6744(2)$, $c = 10.1885(3)$ Å, and $\beta = 115.244(4)\degree$; the site occupancies of Ca0.791(5)Sr0.205, Al0.902(5)Mn0.088, and Mn0.534(5)Fe0.267 at the $A_2$, $M_1$ and $M_3$ sites, respectively.
The refined Sr occupancies using the powder X-ray and TOF neutron diffraction data are consistent with each other, and the Sr population in the A2 site given from the refined Sr occupancy, 0.21 apfu, is close to that of the average composition by EMPA, 0.23 apfu. The sum of Mn and Fe populations derived from the X-ray diffraction data, 0.891 apfu \(= 0.091(M_1) + 0.800(M_3)\), is also close to that from the neutron diffraction data, 0.899 apfu \(= 0.098Mn(M_1) + 0.534Mn(M_3) + 0.267Fe(M_3)\), whereas they are somewhat less than that of EMPA data, Mn\(^{3+}\) + Fe\(^{3+}\) = 1.05 apfu. A possible reason may be attributed to the limited number of the EMPA analysis data. The neutron Rietveld analysis results in Mn population of 0.632 apfu \(= 0.098Mn(M_1) + 0.534Mn(M_3)\) and Fe population of 0.267 apfu \(= Fe(M_3)\), which is fairly consistent with the Mn\(^{3+}\) and Fe\(^{3+}\) contents (Mn\(^{3+}\) = 0.68 apfu and Fe\(^{3+}\) = 0.37 apfu) of the average chemical composition by EMPA (Table 1).

\[\text{Table 3. Site occupancies, atomic positions and equivalent displacement parameters (Å}^2\text{) determined by the single crystal X-ray diffraction analysis}\]

| Site | Site Occupancy | \(x\) | \(y\) | \(U_{eq}\) | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) |
|------|----------------|-------|-------|-----------|-----------|-----------|-----------|
| A1 2e Ca\(_{81}\) | 0.7599(5) | 3/4 | 0.1542(4) | 0.01048(9) | 0.01389(18) | 0.0103(2) | 0.01028(16) |
| A2 2e Ca\(_{0.71(1)}\)Sr\(_{0.29}\) | 0.59902(4) | 3/4 | 0.42349(3) | 0.01163(10) | 0.01193(15) | 0.01472(18) | 0.00757(13) |
| M1 2a Al\(_{0.50(0.02)}\) | 0 | 0 | 0 | 0.00530(16) | 0.00572(2) | 0.0041(3) | 0.0060(2) |
| M2 2c Al\(_{1.0}\) | 0 | 1/2 | 0 | 0.00644(12) | 0.0063(2) | 0.0052(3) | 0.0077(2) |
| M3 2e Mn\(^{3+}\)0.949(0.051)Al\(_{0.51}\) | 0.29338(4) | 1/4 | 0.22173(3) | 0.00637(9) | 0.00535(13) | 0.00667(16) | 0.00691(13) |
| Si1 2e | 0.33947(7) | 3/4 | 0.04481(6) | 0.00634(11) | 0.0068(2) | 0.0061(3) | 0.0065(2) |
| Si2 2e | 0.68522(7) | 1/4 | 0.27649(6) | 0.00631(11) | 0.0064(2) | 0.0061(3) | 0.0067(2) |
| Si3 2e | 0.18245(7) | 3/4 | 0.31719(6) | 0.00619(10) | 0.0065(2) | 0.0061(3) | 0.0067(2) |
| O1 4f | 0.23393(13) | 0.993(2) | 0.03900(11) | 0.00954(19) | 0.0095(4) | 0.0070(5) | 0.0135(4) |
| O2 4f | 0.30224(13) | 0.980(2) | 0.35335(11) | 0.00953(19) | 0.0097(4) | 0.0086(5) | 0.0102(4) |
| O3 4f | 0.79485(13) | 0.0146(2) | 0.34131(11) | 0.00959(19) | 0.0085(4) | 0.0061(5) | 0.0113(4) |
| O4 2e | 0.05408(18) | 1/4 | 0.12974(15) | 0.0074(3) | 0.0083(6) | 0.0069(7) | 0.0074(5) |
| O5 2e | 0.04080(18) | 3/4 | 0.14551(15) | 0.0083(3) | 0.0077(6) | 0.0094(7) | 0.0073(5) |
| O6 2e | 0.06561(18) | 3/4 | 0.40564(16) | 0.0079(3) | 0.0106(6) | 0.0057(7) | 0.0105(6) |
| O7 2e | 0.51485(18) | 3/4 | 0.17643(16) | 0.0119(3) | 0.0086(6) | 0.0137(8) | 0.0109(6) |
| O8 2e | 0.52543(19) | 1/4 | 0.31044(17) | 0.0124(3) | 0.0094(6) | 0.0161(8) | 0.0134(6) |
| O9 2e | 0.6296(2) | 1/4 | 0.10236(17) | 0.0171(3) | 0.0221(8) | 0.0228(10) | 0.0107(6) |
| O10 2e | 0.08134(18) | 1/4 | 0.42865(15) | 0.0076(3) | 0.0093(6) | 0.0070(7) | 0.0083(6) |
| H10 2e | 0.043(5) | 1/4 | 0.3233(6) | 0.05 (U\(_{ij}\)) |

\* Multiplicity and Wyckoff letter.
\** Mn + Fe.

\[\text{57Fe Mössbauer spectroscopy}\]

\[\text{57Fe Mössbauer spectra and hyperfine parameters are shown in Figure 4 and Table 7, respectively. The spectrum consists of three doublets: the doublet AA’ with isomer shift (IS) = 0.35 and quadrupole splitting (QS) = 2.19 mm/s; the doublet BB’ with IS = 0.37 and QS = 1.93 mm/s; and the doublet CC’ with IS = 0.18 and QS = 1.08 mm/s. According to the published Mössbauer studies on the epidote minerals (e.g., Liebscher, 2004; Nagashima and Akasaka, 2010), doublets with IS = 0.24–0.44 and QS = 1.89–2.32 mm/s and with IS = 0.22–0.36 and QS = 1.46–1.67 mm/s are assigned to Fe\(^{3+}\) at the M3 and M1 sites,}\]
respectively. Therefore, the doublets AA' and BB' are assigned to Fe$^{3+}$ at the M$^3$ site. In contrast, the doublet CC' with $IS = 0.18$ and $QS = 1.08$ mm/s and very broad peak width ($FWHH$) of 0.81 mm/s are not assigned to Fe$^{3+}$ nor Fe$^{2+}$ in epidote minerals. Since the powder X-ray and neutron diffraction analyses indicated that the piemontite powder sample contained a very small amount of quartz as an impurity but no Fe-bearing impurity, an undetectable amount of Fe-rich impurity, such as Fe$^{3+}$-rich hydroxide, might have been contaminated in the powder sample. The result of the Mössbauer spectroscopic analysis that Fe$^{3+}$ is distributed only in the M$^3$ site but not the M$^1$ site proves that of the neutron Rietveld analysis.

The presence of two doublets, with $IS = 0.34$ and $QS = 2.04$ mm/s and with $IS = 0.39$ and $QS = 1.95$ mm/s, assigned to Fe$^{3+}$ at the M$3$ site has been reported for synthetic epidote with $0.5 \leq Fe \leq 0.7$ apfu (Fehr and Heuss-Aßbichler, 1997). Two doublets with $IS = 0.34$ and $QS = 2.16-2.22$ mm/s and with $IS = 0.36-0.37$ and $QS = 1.90-1.97$ mm/s due to Fe$^{3+}$ at the M$3$ sites were also found in the synthetic Ca$_2$(Al$_{10.12}$Mn$^{*+0.78-0.73}$Fe$_{0.18}$)Si$_3$O$_{12}$(OH)$_2$-piemontite (Nagashima and Akasaka, 2010). Although aforementioned previous studies supposed a miscibility gap at the compositions of their synthetic epidote and piemontite, the two Fe$^{3+}$ doublets assigned to the M$3$ site in the Tone piemontite may be attributed to the chemical heterogeneity of the piemontite crystals separated for the powder sample.

**DISCUSSION**

**Site populations of Sr and transition metal ions in the studied Tone piemontite**

Based on the site occupancies refined using the single crystal X-ray diffraction data, the structural formula of the Tone piemontite single crystal is derived as $4^2$Ca$^{4+}$(Ca$_{0.711(3)}$Sr$_{0.289}$)$^{3+}$Ca$^{4+}$(Al$_{0.898(3)}$Mn$^{0.012}$)$^{3+}$Al$^{3+}$(Mn$_{0.849(4)}$Al$_{0.051}$)$^{3+}$Si$_3$O$_{12}$(OH)$_2$-piemontite. The presence of two Sr sites with Sr$^{2+}$ and Sr$^{4+}$ populations in the M$3$ site has also been reported for synthetic epidote with $0.5 \leq Fe \leq 0.7$ apfu (Fehr and Heuss-Aßbichler, 1997). Two doublets with $IS = 0.34$ and $QS = 2.16-2.22$ mm/s and with $IS = 0.36-0.37$ and $QS = 1.90-1.97$ mm/s due to Fe$^{3+}$ at the M$3$ sites were also found in the synthetic Ca$_2$(Al$_{10.12}$Mn$^{*+0.78-0.73}$Fe$_{0.18}$)Si$_3$O$_{12}$(OH)$_2$-piemontite (Nagashima and Akasaka, 2010). Although aforementioned previous studies supposed a miscibility gap at the compositions of their synthetic epidote and piemontite, the two Fe$^{3+}$ doublets assigned to the M$3$ site in the Tone piemontite may be attributed to the chemical heterogeneity of the piemontite crystals separated for the powder sample.
Si$_3$O$_{12}$(OH), where Mn* implies sum of Mn and Fe. The results of the neutron Rietveld refinement and Mössbauer spectroscopic analysis for the powder sample indicate that the M1 site is occupied by Al$^{3+}$ and Mn$^{3+}$ but not by Fe$^{3+}$. Therefore, Mn* at the M1 site for the piemontite single crystal is also regarded to be only Mn, and the M1 site population is concluded as M1[Al0.898(4)Mn$^{3+}$0.102] in apfu, which is in agreement with M1[Al0.902(5)Mn$^{0.098}$] in apfu of the powder sample. Consequently, the M3 site in the piemontite single crystal is filled with Al, Mn, and Fe, which is in agreement with the analytical result of the powder sample. Applying the Mn:Fe ratio in the M3 site for the powder piemontite sample, Mn$_{0.633}$Fe$_{0.316}$Si$_3$O$_{12}$(OH). The obtained total Mn$^{3+}$ and Fe$^{3+}$, 0.735 and 0.316 apfu, respectively, are fairly close to those of the EMPA data, 0.68(8) Mn$^{3+}$ and 0.37(8) Fe$^{3+}$ (Table 1).

Table 5. Details of powder X-ray and TOF neutron diffraction data collection and refined results of piemontite

|                        | X-ray     | TOF neutron |
|------------------------|-----------|-------------|
| 20 range (°)           | 5-150     | -           |
| d range (Å)            | 0.55-5.28$^*$ |            |
| Space group            | $P2_1/m$  |             |
| a (Å)                  | 8.8769(3) | 8.8817(2)   |
| b (Å)                  | 5.66844(7)| 5.6744(2)   |
| c (Å)                  | 10.1881(4)| 10.1885(3)  |
| $\beta$ (°)           | 115.199(3)| 115.244(4)  |
| $V$ (Å$^3$)            | 463.86(3) | 464.45(3)   |
| $R_B$ (%)              | 2.05      | 6.63        |
| $R_F$ (%)              | 1.16      | 4.22        |
| $R_p$ (%)              | 2.20      | 1.65        |
| $R_w$ (%)              | 2.95      | 2.11        |
| $R_e$ (%)              | 2.13      | 0.88        |
| S$^*$                  | 1.38      | 2.39        |
| D-W d$^*$              | 0.727     | 0.568       |
| r$^*$                  | 1.037     | 1.035       |
| Mass fraction          |           |             |
| Piemontite             | 0.991     | 0.948       |
| Quartz                 | 0.009     | 0.052       |

* Corresponding to range of TOF data 5200–49998.
** $R_B$, R-Bragg factor; $R_F$, R-structure factor; $R_p$, R-pattern; $R_w$, R-weighted pattern; $R_e$, R-expected.
S = ($R_w$/($R_e$), Goodness of fit (Young, 1993); D-W d, Durbin-Watson d-statistic (Hill and Flack, 1987); r, Preferred-orientation parameter in the March-Dollase function.

It has been suggested that piemontites rich in Sr and/or Ba tend to be rich in Mn$^{3+}$ and Fe$^{3+}$: in piemontite from the Fukuyama manganiferous iron ore deposit, Tokoro, Hokkaido, Japan, Sr/(Sr + Ca), Mn$^{3+}$/(Al + Mn$^{3+}$ + Fe$^{3+}$), and (Mn$^{3+}$ + Fe$^{3+}$)/(Al + Mn$^{3+}$ + Fe$^{3+}$) ratios attain 0.48, 0.51, and 0.58, respectively, corresponding to 0.96 Sr apfu, 1.53 Mn$^{3+}$ apfu, and, 1.74 (Mn$^{3+}$ + Fe$^{3+}$) apfu, respectively (Togari et al., 1988; Akasaka et al., 1988); in the Kalahari manganese field, South Africa, the Sr, Mn$^{3+}$, and Fe$^{3+}$ contents in tweddillite with the lowest Al concentration are 0.99, 1.52, and 0.41 apfu, respectively (Armbruster et al., 2002); and from Sambagawa metamorphic rocks, central Shikoku, Japan, piemontite with 0.58 apfu Sr, 1.42 apfu Mn$^{3+}$, and 0.81 apfu Fe$^{3+}$ and (Mn$^{3+}$ + Fe$^{3+}$) of 2.23 apfu was reported (Enami and Banno, 2001). In fact, Sr-rich zone within the Tone piemontite crystal tends to be richer in Mn and Fe than Sr-poor core and zone, as shown in Figure 1. However, the Mn$^{3+}$, and Fe$^{3+}$ and (Mn$^{3+}$ + Fe$^{3+}$) contents in the Tone piemontite with Sr = 0.289 apfu are 0.735, and 0.316 and 1.051 apfu, respectively, and less than those of the piemontites with lower Sr contents from St. Marcel, Italy, and from the Kamisugai deposit, central Shikoku, Japan: in the former, Mn$^{3+} = 0.78, and Fe^{3+} =
0.35 and \((\text{Mn}^{3+} + \text{Fe}^{3+}) = 1.13\) apfu against \(\text{Sr} = 0.16\) apfu (Ferraris et al., 1989); in the latter \((\text{Mn}^{3+} + \text{Fe}^{3+}) = 1.17\) apfu against \(\text{Sr} = 0.19\) apfu (Nagashima et al., 2010). Therefore, piemontite with high \(\text{Sr}\) content is not necessarily richer in \((\text{Mn}^{3+} + \text{Fe}^{3+})\) content than \(\text{Sr}\)–poor piemontite. The presence of niigataite, \(\text{Sr}\)–analogue of clinzoisite (Miyajima et al. 2003), also supports this consideration. Above result is understandable by the proposed factors controlling \(\text{Sr}, \text{REE}\) and transition element contents in piemontite and epidote, that is (1) the chemical composition of the host rocks, (2) the local availability of these elements, and (3) hydrothermal and/or metamorphic fluids supplying these elements, as discussed by e.g., Togari et al. (1988) and Akasaka et al. (1988) for \(\text{Mn}^{3+}, \text{Fe}^{3+}, \) and \(\text{Sr};\) Nagashima et al. (2010) for \(\text{Mn}, \text{Fe}, \text{Sr}, \) and \(\text{REE};\) Nagashima et al. (2006) for \(\text{Cr}, \text{Sr}, \) and \(\text{REE};\) and Treloar (1987) and Torres–Ruiz et al. (2003) for \(\text{Cr}.\) In the experimental studies on piemontite in the join \(\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\)

### Table 6. Refined site occupancies, atomic positions and site occupancies obtained by X-ray and TOF neutron Rietveld analyses

| Site | Occupancy | X-ray | TOF | \(x\) | \(y\) | \(z\) | \(b^*\) |
|------|-----------|-------|-----|-------|-------|-------|--------|
| A1   | \(\text{Ca}_{1.0}\) | 0.7574(5) | 3/4 | 0.1460(5) | 0.77 |
|      | \(\text{Ca}_{1.0}\) | 0.7628(10) | 3/4 | 0.1644(11) |
| A2   | \(\text{Ca}_{0.79(6)}\text{Sr}_{0.205}\) | 0.5966(5) | 3/4 | 0.4238(4) | 0.81 |
|      | \(\text{Ca}_{0.79(5)}\text{Sr}_{0.209}\) | 0.6009(9) | 3/4 | 0.4228(9) |
| M1   | \(\text{Al}_{0.90(7)}\text{Mn}^{2+}_{0.091}\) | 0 | 0 | 0 | 0.47 |
|      | \(\text{Al}_{0.902(5)}\text{Mn}_{0.098}\) | 0 | 0 | 0 |
| M2   | \(\text{Al}_{1.0}\) | 0 | 0 | 1/2 | 0.56 |
|      | \(\text{Al}_{1.0}\) | 0 | 0 | 1/2 |
| M3   | \(\text{Mn}^{2+}_{0.80(1)}\text{Al}_{0.20}\) | 0.2964(5) | 1/4 | 0.2210(4) | 0.39 |
|      | \(\text{Mn}_{0.34(6)}\text{Fe}_{0.267}\text{Al}_{0.20}\) | 0.2935(4) | 1/4 | 0.222(3) |
| Si1  | \(\text{Si}_{1.0}\) | 0.3402(7) | 3/4 | 0.0457(6) | 0.52 |
|      | \(\text{Si}_{1.0}\) | 0.3391(9) | 3/4 | 0.0507(10) |
| Si2  | \(\text{Si}_{1.0}\) | 0.6891(8) | 1/4 | 0.2736(7) | 0.51 |
|      | \(\text{Si}_{1.0}\) | 0.67937(13) | 1/4 | 0.27346(11) |
| Si3  | \(\text{Si}_{1.0}\) | 0.1832(7) | 3/4 | 0.3117(7) | 0.35 |
|      | \(\text{Si}_{1.0}\) | 0.17187(10) | 3/4 | 0.30646(10) |
| O1   | \(\text{Si}_{1.0}\) | 0.2370(10) | 0.9898(14) | 0.0331(8) | 0.81 |
|      | \(\text{Si}_{1.0}\) | 0.23426(6) | 0.9988(11) | 0.03838(3) |
| O2   | \(\text{Si}_{1.0}\) | 0.3006(10) | 0.9855(12) | 0.3478(9) | 0.80 |
|      | \(\text{Si}_{1.0}\) | 0.30371(6) | 0.98867(8) | 0.35076(6) |
| O3   | \(\text{Si}_{1.0}\) | 0.7859(11) | 0.0083(13) | 0.3419(8) | 0.81 |
|      | \(\text{Si}_{1.0}\) | 0.79504(6) | 0.01826(8) | 0.342(4) |
| O4   | \(\text{Si}_{1.0}\) | 0.0563(13) | 1/4 | 0.1440(12) | 0.59 |
|      | \(\text{Si}_{1.0}\) | 0.05493(7) | 1/4 | 0.13684(8) |
| O5   | \(\text{Si}_{1.0}\) | 0.0440(11) | 3/4 | 0.1489(13) | 0.70 |
|      | \(\text{Si}_{1.0}\) | 0.04266(7) | 3/4 | 0.1427(10) |
| O6   | \(\text{Si}_{1.0}\) | 0.0712(13) | 3/4 | 0.4117(14) | 0.62 |
|      | \(\text{Si}_{1.0}\) | 0.06056(9) | 3/4 | 0.39544(9) |
| O7   | \(\text{Si}_{1.0}\) | 0.5214(13) | 3/4 | 0.1724(10) | 0.80 |
|      | \(\text{Si}_{1.0}\) | 0.5201(8) | 3/4 | 0.17851(8) |
| O8   | \(\text{Si}_{1.0}\) | 0.5221(13) | 1/4 | 0.3188(12) | 0.92 |
|      | \(\text{Si}_{1.0}\) | 0.51521(9) | 1/4 | 0.31032(9) |
| O9   | \(\text{Si}_{1.0}\) | 0.6132(14) | 1/4 | 0.0987(13) | 0.99 |
|      | \(\text{Si}_{1.0}\) | 0.62041(8) | 1/4 | 0.09637(8) |
| O10  | \(\text{Si}_{1.0}\) | 0.0870(13) | 1/4 | 0.4308(12) | 0.60 |
|      | \(\text{Si}_{1.0}\) | 0.08552(8) | 1/4 | 0.44344(8) |
| H10  | \(\text{TOF}\) | 0.04978(18) | 1/4 | 0.31779(17) | 3.95 |

* Isotropic thermal parameters, \(b\), were fixed at the values obtained by Dollase (1969).

** Mn + Fe.
(OH)-Ca$_2$Mn$_{3+}$Si$_3$O$_{12}$(OH) by Langer et al. (2002) and Nagashima and Akasaka (2004), piemontites containing as much as 1.48 and 1.26 Mn$^{3+}$ apfu, respectively, were synthesized from the starting materials of Ca$_2$Al$_{1.2}$Mn$_{3+1.8}$Si$_3$O$_{12}$(OH) and Ca$_2$Al$_{1.5}$Mn$_{3+1.5}$Si$_3$O$_{12}$(OH) in composition, respectively, indicating that the Mn$^{3+}$-rich piemontite is formed from the starting material with high Mn$^{3+}$ content irrespective of whether Sr is present or absent. The Mn$^{3+}$ content in the host material, thus, is the most important factor for the formation of Mn$^{3+}$-rich piemontite. Therefore, Sr, REE and transition element contents in piemontite and epidote depend on their activity in the wall rocks and metamorphic or hydrothermal fluids, but Sr content in piemontite and epidote is not an essential factor for the transition element contents.

On the other hand, at first glance, the Sr content appears to affect the (Mn + Fe) content in the M$_1$ and M$_3$ sites. The intracrystalline partitioning coefficient for (Mn$^{3+}$ + Fe$^{3+}$)-Al partitioning, defined as $K_D = ([\text{Fe}^{3+} + \text{Mn}^{3+}] / \text{Al})_M / ([\text{Fe}^{3+} + \text{Mn}^{3+}] / \text{Al})_M$, in the Tone piemontite is calculated as 0.006 (Fig. 5). Since the $K_D$ values for (Mn$^{3+}$ + Fe$^{3+}$)-Al partitioning in the synthetic Ca$_2$Al$_2$(Fe$^{3+}$,Mn$^{3+}$)Si$_3$O$_{12}$(OH)–epidote and piemontite are 0.05–0.13 (Nagashima and Akasaka, 2010), the $K_D$ value of the Tone piemontite is significantly lower than those of Sr-free Ca–epidote and Ca–piemontite (Fig. 5), indicating that the M$_3$ site preference of (Mn$^{3+}$ + Fe$^{3+}$) in the Tone piemontite is stronger than that in the Sr–free Ca–epidote–piemontite series. However, the $K_D$ value for Mn$^{3+}$–Al partitioning [$K_D = ([\text{Mn}^{3+} / \text{Al})_M / ([\text{Mn}^{3+} / \text{Al})_M]$ in the Tone piemontite is 0.066, which is in a range of the values for the synthetic Ca–piemontites, that is $K_D = 0.063$–0.080 after Langer et al. (2002) and $K_D = 0.038$–0.063 after Nagashima and Akasaka (2004). Moreover, the Mn$^{3+}$ occupancies at M$_3$ and M$_1$ sites in the Tone piemontite, 0.633 and 0.102, respectively, agree to the calculated values, 0.63 for the M$_3$ site and 0.08 for the M$_1$ site using the regression equations on the Mn$^{3+}$ occupancy at the M$_3$ and M$_1$ sites against total Mn$^{3+}$ apfu in the synthetic Ca$_2$(Al,Mn$^{3+}$)$_3$Si$_3$O$_{12}$(OH)–piemontites formulated by Nagashima and

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**Figure 3.** Crystal structure of Sr–rich piemontite projected down [010] using the program VESTA3 (Momma and Izumi, 2011).

**Figure 4.** $^{57}$Fe Mössbauer spectrum of piemontite at 293K. The refined Mössbauer hyperfine parameters are listed in Table 7.

**Table 7.** Mössbauer hyperfine parameters of Tone piemontite*

| IS (mm/s) | QS (mm/s) | FWHH (mm/s) | Area Ratio (%) | Assignment |
|----------|-----------|-------------|---------------|------------|
| AA$'$    | 0.351(2)  | 2.185(5)    | 0.244(9)      | Fe$^{3+}$(M3) in piemontite |
| BB$'$    | 0.367(6)  | 1.93(1)     | 0.35(1)       | Fe$^{3+}$(M3) in piemontite |
| CC$'$    | 0.18(2)   | 1.08(4)     | 0.81(6)       | Unassignable |

*Estimated standard deviation are in parentheses (1σ). IS, isomer shift relative to metallic iron absorber; QS, quadrupole splitting; FWHH, full width at half height.
sites of the site. Such strong preferential incorporation of Fe$^{3+}$ in the M$^{1}$ site but due to the selective distribution of Fe$^{3+}$ in the M$^{3}$ site. Therefore, the stronger preference of Fe$^{3+}$ at the M$^{1}$ site is similar to that of Mn$^{3+}$: the substitution of Sr for Ca at the M$^{1}$ site is not in the M$^{3}$ site.

At first glance, these results seem to indicate that the substitution of Sr for Ca at the A2 site affect the distribution of Fe$^{3+}$ in the M$^{3}$ and M$^{1}$ sites. However, Dollase (1973) showed that $K_D$ values of Fe$^{3+}$-Al partitioning in natural epidotes are $\sim 0.01-0.02$, and that epidotes with Fe$^{3+} > 0.63$ apfu in the M$^{3}$ site have no detectable Fe$^{3+}$ in the M$^{1}$ site. Fehr and Heuss-Albfichler (1997) also got $K_D$ values of Fe$^{3+}$-Al partitioning, 0.012-0.022, for annealed natural epidotes and supported the result by Dollase (1973). Since the Fe$^{3+}$ in the M$^{3}$ site is 0.316 apfu for the Tone piemontite single crystal and 0.267 apfu in average for the piemontite powder sample, the Fe$^{3+}$ distribution only in the M$^{3}$ site but not in the M$^{1}$ site in the Tone piemontite is consistent with the result for the natural epidotes after Dollase (1973) and Fehr and Heuss-Albfichler (1997). There is no topological reason for the stronger preference of Fe$^{3+}$ than Mn$^{3+}$ to the M$^{3}$ site.

After all, in the Tone piemontite, Al, Mn$^{3+}$ and Fe$^{3+}$ occupancies in the M$^{1}$ and M$^{3}$ sites are not affected by Sr content. In their study on the synthetic epidote and piemontite with the compositions of Ca$_2$Al$_2$(Fe$^{3+}$,Mn$^{3+}$)$_3$Si$_3$O$_{12}$(OH), Nagashima and Akasaka (2010) found a rule that Fe$^{3+}$ and Mn$^{3+}$ distribute among octahedral sites according to their individual distribution schemes by the substitutions of Fe$^{3+} \leftrightarrow$ Al and Mn$^{3+} \leftrightarrow$ Al, respectively. This rule is valid not only for Ca-epidote and Ca-piemontite but also for Sr-rich and -bearing ones.

No dependence of Mn$^{3+}$ and Fe$^{3+}$ contents in the M$^{1}$ and M$^{3}$ sites against Sr content can be also confirmed in terms of the relationship between Sr content and mean $<M^{3}O>$ and $<M^{1}O>$ distances, as discussed below. As shown in Table 8, mean $<M^{3}O>$ and $<M^{1}O>$ distances of the Tone piemontite, $<M^{3}O> = 2.050$ Å and $<M^{1}O> = 1.923$ Å, are similar to those of synthetic Ca-piemontite, $<M^{3}O> = 2.047-2.063$ Å and $<M^{1}O> = 1.926-1.956$ Å after Langer et al. (2002), Almen (1987) and Nagashima and Akasaka (2004), 2010), and of Sr-rich and -bearing piemontites, $<M^{3}O> = 2.057-2.077$ Å and $<M^{1}O> = 1.929-1.946$ Å (Ferraris et al., 1989; Bonazzi et al., 1990: Nagashima et al., 2010). Therefore, there is no systematic variations of the bond distances and volumes of the M$^{3}$O$_{6}$ and M$^{1}$O$_{6}$ octahedra against Sr content at the A2 site for these piemontites. This conclusion is well illustrated in Figure 6, in which $<M^{3}O>$ and $<M^{1}O>$ distances listed in Table 8 are plotted against Sr content in the A2 site. The $<M^{1}O>$ distance of a tweddllite from Kalahari, South Africa, in which the A2 site is filled with Sr, is 1.969 Å (Armbuster et al., 2002) and, thus, is greater than those of other stronlitan piemontite and Sr-free Ca-piemontite. However, since the (Mn + Fe) content in the M$^{1}$ site of the Kalahari tweddllite attains 0.57 apfu, Armbuster et al. (2002) explained that the large mean $<M^{1}O>$ distance is due to

![Figure 5. Mn$^{3+}$ + Fe$^{3+}$ occupancy at the M$^{1}$ site versus Mn$^{3+}$ + Fe$^{3+}$ occupancy at the M$^{3}$ site with intracrystalline partitioning. $K_D = [Al(Mn^{3+} + Fe^{3+})]_M[Al(Mn^{3+} + Fe^{3+})]_A].$ Ideal fractionation $K_D$ of 0.01, 0.02, 0.04, 0.08, 0.10, 0.12, and 0.14 are shown. Numbers written with closed symbols are Sr content (apfu).](image-url)
Table 8. Site populations in the $A2$, $M1$, and $M3$ sites, ($Mn^{3+} + Fe^{3+}$)-content in the octahedral sites and selected bond distances of the synthetic Ca-piemontites and natural Sr-rich piemontites

|                  | Synthetic piemontites*1 (Langer et al., 2002; Almen, 1987) | Synthetic piemontite*1 (Nagashima and Akasaka, 2004) | Synthetic piemontite*1 (Nagashima and Akasaka, 2010) | Sr-bearing piemontite (Dollase, 1969) | Sr-rich piemontite (Ferraris et al., 1989) | Sr-REE-rich piemontite (Nagashima et al., 2010) | Tone Sr-rich piemontite (This study) | Strontiopie montite (Bonazzi et al., 1990) | Tweddil tide (Armbruster et al., 2002) |
|------------------|-------------------------------------------------------------|-------------------------------------------------------|--------------------------------------------------------|--------------------------------------|-------------------------------------------|---------------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
|                  | MK-35/8 PF-66/14 MK-42/1 PM81 Run No. 30                    |                                                        |                                                        |                                      |                                           |                                             |                                        |                                        |                                        |
| Sr in $A2$ (apfu)| -                                                           | -                                                     | -                                                      | 0.13                                 | 0.16                                      | 0.19                                         | 0.289                                  | 0.73                                   | 1.00                                   |
| REE in $A2$ (apfu)| -                                                           | -                                                     | -                                                      | 0.10                                 |                                           |                                             |                                        |                                        |                                        |
| $Me^{3+}$ in $M1$+$M3$ (apfu) |                                                        |                                                        |                                                        |                                      |                                           |                                             |                                        |                                        |                                        |
| $Mn^{3+}$        | 0.83                                                         | 0.98                                                   | 1.39                                                   | 1.03                                 | 0.73                                      | 0.72                                         | 0.78                                    | 0.72                                   | 0.735                                  | 0.86                                       | 1.360-1.577*3                          |
| $Fe^{3+}$        | -                                                            | -                                                     | -                                                      | 0.12                                 | 0.31                                      | 0.35                                         | 0.45                                    | 0.316                                  | 0.32                                   | 0.278-0.191*3                            |
| $Mn^{3+} + Fe^{3+}$ | -                                                           | -                                                     | -                                                      | 0.85                                 | 1.03                                      | 1.13                                         | 1.17                                    | 1.051                                  | 1.18                                   | 1.58*4                                    |
| Refinement method| Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld | Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld Single-crystal Rietveld | | | | | | | | |
| $A1$- O7         | n.g.*2                                                       | n.g.                                                   | 2.296(2)                                               | 2.32(2)                              | 2.272(9)                                  | 2.288(6)                                    | 2.281(7)                                | 2.253(5)                               | 2.285(2)                               | 2.227(13)                              | 2.260(7)                                   | |
| $A2$- O2 (<2)    | n.g.                                                         | n.g.                                                   | 2.669(2)                                               | 2.68(1)                              | 2.726(6)                                  | 2.711(4)                                    | 2.737(3)                                | 2.683(3)                               | 2.753(1)                               | 2.715(8)                               | 2.757(4)                                   | |
| $A2$- O2 (<2)    | n.g.                                                         | n.g.                                                   | 2.534(3)                                               | 2.52(1)                              | 2.554(7)                                  | 2.548(4)                                    | 2.553(3)                                | 2.557(3)                               | 2.562(1)                               | 2.614(8)                               | 2.663(4)                                   | |
| $A3$- O2 (<2)    | n.g.                                                         | n.g.                                                   | 2.832(2)                                               | 2.74(1)                              | 2.709(6)                                  | 2.745(4)                                    | 2.716(3)                                | 2.800(4)                               | 2.686(1)                               | 2.722(9)                               | 2.757(4)                                   | |
| O7               | n.g.                                                         | n.g.                                                   | 2.254(4)                                               | 2.24(2)                              | 2.268(9)                                  | 2.277(6)                                    | 2.283(7)                                | 2.300(5)                               | 2.303(2)                               | 2.374(12)                              | 2.405(6)                                   | |
| O6               | n.g.                                                         | n.g.                                                   | 2.489(3)                                               | 2.55(1)                              | 2.542(8)                                  | 2.541(7)                                    | 2.566(6)                                | 2.565(5)                               | 2.592(2)                               | 2.608(10)                              | 2.657(6)                                   | |
| $<^{8}$ A2-O>    | 2.587                                                        | 2.598                                                  | 2.602                                                   | 2.58                                  | 2.60                                      | 2.603                                       | 2.608                                   | 2.618                                  | 2.612                                  | 2.636                                  | 2.677                                       | |
| $A2$- O8 (<2)    | n.g.                                                         | n.g.                                                   | 3.079(1)                                               | 3.04(1)                              | 3.027(3)                                  | 3.03(1)                                     | 3.031(1)                                | 2.999(2)                               | 3.018(0)                               | 3.019(4)                               | 3.044(2)                                   | |
| $<^{8}$ A2-O>    | -                                                            | -                                                      | 2.689                                                   | 2.68                                  | 2.684                                     | 2.69                                        | 2.692                                   | 2.694                                  | 2.693                                  | 2.712                                  | 2.750                                       | |
| $<^{M1}$ O>    | 1.926                                                        | 1.927                                                  | 1.956                                                   | 1.95                                  | 1.935                                     | 1.933                                       | 1.932                                   | 1.946                                  | 1.923                                  | 1.929                                  | 1.969                                       | |
| $<^{M3}$ O>    | 2.047                                                        | 2.047                                                  | 2.063                                                   | 2.07                                  | 2.049                                     | 2.062                                       | 2.057                                   | 2.077                                  | 2.050                                  | 2.061                                  | 2.068                                       | |

*1 Synthesis conditions: MK-35/8, 1.5 GPa and 800°C; PF-66/14, 1.82 GPa and 820°C; MK-42/1, 1.5 GPa and 750°C; PM81, 0.35 GPa and 500°C; Run No. 30, 0.37 GPa and 500°C.
*2 n.g., not given in the original paper.
*3 EMPA data. *4 X-ray structural refinement result.
the high (Mn + Fe) content in this site. It is noted that the mean \(<M_3-O>\) distance, 2.068 Å, of the Kalahari tweddellite is not the largest among the piemontites referred to above, despite the M3 site fully occupied with (Mn + Fe). Figure 6b shows that the \(<M_3-O>\) and \(<M_1-O>\) distances essentially depend on the Mn\(^{3+}\) and Fe\(^{3+}\) contents in the M3 and M1 sites and supports above discussion and conclusion.

**Effect of substitution of Sr for Ca in the A2 site on the A2O\(_{10}\) polyhedra and overall crystal structure**

The increase of the mean \(<A_2-O>\) distance with Sr content in the A2 site is a characteristic geometric change of the A2O\(_{10}\) polyhedron by the Sr substitution for Ca (e.g., Bonazzi and Menchetti, 2004; Nagashima et al., 2010). As shown in Table 8 and Figure 7, the relationships of the \(<VIII A_2-O>\) (= 2.617 Å) and \(<X A_2-O>\) (= 2.693 Å) against Sr content in the A2 site (= 0.289 apfu) are in harmony with those of other Sr–bearing piemontites. However, it has been found that the A2O\(_8\) and A2O\(_{10}\) coordination polyhedra do not expand isotropically with the increase of the Sr content in the A2 site (Bonazzi et al., 1990; Nagashima et al., 2010): Bonazzi et al. (1990) found main lengthening of the A2–O7 distance with Sr in the A2 site; in addition, Nagashima et al. (2010) found that the A2–O2' and A2–O10 distances also increase with increasing Sr population in the A2 site. In fact, the A2–O7 distance (= 2.303 Å) of the Tone piemontite with 0.289 apfu Sr is longer than A2–O7 = 2.254(4)–2.268(9) Å of the synthetic Sr-free Ca-piemontite (Almen, 1987; Nagashima and Akasaka, 2004, 2010) and close to A2–O7 = 2.300(5) Å of the Kamisugai piemontite with Sr = 0.19 apfu (Nagashima et al., 2010). The lengthening of the A2–O2' and A2–O10 distances by the substitution of Sr for Ca in the A2 site is also the case of the Tone piemontite: A2–O2' = 2.562(1) and A2–O10 = 2.592(2) Å of the Tone piemontite are longer than A2–O2' = 2.52(1)–2.554(7) and A2–O10 = 2.489(3)–2.55(1) Å of Sr-free Ca-piemontite after Almen (1987) and Nagashima and Akasaka (2004, 2010). The A2–O2, A2–O3 and A2–O8 distances do not show any systematic variation against Sr content, as noted by Nagashima et al. (2010).

Although Bonazzi and Menchetti (2004) noticed that the increase of the A2–O7 distance leads to the decrease of the A1–O7 distance, the A1–O7 distance of the Tone piemontite, 2.285(2) Å, is in a range of those of synthetic Sr-free Ca-piemontites, 2.272(9)–2.296(2) Å (Table 8; Almen, 1987; Nagashima and Akasaka, 2004, 2010). Moreover, as shown in Table 8, the A1–O7 distance of the published Sr-bearing or Sr-rich piemontites is in a range between 2.227(13) and 2.288(6) Å. Thus, the A1–O7 distance does not seem to be influenced by the
increase of the A2–O7 distance due to the substitution of Sr for Ca at the A2 site.

Anisotropic changes in the A2O10 coordination polyhedra due to the substitution of Sr for Ca on the overall crystal structure, which is characterized by the change of the unit-cell parameters and Si1–O9–Si2 angle. The increase of unit-cell parameters of synthetic piemontite in the join Ca2Al3Mn3+Si5O12(OH)–Sr2Al3Mn3+O12(OH) and synthetic clinozoisite in the join Ca2Al3Si5O12(OH)–Sr2Al3Si5O12(OH) with increasing Sr content in the A2 site has been already shown by Akasaka et al. (2000) and Dörsam et al. (2007), respectively. The unit-cell parameters of the Tone piemontite obtained from the X-ray single-crystal analysis ([42]Sr = 0.289 apfu; Mn3+ + Fe3+ = 1.051 apfu), \( a = 8.8942(1) \) Å, \( b = 5.6540(1) \) Å, \( c = 10.1928(2) \) Å, \( \beta = 115.100(1) \)°, and \( V = 464.17(2) \) Å³, are fairly consistent with those of the synthetic (Ca 2.0 – Sr460.6 Å³, the volume of Sr-free Sr for Ca at the A1 site does not directly effect on other coordination polyhedra at the A1, octahedral and tetrahedral sites, it causes the anisotropic change in the A2O12– and A2O10- coordination polyhedra and the Si1–O9–Si2 angle and influences the overall crystal structure of piemontite, which is reflected in the variation of the unit-cell parameters.

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