New data on ferri-ghoseite in Sanbagawa quartz schist from the Imori region, Wakayama Prefecture, Japan: solid solution between magnesio-riebeckite and clino-suenoite

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Chemically heterogeneous amphibole, ranging in composition from magnesio-riebeckite through ferri-ghoseite to clino-suenoite, was found in a specimen of Sanbagawa quartz schist from the Imori region of the western Kii Peninsula, central Japan. The amphibole exhibits a continuous solid solution between ^BNa and $^B\text{Mn}^{2+}$ ($^B\text{Mn}^{2+} = 0\text{--}1.82$ atoms per formula unit). Most of the amphibole crystals comprise a Mn-poor core and a Mn-rich rim, and ferri-ghoseite often occurs near the boundary between core and rim. The crystal structure of a single crystal fragment of ferri-ghoseite, which has an averaged composition of $^A(\text{Na}_{0.16}\text{K}_{0.02})_{\Sigma 0.18}^B(\text{Na}_{0.83}\text{Ca}_{0.09}\text{Mn}_{1.08}^{2+})_{\Sigma 2.00}^C(\text{Mg}_{3.78}\text{Mn}_{0.52}\text{Fe}_{0.66}^{3+}\text{Al}_{0.04})_{\Sigma 5.00}^T(\text{Si}_{7.95}\text{Al}_{0.05})_{\Sigma 8.00}\text{O}_{22}^W[(\text{OH})_{1.90}\text{F}_{0.10}]_{\Sigma 2.00}$ based on electron-microprobe analyses, was refined to a $R1$ of 6.7%, has unit cell parameters of $a = 9.6389(7)$, $b = 18.0534(10)$, $c = 5.3138(3)$ Å, and $\beta = 102.896(2)^\circ$, and is in space group $C2/m$ with $Z = 2$. The site populations for B cations of the ferri-ghoseite are $^{M4}(\text{Na}_{0.83}\text{Ca}_{0.09})^{M4'}\text{Mn}_{1.08}^{2+}$, which also confirms the $^B(\text{Na}, \text{Mn}^{2+})$ solid solution. Sector-zoned aegirine occurs in the amphibole-bearing quartz schist from Imori, and it is assumed that most of the metamorphic minerals in the quartz schist formed under non-equilibrium conditions. Therefore, taking into account the miscibility gap between sodium amphibole and clino-suenoite, the solid solution between ^BNa and $^B\text{Mn}^{2+}$ in the amphibole can be inferred to have resulted from rapid, non-equilibrium crystallization rather than high- T equilibrium crystallization.

Keywords: Amphibole, Ferri-ghoseite, Magnesio-riebeckite, Clino-suenoite, Solid solution

INTRODUCTION

Ferri-ghoseite, $^A\Box^B(\text{NaMn}^{2+})^C(\text{Mg}_4\text{Fe}^{3+})^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$, is a recently approved member of the sodium-(magnesium-iron-manganese) subgroup of the amphibole supergroup (Hawthorne et al., 2012; Williams et al., 2013). This amphibole subgroup, in which ^BNa and $^B(\text{Mg} + \text{Fe}^{2+} + \text{Mn}^{2+})$ ideally occur in a 1:1 ratio, has been newly introduced to the amphibole nomenclature scheme in force (Hawthorne et al., 2012). Within this subgroup, the composition $^A\Box^B(\text{NaMn}^{2+})^C(\text{Mg}_4\text{Al})^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$ was provisionally defined as ‘rootname 11’ (cf. table 7 in Hawthorne et al., 2012). A subsequent decision by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA)

to use the root name ghoseite for this composition was made in consideration of its Fe^{3+} -dominant counterpart (Oberti and Ghose, 1993), ferri-ghoseite (IMA 12-F; Williams et al., 2013), which has an ideal chemical formula of $^A\Box^B(\text{NaMn}^{2+})^C(\text{Mg}_4\text{Fe}^{3+})^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$.

Oberti and Ghose (1993) reported monoclinic Mn-rich amphibole with a composition $^A(\text{Na}_{0.30}\text{K}_{0.03})_{\Sigma 0.33}^B(\text{Na}_{0.87}\text{Ca}_{0.39}\text{Mn}_{0.57}^{2+}\text{Mg}_{0.17})_{\Sigma 2.00}^C(\text{Mg}_{3.84}\text{Mn}_{0.38}\text{Fe}_{0.72}^{3+}\text{Li}_{0.06})_{\Sigma 5.00}^T(\text{Si}_{7.88}\text{Al}_{0.12})_{\Sigma 8.00}\text{O}_{22}^W[(\text{OH})_{1.60}\text{F}_{0.40}]_{\Sigma 2.00}$ from Tidodi, India, which exhibited no evidence of exsolution as determined by crystal-structure refinement. Based on the amphibole nomenclature employed in 1993 (Leake, 1978), this Mn-rich amphibole was not considered a new mineral species, but later it was approved as a new mineral and given the name ‘parvowinchite’ based on revisions to the amphibole nomenclature (Leake et al., 2004). After the approval of the current nomenclature (Hawthorne et al., 2012), the nomenclature scheme re-

quired a new name for this Mn-rich amphibole, and 'parvowinchite' was renamed ferri-ghoseite (Williams et al., 2013).

Previous studies have characterized the exsolution between the sodium and magnesium-iron-manganese amphibole subgroups, indicating immiscibility between them (e.g., Smelik and Veblen, 1991; Shau et al., 1993). Therefore, the sodium-(magnesium-iron-manganese) amphibole subgroup has been investigated in terms of its solid solution with particular interest in the isomorphous substitution between large ^BNa and small $^B(\text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+})$ cations, but none have reported a wide compositional range between them, as far as we know. We found chemically heterogeneous amphibole, ranging in composition from magnesio-riebeckite [$^A\Box^B\text{Na}_2^C(\text{Mg}_3\text{Fe}_2^{3+})^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$] through ferri-ghoseite to clino-suenoite [$^A\Box^B\text{Mn}_2^{2+}\text{Mg}_5^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$], in a quartz schist of the Sanbagawa metamorphic belt of the Iimori region, Wakayama Prefecture, Japan. This amphibole from Iimori is suitable for investigating the solid solution between ^BNa and $^B\text{Mn}^{2+}$ in amphiboles. We present mineral data for this amphibole, including a single crystal study of ferri-ghoseite, and discuss the solid solution between magnesio-riebeckite and clino-suenoite. The specimen has been stored at the Geological Museum of the Geological Survey of Japan (GSJ), AIST, Tsukuba, under the registration number GSJ M41558.

GEOLOGIC SETTING AND PETROGRAPHY

The Sanbagawa metamorphic belt belongs to the high-pressure intermediate group of the metamorphic facies series (Miyashiro, 1961). It represents the deeply subducted portion of a Mesozoic accretionary complex at the eastern margin of the Eurasian continent. The Sanbagawa metamorphic belt in the Iimori region is divided into three mineral zones: chlorite, garnet, and biotite (in order of increasing metamorphic grade) on the basis of mineral paragenesis in the pelitic schists (e.g., Wang and Maekawa, 1997; Makimoto et al., 2004).

The ferri-ghoseite-bearing quartz schist was collected from a waste-rock pile at the Iimori mine (34°15'N, 135°26'E). This mine is located in the garnet zone, according to the metamorphic zonation maps of Wang and Maekawa (1997) and Makimoto et al. (2004). The quartz schist consists mainly of quartz, aegirine, albite, amphibole, and garnet with minor pyrophanite, apatite, rhodochrosite and jacobsonite. The amphibole is pale yellowish green and occurs as euhedral to subhedral crystals with lengths up to 500 μm .

MINERAL CHEMISTRY OF AMPHIBOLE

Chemical analyses of the amphibole were performed on JEOL JXA-8800R and JEOL JXA-8900R electron microprobes at the GSJ Laboratory, AIST. The accelerating voltage and specimen current were set to 15 kV and 12 nA, respectively, on the Faraday cup. The beam diameter was 5 μm for analyses of F and Cl, and 2 μm for analyses of other elements. Synthetic quartz (for Si), rutile (Ti), corundum (Al), eskolaite (Cr), hematite (Fe), manganosite (Mn), periclase (Mg), wollastonite (Ca), F-phlogopite (F), natural albite (Na), adularia (K), and Cl-rich hastingsite (Cl) were used as standard materials. Matrix corrections followed Bence and Albee (1968) method. Detection limits for Cl and F were ~ 0.02 and ~ 0.12 wt% (3σ level), respectively, for most analyses. The chemical compositions of the amphibole are given in Table 1. Cl content of the amphibole is below the detection limit. Structural formulae for the amphibole were calculated on the basis of 23 O and assuming (1) $\text{OH} = 2 - \text{F} - \text{Cl}$; and (2) that all cations, apart from H^+ , are allocated into the T, C, B, and A groups of cations based on their ionic size and the relationship $\text{T} < \text{C} < \text{B} < \text{A}$, as suggested by Leake et al. (1997). Based on the relatively high oxygen fugacity indicated by the high $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios (0.99–1.0) of associated aegirine and garnet (Banno and Yamada, 2012), the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of the amphibole were estimated using the maximum ferric method of Leake et al. (1997). Total Mn was expressed as Mn^{2+} , because, in this way, formulae calculated using the maximum ferric method satisfied the six criteria for calculation of amphibole formulae outlined by Leake et al. (1997).

Backscattered electron images of the amphibole crystals show that they are chemically heterogeneous, with dark and bright areas, corresponding to Mn-poor and Mn-rich compositions, respectively (Fig. 1). Numbers shown in Figure 1 indicate $^B\text{Mn}^{2+}$ [atoms per formula unit (apfu)]. The amphibole crystals do not show clear concentric zoning, but most consist of a dark core (Mn-poor core) and a bright rim (Mn-rich rim) (Figs. 1a–1c). This texture indicates that the dark areas formed earlier than the bright areas. Some amphibole grains do not possess a dark core (Figs. 1d–1f). Moreover, gray areas, which shows a composition intermediate between those of the dark and bright areas, occur in some amphibole crystals near the boundary between the dark core and the bright rim (Figs. 1a–1c), or as patches in the bright areas (Fig. 1f). The dark areas in the amphibole crystals range from magnesio-riebeckite to $^B\text{Mn}^{2+}$ -poor ferri-ghoseite ($^B\text{Mn}^{2+} = 0\text{--}0.44$ apfu), whereas the bright areas range from $^B\text{Mn}^{2+}$ -rich ferri-ghoseite to clino-suenoite ($^B\text{Mn}^{2+} = 1.19\text{--}1.82$ apfu) (Figs. 2 and 3a). The gray

Table 1. Chemical compositions of amphibole from Iimori

Area	D	D	G	G	G	G	G	B	B	B	B	B
Mineral	Mrbk	Mrbk	Fgho	Fgho [#]	Fgho [#]	Fgho [#]	Fgho [#]	Fgho	Csue	Csue	Csue	Csue
Weight percentage												
SiO ₂	57.30	57.23	56.38	55.73	55.92	55.80	55.49	55.42	55.18	55.21	55.43	55.93
TiO ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al ₂ O ₃	4.00	3.71	0.73	0.62	0.49	0.52	0.48	0.38	0.30	0.22	0.18	0.14
Cr ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO [*]	9.55	8.80	7.16	6.46	5.73	5.02	4.93	4.05	3.59	2.55	2.17	1.74
MnO	1.05	3.53	9.95	11.44	13.59	13.98	13.86	15.16	16.38	17.64	19.01	19.44
MgO	15.26	14.91	17.26	17.42	17.18	18.03	18.44	18.81	18.71	19.14	19.24	20.01
CaO	0.66	0.66	0.70	0.63	0.64	0.57	0.58	0.49	0.48	0.43	0.45	0.34
Na ₂ O	7.89	7.31	5.20	4.31	3.48	3.12	3.47	3.01	2.74	2.07	1.55	1.04
K ₂ O	0.30	0.29	0.20	0.14	0.07	0.09	0.08	0.08	0.07	n.d.	n.d.	n.d.
F	0.38	0.25	0.37	0.29	0.15	0.12	0.30	0.19	0.19	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
-O=F+Cl	0.16	0.11	0.16	0.12	0.06	0.05	0.13	0.08	0.08	0.00	0.00	0.00
Total	96.23	96.58	97.79	96.92	97.19	97.20	97.50	97.51	97.56	97.26	98.03	98.64
H ₂ O ^{**}	1.98	2.04	1.95	1.96	2.03	2.04	1.96	2.00	1.99	2.08	2.09	2.10
Fe ₂ O ₃ ^{***}	10.17	9.78	7.96	7.18	6.37	5.58	5.16	3.57	2.08	1.57	0.55	0.11
FeO ^{***}	0.40	0.00	0.00	0.00	0.00	0.00	0.29	0.83	1.71	1.14	1.67	1.64
Total	99.23	99.60	100.54	99.60	99.86	99.80	99.98	99.86	99.75	99.50	100.17	100.75
Formulae on the basis of O = 23												
Si	7.96	7.97	7.95	7.95	7.98	7.96	7.92	7.94	7.95	7.96	7.97	7.98
Al	0.04	0.03	0.05	0.05	0.02	0.04	0.08	0.06	0.05	0.04	0.03	0.02
Sum T	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al	0.61	0.58	0.07	0.06	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Ti	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe ³⁺	1.06	1.02	0.84	0.77	0.68	0.60	0.56	0.39	0.22	0.17	0.06	0.01
Fe ²⁺	0.05	0.00	0.00	0.00	0.00	0.00	0.03	0.10	0.21	0.14	0.20	0.20
Mn ²⁺	0.12	0.31	0.46	0.47	0.60	0.52	0.49	0.50	0.55	0.58	0.62	0.54
Mg	3.16	3.09	3.63	3.70	3.66	3.83	3.92	4.01	4.02	4.11	4.12	4.25
Sum C	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Mn ²⁺	0.00	0.11	0.73	0.91	1.05	1.17	1.19	1.34	1.45	1.58	1.70	1.81
Ca	0.10	0.10	0.11	0.10	0.10	0.09	0.09	0.07	0.07	0.07	0.07	0.05
Na	1.90	1.79	1.16	0.99	0.85	0.74	0.72	0.59	0.48	0.35	0.23	0.14
Sum B	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Na	0.22	0.18	0.26	0.20	0.11	0.12	0.24	0.25	0.29	0.22	0.20	0.15
K	0.05	0.05	0.04	0.03	0.01	0.02	0.02	0.02	0.01	n.d.	n.d.	n.d.
Sum A	0.27	0.23	0.30	0.23	0.12	0.14	0.26	0.27	0.30	0.22	0.20	0.15
F	0.17	0.11	0.17	0.13	0.07	0.05	0.14	0.09	0.09	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OH	1.83	1.89	1.83	1.87	1.93	1.95	1.86	1.91	1.91	2.00	2.00	2.00
Sum W	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

* Total Fe as FeO.

** H₂O was calculated assuming OH + F + Cl = 2.0 apfu.*** Fe³⁺/Fe²⁺ was calculated by maximum ferric estimation (Leake et al., 1997).

Chemical composition of ferri-ghoseite for the X-ray study.

Abbreviations: D, dark area; G, gray area; B, bright area; Mrbk, magnesio-riebeckite; Fgho, ferri-ghoseite; Csue, clino-suenoite; n.d., not detected.

Figure 1. (a)–(f) Backscattered electron images of amphibole crystals from Iimori. Numbers indicate $^B\text{Mn}^{2+}$ (apfu). Abbreviations: Aeg, aegirine; Qtz, quartz; Rds, rhodochrosite.

areas range from $^B\text{Mn}^{2+}$ -rich magnesio-riebeckite to ferri-ghoseite ($^B\text{Mn}^{2+} = 0.32$ – 1.29 apfu) (Figs. 2 and 3a). The empirical formula of the gray areas, based on the average chemical composition ($n_{\text{spots}} = 37$), is $^A(\text{Na}_{0.21}\text{K}_{0.02})\Sigma 0.23$ $^B(\text{Na}_{0.95}\text{Ca}_{0.10}\text{Mn}_{0.95})\Sigma 2.00$ $^C(\text{Mg}_{3.72}\text{Mn}_{0.50}\text{Fe}_{0.72}^{\text{Al}_{0.06}})\Sigma 5.00$ $^T(\text{Si}_{7.95}\text{Al}_{0.05})\Sigma 8.00$ $\text{O}_{22}^W[(\text{OH})_{1.88}\text{F}_{0.12}]\Sigma 2.00$.

The amphibole shows positive correlations in $^C(\text{Mg} + \text{Mn}^{2+} + \text{Fe}^{2+})$ versus $^B\text{Mn}^{2+}$ (Fig. 3a), and $^C(\text{Fe}^{3+} + \text{Al})$ versus ^BNa diagrams (Fig. 3b), indicating the substitu-

tion mechanism $^B\text{Mn}^{2+} + ^C(\text{Mg}, \text{Mn}^{2+}, \text{Fe}^{2+}) = ^B\text{Na}^+ + ^C(\text{Fe}^{3+}, \text{Al})$.

X-RAY CRYSTALLOGRAPHY OF FERRI-GHOSEITE

A single crystal fragment of ferri-ghoseite extracted from the gray area of an amphibole crystal in a polished thin section used for the electron microprobe analyses was

Figure 2. B_{Ca} - $B_{Mn^{2+}}$ - B_{Na} ternary diagram showing the compositional range of amphibole from Iimori. Also plotted for comparison are a richterite—clino-suenoite pair from Robinson et al. (1971), and Mn-rich amphibole (bulk composition) and two secondary amphiboles from Shau et al. (1993).

mounted on a glass fiber and analyzed by X-ray diffraction. Single crystal diffraction data were obtained using a RIGAKU R-AXIS RAPID II diffractometer equipped with a curved imaging plate and $MoK\alpha$ radiation monochromatized, focused by a VariMax confocal multilayer mirror. Each of X-ray diffraction spots did not show splitting and streaks caused by a variance of d_{hkl} . The Rigaku RAPID AUTO software package was used to process the diffraction data and correct the data for a numerical absorption. The crystal structure was solved using the software SUPERFLIP (Palatinus and Chapuis, 2007) and employing the charge-flipping method. The SHELXL-2018 software package (Sheldrick, 2008) was used for crystal structure refinement. Scattering factors for neutral atoms were taken from the International Tables for Crystallography, Volume C (1992). The C cations reside in the $M1$, $M2$, and $M3$ sites, whereas the B cations occur at the $M4$ site (Hawthorne et al., 2012). The W anions occur at the O3 site (Hawthorne et al., 2012). Site-scattering values of the $M1$ and $M2$ sites were refined by sharing the sites with Mg and Fe atoms, which are representative elements in these sites. Occupancy of Mg in the $M3$ site was fixed at 1 because the refined site-scattering value

Figure 3. (a) $C(Mg + Mn^{2+} + Fe^{2+})$ versus $B_{Mn^{2+}}$, and (b) $C(Fe^{3+} + Al)$ versus B_{Na} diagrams for amphibole from Iimori.

was close to 12. Residual electron density, which is near to the $M4$ site and displaced along the 2-fold axis towards the octahedral strip, was detected on a difference-Fourier map after convergence of the first refinement based on a model containing eight cation sites ($T1$, $T2$, $M1$, $M2$, $M3$, $M4$, A , and H). The position of the residual electron density was called $M4'$ by Ungaretti et al. (1981). The presence of the split position $M4'$ was also reported in ferri-ghoseite from Tidodi, India (Oberti and Ghose, 1993). All the atomic positions, apart from A and H , were refined using anisotropic thermal factors.

Table 2. Experimental details and crystallographic data of ferri-ghoseite

<i>a</i> (Å)	9.6389(7)
<i>b</i> (Å)	18.0534(10)
<i>c</i> (Å)	5.3138(3)
β (°)	102.896(2)
<i>V</i> (Å ³)	901.37(10)
Space group	<i>C2/m</i>
<i>Z</i>	2
<i>D</i> _{calc.} (g/cm ³)	3.146
μ (mm ⁻¹)	2.502
Radiation	MoK α
Reflection range	-13 $\leq h \leq$ 13 -23 $\leq k \leq$ 21 -7 $\leq l \leq$ 7
No. of measured reflections	5172
No. of unique reflections	1335
No. of observed reflections [$F^2 > 2\sigma(F^2)$]	1257
<i>R</i> _{int}	0.0427
Variable parameters	105
<i>R</i> 1 [$F^2 > 2\sigma(F^2)$], <i>R</i> 1 (all reflections)	0.0626, 0.0672
<i>wR</i> 2 (all reflections)	0.1251
Weighting parameters, <i>a</i> , <i>b</i>	0.0001, 14.6777
Goodness of Fit	1.253
Final $\Delta\rho_{\max}$ (e/Å ³)	0.955
Final $\Delta\rho_{\min}$ (e/Å ³)	-0.865

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{0.5}.$$

$$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP].$$

$$P = (2F_c^2 + F_o^2) / 3.$$

Full-matrix refinement on F^2 of 1335 independent reflections ($R_{\text{int}} = 0.0427$), of which 1257 have criteria to be larger than $2\sigma(I)$, yielded $R1 = 0.0672$ and $wR2 = 0.1251$. The unit cell dimensions are $a = 9.6389(7)$, $b = 18.0534(10)$, $c = 5.3138(3)$ Å, and $\beta = 102.896(2)^\circ$, and the space group is *C2/m* with $Z = 2$. The results of the refinement are summarized in Table 2. The final atomic coordinates, refined site-scattering values [electrons per formula unit (epfu)], and displacement parameters (Å²) are given in Table 3.

The average chemical composition of the ferri-ghoseite fragment used for the X-ray diffraction, based on four microprobe spot analyses (Table 1), is ${}^A(\text{Na}_{0.16}\text{K}_{0.02})_{\Sigma 0.18}{}^B(\text{Na}_{0.83}\text{Ca}_{0.09}\text{Mn}_{1.08}^{2+})_{\Sigma 2.00}{}^C(\text{Mg}_{3.78}\text{Mn}_{0.52}^{2+}\text{Fe}_{0.66}^{3+}\text{Al}_{0.04})_{\Sigma 5.00}{}^T(\text{Si}_{7.95}\text{Al}_{0.05})_{\Sigma 8.00}\text{O}_{22}{}^W[(\text{OH})_{1.90}\text{F}_{0.10}]_{\Sigma 2.00}$. The site populations were obtained by distributing the ions of the empirical formula under the constraints of the refined site-scattering values (Hawthorne et al. 1995). The site populations of the ferri-ghoseite from Iimori indicate that the *M4* and *M4'* sites are occupied by (Na,Ca) and Mn^{2+} , respectively (Table 4). Site-scattering values calculated from the site populations are given in Table 4. Minor differences between the refined and calculated site-scattering values are probably due to chemical zon-

ing with depth in the amphibole fragment in thin section.

DISCUSSION

Robinson et al. (1971) reported exsolution lamellae in coexisting richterite and clino-suenoite from Southwestern Labrador, Canada, indicating a miscibility gap between sodium-calcium amphibole and clino-suenoite. Shau et al. (1993) described submicroscopic exsolution lamellae in Mn-rich amphibole from Tirodi, India, with an average bulk composition of ${}^A(\text{Na}_{0.55}\text{K}_{0.11})_{\Sigma 0.66}{}^B(\text{Na}_{0.93}\text{Ca}_{0.41}\text{Mn}_{0.66}^{2+})_{\Sigma 2.00}{}^C(\text{Mg}_{4.08}\text{Fe}_{0.52}^{2+}\text{Mn}_{0.05}^{2+}\text{Fe}_{0.29}^{3+}\text{Al}_{0.05}\text{Ti}_{0.01})_{\Sigma 5.00}{}^T(\text{Si}_{7.90}\text{Al}_{0.10})_{\Sigma 8.00}\text{O}_{22}{}^W(\text{OH})_{2.00}$. This Mn-rich amphibole is characterized by ($\bar{1}01$) and (100) exsolution lamellae, as well as inclusions of two secondary amphiboles, magnesio-arfvedsonite and clino-suenoite with a richterite component, neither of which contain exsolution lamellae. The compositions of the above-mentioned amphiboles are plotted in Figure 2. The submicroscopic exsolution lamellae and the presence of coexisting secondary amphiboles indicate a miscibility gap between sodium amphibole and clino-suenoite, caused mainly by differences in the radii of the cations in the *M4* (${}^B\text{Na}$ versus ${}^B\text{Mn}^{2+}$) and *M2* (${}^C\text{Fe}^{3+}$ versus ${}^C\text{Mg}$) sites (Shau et al., 1993).

The selected-area electron diffraction patterns for the Mn-rich amphibole from Tirodi show that diffraction spots reveal splitting and streaks derived from the submicroscopic exsolution lamellae (the Mn^{2+} -Mg-rich phase) of which *a*-axis and β are slightly smaller than those of the host (the Na- Fe^{3+} -rich phase) (Shau et al., 1993). On the other hand, the single crystal study for the crystal fragment of ferri-ghoseite from Iimori exhibits that each of X-ray spots do not show splitting and streaks caused by a variance of d_{hkl} . Therefore, we concluded that submicroscopic exsolution lamellae are not present in the studied crystal fragment.

The studied amphibole from Iimori is chemically heterogeneous, with compositions that range from magnesio-riebeckite through ferri-ghoseite to clino-suenoite, indicating a continuous solid solution between ${}^B\text{Na}$ and ${}^B\text{Mn}^{2+}$ (Fig. 2). The ${}^B(\text{Na},\text{Mn}^{2+})$ solid solution is also confirmed by the occupation of the *M4* and *M4'* sites by (Na,Ca) and Mn^{2+} , respectively (Tables 3 and 4). The presence of the *M4'* split position was also reported in ferri-ghoseite from Tirodi, India (Oberti and Ghose, 1993), and in richterite containing significant ${}^B(\text{Mn}^{2+}, \text{Mg})$ from Långban, Sweden (Oberti et al., 1993). The *M4'* position allows small ($\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}$) cations to assume a more suitable $[6 + 2]$ coordination, similar to the coordination in iron-magnesium-manganese amphiboles. That is, the O2 and O4 oxygens are closer to, and the O6 oxygens are farther from, the *M4'* position than from the

Table 3. Atomic coordinates, refined site-scattering values (epfu), and displacement parameters ($\text{\AA}^2$) for ferri-ghoseite

Site	Site-scattering value	x	y	z	U_{eq}	
$T1$	56.0	0.28516(12)	0.08465(6)	0.2819(2)	0.0094(3)	
$T2$	56.0	0.29377(12)	0.17044(6)	0.7900(2)	0.0102(3)	
$M1$	27.6(5)	0	0.08772(9)	0.5	0.0096(6)	
$M2$	32.7(5)	0	0.17957(8)	0	0.0101(5)	
$M3$	12.0	0	0	0	0.0066(5)	
$M4$	8.8(2)	0	0.2769(11)	0.5	0.0133(7)	
$M4'$	30.1(5)	0	0.26293(19)	0.5	0.0133(7)	
A	1.2	0.062(5)	0.5	0.137(10)	0.015(9)*	
$O1$		0.1135(3)	0.08678(17)	0.2130(6)	0.0111(6)	
$O2$		0.1214(3)	0.17137(17)	0.7236(6)	0.0129(6)	
$O3$		0.1119(5)	0	0.7091(9)	0.0118(9)	
$O4$		0.3714(3)	0.24785(18)	0.7842(7)	0.0169(7)	
$O5$		0.3500(3)	0.13037(18)	0.0711(6)	0.0144(6)	
$O6$		0.3470(3)	0.12077(19)	0.5660(6)	0.0162(7)	
$O7$		0.3414(5)	0	0.2865(9)	0.0144(9)	
H		0.172(11)	0	0.72(2)	0.04(4)*	
Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$T1$	0.0082(5)	0.0083(6)	0.0109(5)	-0.0003(4)	0.0005(4)	-0.0008(4)
$T2$	0.0100(5)	0.0086(6)	0.0115(5)	0.0005(4)	0.0011(4)	-0.0010(4)
$M1$	0.0127(9)	0.0066(10)	0.0101(9)	0	0.0039(6)	0
$M2$	0.0088(7)	0.0106(8)	0.0103(7)	0	0.0009(5)	0
$M3$	0.0062(12)	0.0051(13)	0.0075(12)	0	-0.0005(10)	0
$M4$	0.0163(7)	0.0100(18)	0.0157(7)	0	0.0082(5)	0
$M4'$	0.0163(7)	0.0100(18)	0.0157(7)	0	0.0082(5)	0
$O1$	0.0078(13)	0.0112(15)	0.0135(15)	-0.0009(11)	0.0005(11)	-0.0007(10)
$O2$	0.0119(14)	0.0130(15)	0.0130(14)	0.0002(12)	0.0007(11)	0.0001(11)
$O3$	0.011(2)	0.013(2)	0.012(2)	0	0.0032(17)	0
$O4$	0.0171(15)	0.0117(15)	0.0207(17)	0.0026(13)	0.0015(13)	-0.0047(12)
$O5$	0.0125(14)	0.0169(16)	0.0135(15)	0.0047(12)	0.0020(11)	0.0007(11)
$O6$	0.0129(14)	0.0195(17)	0.0147(15)	-0.0047(13)	0.0000(12)	0.0014(12)
$O7$	0.013(2)	0.009(2)	0.023(2)	0	0.0052(17)	0

* Isotropic displacement parameter.

Table 4. Site populations and a comparison between refined and calculated site-scattering values for ferri-ghoseite

Site	Site population (apfu)	Site-scattering value (epfu)	
		Refined	Calculated
<i>T</i> 1	3.95Si + 0.05Al	56.0	56.0
<i>T</i> 2	4.00Si	56.0	56.0
<i>M</i> 1	1.60Mg + 0.40Mn ²⁺	27.6	29.2
<i>M</i> 2	1.30Mg + 0.66Fe ³⁺ + 0.04Al	32.7	33.3
<i>M</i> 3	0.88Mg + 0.12Mn ²⁺	12.0	13.6
Σ C cations		72.3	76.1
<i>M</i> 4	0.83Na + 0.09Ca	8.8	10.9
<i>M</i> 4'	1.08Mn ²⁺	30.1	27.0
Σ B cations		38.9	37.9
A cations	0.16Na + 0.02K	1.2	2.1
W anions	1.90(OH) ⁻ + 0.10F ⁻	16.0	16.1

standard *M*4 position, which is occupied by large (Na,Ca) cations having a coordination number [8] in sodium-calcium amphiboles (Oberti and Ghose, 1993).

Occurrences of ferri-ghoseite are very rare. Until this

study, ferri-ghoseite having chemical composition close to the ideal formula had been found only in Tidodi, India (Oberti and Ghose, 1993). This study in the Iimori region of Japan describes the second worldwide occurrence of

ferri-ghoseite with its chemical composition close to the ideal formula. Although the phase relations in the magnesio-riebeckite and clino-suenoite join have not been experimentally characterized, the extremely rare occurrence of ferri-ghoseite suggests a miscibility gap between magnesio-riebeckite and clino-suenoite under a range of P - T conditions. A wide compositional range between magnesio-riebeckite and clino-suenoite has not been reported from natural samples, as far as we know. Therefore, the continuous solid solution between ${}^{\text{B}}\text{Na}$ and ${}^{\text{B}}\text{Mn}^{2+}$ in the magnesio-riebeckite—clino-suenoite series from Iimori is unusual in comparison with amphiboles from other localities. Banno and Yamada (2012) reported sector-zoned aegirine in ferri-ghoseite-bearing quartz schist from the Sanbagawa belt at Iimori and concluded that the zoning developed as a result of rapid, non-equilibrium crystallization. These authors also found garnet showing a sector structure under the optical microscope, which is similarly indicative of non-equilibrium crystallization. Therefore, if it is assumed that most of the metamorphic minerals in the quartz schist formed under non-equilibrium conditions, then the unusual solid solution between ${}^{\text{B}}\text{Na}$ and ${}^{\text{B}}\text{Mn}^{2+}$ in the amphibole can be inferred to have resulted from rapid, non-equilibrium crystallization rather than high- T equilibrium crystallization.

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