

Structural variation of babingtonite depending on cation distribution at the octahedral sites

Mariko Nagashima · Keiko Mitani · Masahide Akasaka

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Abstract Babingtonite, $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}(\text{OH})]$ ($Z=2$, space group $P\bar{1}$) from Yakuki mine (Japan), Grönsjöberget (Sweden), Kandivali Quarry (India), Baveno Quarry (Italy), Bråstad Mine (Norway), and Kouragahana (Japan), and manganbabingtonite, $\text{Ca}_2(\text{Mn}^{2+}, \text{Fe}^{2+})\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}(\text{OH})]$, from Iron Cap mine (USA) were studied using electron-microprobe analysis (EMPA), ^{57}Fe Mössbauer analysis and single-crystal X-ray diffraction methods to determine the cation distribution at M1 and M2 and to analyze its effect on the crystal structure of babingtonite. Although all studied babingtonite crystals are relatively homogeneous, chemical zonation due to mainly $\text{Fe} \leftrightarrow \text{Mn}$ substitution is observed in manganbabingtonite. Mössbauer spectra consist of two doublets with isomer shift ($I.S.$)=1.16–1.22 mm/s and quadrupole splitting ($Q.S.$)=2.33–2.50 mm/s and with $I.S.$ =0.38–0.42 mm/s and $Q.S.$ =0.82–0.90 mm/s, assigned to Fe^{2+} and Fe^{3+} at the M1 and M2 octahedral sites, respectively. The determined ratio of Fe^{2+} /total Fe in manganbabingtonite

(0.26) was smaller than that in the others (0.35–0.44) because of high Mn^{2+} content instead of Fe^{2+} . The unit-cell parameters of babingtonite are $a=7.466\text{--}7.478$, $b=11.624\text{--}11.642$, $c=6.681\text{--}6.690$ Å, $\alpha=91.53\text{--}91.59$, $\beta=93.86\text{--}93.94$, $\gamma=104.20\text{--}104.34^\circ$, and $V=560.2\text{--}562.3$ Å³, and those of manganbabingtonite are $a=7.4967(3)$, $b=11.6632(4)$, $c=6.7014(2)$ Å, $\alpha=91.602(2)$, $\beta=93.989(2)$, $\gamma=104.574(3)^\circ$, and $V=565.09(5)$ Å³. Structural refinements converged to R_1 values of 1.64–3.16 %. The $\langle \text{M1-O} \rangle$ distance was lengthened due to the substitution of large octahedral cations such as Mn^{2+} for Fe^{2+} . The increase of the M1-O8, M1-O8' and M1-O13 lengths with mean ionic radii is slightly more pronounced than of the other M1-Oi lengths. The lengthened M1-O13 distance leads the positive correlation between Si5-O15-Si1 angle and M1-O13 distance. The increase of Si2-O3-Si1 and Si5-O12-Si4 angles due to the increase of mean ionic radius of M2 is also observed.

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M. Nagashima (✉)
Graduate School of Science and Engineering, Yamaguchi University, Yoshida 1677-1, Yamaguchi 753-8512, Japan
e-mail: nagashim@yamaguchi-u.ac.jp

K. Mitani
Department of Geosphere Sciences, Yamaguchi University, Yoshida 1677-1, Yamaguchi 753-8512, Japan

M. Akasaka
Department of Geoscience, Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan

Introduction

Babingtonite is one of the hydro-pyroxenoid group minerals with 5-periodic single chain, and its simplified formula is $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}(\text{OH})]$ ($Z=2$). Manganbabingtonite, Mn^{2+} substitutes for Fe^{2+} , and scandiobabingtonite, Sc^{3+} for Fe^{3+} , also exist as independent mineral species (Vinogradova et al. 1966; Orlandi et al. 1998). The crystal structure of babingtonite was firstly solved by Araki and Zoltai (1972). The structure contains an undulating chain built by SiO_4 containing five tetrahedra per repeat unit, two Ca sites (Ca1 and Ca2), which are 8-coordinated by O, and two crystallographically independent octahedral sites, M1 and M2.

The ordered arrangement of the divalent cations, such as Fe^{2+} , Mg^{2+} and Mn^{2+} , at M1 and the trivalent cation of Fe^{3+}

and Al^{3+} at M2 has been repeatedly examined by X-ray diffraction and ^{57}Fe Mössbauer spectroscopy (Araki and Zoltai 1972; Amthauer 1980; Amthauer and Rossman 1984; Burns and Dyar 1991; Akasaka et al. 2013). All ^{57}Fe Mössbauer studies reported ferrous and ferric iron separated onto the M1 and M2 sites, respectively.

The distribution of cations including H^+ was also studied using neutron diffraction by Tagai et al. (1990). As a result of their study, the distribution of Mg and Mn at the larger M1 site and of Al at the smaller M2 site was directly determined. Then it was simply concluded that the divalent cations distribute at the larger M1 site and, on the other hand, the trivalent cations in the smaller M2 site. However, as the result of X-ray single-crystal study of babingtonite from Arvigo, Grisons (type loc.), Armbruster (2000) estimated that Mg occupies not only M1 but also M2 based on the M2-O elongation and the number of electrons in this site; consequently Fe^{3+} can occupy the larger M1 site. He also pointed out that the degree of Fe^{2+} - Fe^{3+} ordering was possibly due to the variable formation temperature. As the result of high-resolution transmission microscopy, Czank (1981) discussed that the frequency of chain periodicity faults is influenced by the genetic conditions and chemical composition.

In this study, we examined six babingtonite and one manganbabingtonite specimens from different localities using electron microprobe analysis (EMPA), ^{57}Fe Mössbauer spectroscopic analysis and X-ray single-crystal refinement to determine the cation distribution at M1 and M2 and to find its effect on the crystal structure of babingtonite. This is also the first report of the crystal structure of manganbabingtonite. We focus on the variation of size of octahedra and Si-O-Si angles in the undulated chain consisting of SiO_4 -tetrahedra, due to variations of the chemical composition, and bond valence and hydrogen bonding of babingtonite.

Experimental methods

Studied specimens

The studied babingtonite and manganbabingtonite specimens are from seven different localities. All babingtonite crystals show vitreous luster and are black in hand specimen. The localities and other features of each specimen are;

- (1) Yakuki mine, Japan: euhedral to subhedral short prismatic babingtonite crystals (< 4 mm) are mainly associated with hedenbergite, grossular-andradite garnets, quartz, and ilvaite. Pyrite and chalcopyrite were confirmed as associated opaque phases. The Yakuki mine is a copper deposit, which formed in a contact aureole between a granodiorite intrusion and Carboniferous slates and limestones (Nambu et al. 1970).

- (2) Grönsjöberget, Sweden: euhedral to subhedral babingtonite (< 5 mm) and quartz (< 1 mm) crystals were attached to a fine-grained epidote-calcite skarn mass. Babingtonite is found in the contact zone between skarn and marble (Forsberg 1996).
- (3) Kandivali Quarry, India: babingtonite crystals (< 0.5 mm) cover cauliflower-like shaped prehnite aggregates. Euhedral quartz (< 1 cm) occurs together with prehnite. Chlorite and epidote are associated with babingtonite. After Wise and Moller (1990), Ca-Fe silicate minerals in this district formed in cavities of altered basalt.
- (4) Baveno Quarry, Italy: babingtonite crystals (< 1 mm) partly cover quartz in a granitic pegmatite. The Seula mine (former name was Montecatini granite quarry) near Baveno is known as the occurrence of a variety of Sc-bearing minerals, and is also the type locality of scandiobabingtonite (Orlandi et al. 1998).
- (5) Bråstad Mine, Norway: subhedral babingtonite crystals (< 10 mm) are mainly associated with feldspar (oligoclase). The Bråstad mine located in the Arendal district is a skarn-iron ore deposit. The skarn in this district was formed by metasomatic processes in Precambrian limestones, in association with the intrusion of igneous rocks ranging in composition from diorite to granite (Bugge 1940).
- (6) Iron Cap mine, Graham County, Arizona, USA: platy manganbabingtonite crystals (< 7 mm) are closely associated with brownish johannsenite crystals. The Iron Cap mine is a lead-zinc mine. Manganbabingtonite was considered to be formed due to very late, low temperature alteration of earlier clinopyroxene skarn assemblages (Burt and London 1978).
- (7) Kouragahana, Japan: euhedral to subhedral babingtonite crystals are associated with prehnite (Akasaka et al. 2003) and calcite. They occur in cavities of hydrothermally altered dolerite (Nomura et al. 1984). Other details of this specimen have been described by Akasaka et al. (2013)

Chemical analysis (EMPA-WDX)

The chemical compositions of babingtonite samples (1)–(6) were analysed using the JEOL JXA-8230 electron-microprobe analyzer at Yamaguchi University. Si, Ti, Al, Cr, V, Fe, Mn, Mg, Ca, Sr, Ba, Na, K, Ni, Cu, Zn, Pb, P, F, and Cl were measured using an accelerating voltage of 15 kV and a beam current of 20 nA, with a beam diameter of 1–10 μm . The following standards were used: natural wollastonite (Si, Ca), synthetic KTiPO_4 (P, K), synthetic $\text{Ca}_3(\text{VO}_4)_2$ (V), synthetic rutile (Ti), synthetic corundum (Al), synthetic eskolaite (Cr), synthetic hematite (Fe), synthetic tephroite (Mn), synthetic periclase (Mg), synthetic bunsenite (Ni), PbVGe -oxide (Pb), $\text{SrBaNb}_4\text{O}_{12}$ (Sr, Ba), albite (Na), orthoclase (K), native copper (Cu), zinc oxide (Zn), synthetic fluorite (F) and synthetic

halite (Cl). The Pb, F and Cl contents, which are not shown in Table 1, are negligible in all specimens. The ZAF method was used for data correction. The scandium content in the Bråstad babingtonite crystals was carefully confirmed using qualitative analysis. Quantitative analyses were performed for several babingtonite crystals from each sample (except for Kouragahana) to confirm compositional variation. However, the average chemical composition of manganbabingtonite was obtained from the crystal used for the structural analysis.

⁵⁷Fe Mössbauer analysis

The ⁵⁷Fe Mössbauer spectra of the babingtonite samples (1)–(6) were measured at room temperature, using 370 MBq ⁵⁷Co in Pd as a source. The absorber was about 50 mg of finely ground sample. Mössbauer data were obtained using a constant acceleration spectrometer fitted with a 1,024 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 width and intensities constrained to be equal at each site. The QBMOSS program written by Akasaka and Shinno (1992) was used for computer analysis. The quality of the fit was judged using the χ^2 value and standard deviations of Mössbauer parameters.

Single-crystal structure analysis

X-ray diffraction data for single-crystals of babingtonite samples from seven different localities were collected using a Bruker SMART APEX II CCD diffractometer installed at Shimane University, Japan. Crystals were mounted on glass fibres and intensity data were measured at room temperature using graphite-monochromatized MoK α radiation ($\lambda=0.71069$ Å). Preliminary lattice parameters and an orientation matrix were obtained from twelve sets of frames and refined during the integration process of the intensity data. Diffraction data were collected with ω scans at different φ settings (φ - ω scan) (Bruker 1999). Data were processed using SAINT (Bruker 1999). An empirical absorption correction using SADABS (Sheldrick 1996) was applied. The reflection statistics and systematic absences were consistent with space groups $P1$ and $P\bar{1}$. Subsequent attempts to solve the structure indicated that the observed average structure is centrosymmetric, and for this reason $P\bar{1}$ is the correct space group. Structural refinement was performed using SHELXL-97 (Sheldrick 2008). Scattering factors for neutral atoms were employed. The site occupancies of Ca at Ca1 and Ca2, and Si at Si1-5 were fixed based on the data derived from the electron microprobe analysis to reduce the correlations among site occupancies, scale factor, and displacement parameters. However, Fe introduced as “dummy occupant” at M1 and M2, which was

subsequently refined. The refined number of electrons at M1 and M2 and corresponding esd's, expressed as site scattering, were used as guide to final cation assignment. Because the obtained site-scattering values of M1 and M2 showed good correspondence with electron microprobe analyses, a second series of refinements has been performed. On the basis of the site-scattering values, Al and Fe were assigned to M2, and Mg, Mn and Fe to M1. Positions of the hydrogen atoms of the hydroxyl groups were derived from difference-Fourier syntheses. Subsequently, hydrogen positions were refined at a fixed value of $U_{\text{iso}}=0.05$ Å². The hydrogen position was refined with a bond distance restraint of O–H=0.980(1) Å (Franks 1973).

Results

Chemical compositions of babingtonites

The average chemical compositions of babingtonite are given in Table 1, in which Fe²⁺ and Fe³⁺ are recalculated from stoichiometry (total cations = 9 per O=14.5). The average composition of Kouragahana babingtonite is from Akasaka et al. (2013; see for details on chemical analyses and charge balance). Specimens except for the Iron Cap mine and Kouragahana are almost homogeneous. Average chemical composition of this manganbabingtonite in Table 1 was obtained from the crystal used for structural analysis. In addition, the data showing the highest Mn content among all analytical points is also shown in Table 1, which has not been used for the structural analysis. Qualitative analysis did not indicate presence of Sc in the Baveno babingtonite. Thus, Sc content in our studied crystal was considered to be negligible despite the fact that it comes from the type locality of scandiobabingtonite.

Babingtonite: Babingtonite from Bråstad, Yakuki and Grönsjöberget is characterized by high MnO contents; i.e. 4.24, 4.02 and 3.42 wt.%, respectively. The variation of MnO and MgO contents in babingtonite directly affects the iron content in each specimen. The Fe²⁺/total Fe varies from 0.34 (Bråstad) to 0.48 (Kouragahana). However, the Fe²⁺/total Fe ratio of Kouragahana babingtonite can be variable because of sector zonation; Fe²⁺-Al³⁺-rich and Fe³⁺-Mn²⁺-rich sectors were confirmed (Akasaka et al. 2013).

Manganbabingtonite: Each manganbabingtonite crystal from the Iron Cap mine was slightly zoned (mainly Fe $\leftrightarrow$ Mn zonation). The crystal used for the structural analysis has a relatively high Fe content (16.82 Fe₂O₃ wt.%; 9.26 MnO wt.%). The chemical compositions of individual crystals in this specimen are variable. In Mn-rich crystals, the MnO content reaches 14.1 MnO wt.% corresponding to *c.* 1.15 Mn apfu, Fe and Ca contents decrease accordingly (Table 1). This implies that Ca ions at the large coordination polyhedra can be partly substituted by a small amount of Mn²⁺. The

Table 1 Chemical compositions of babingtonite and manganbabingtonite

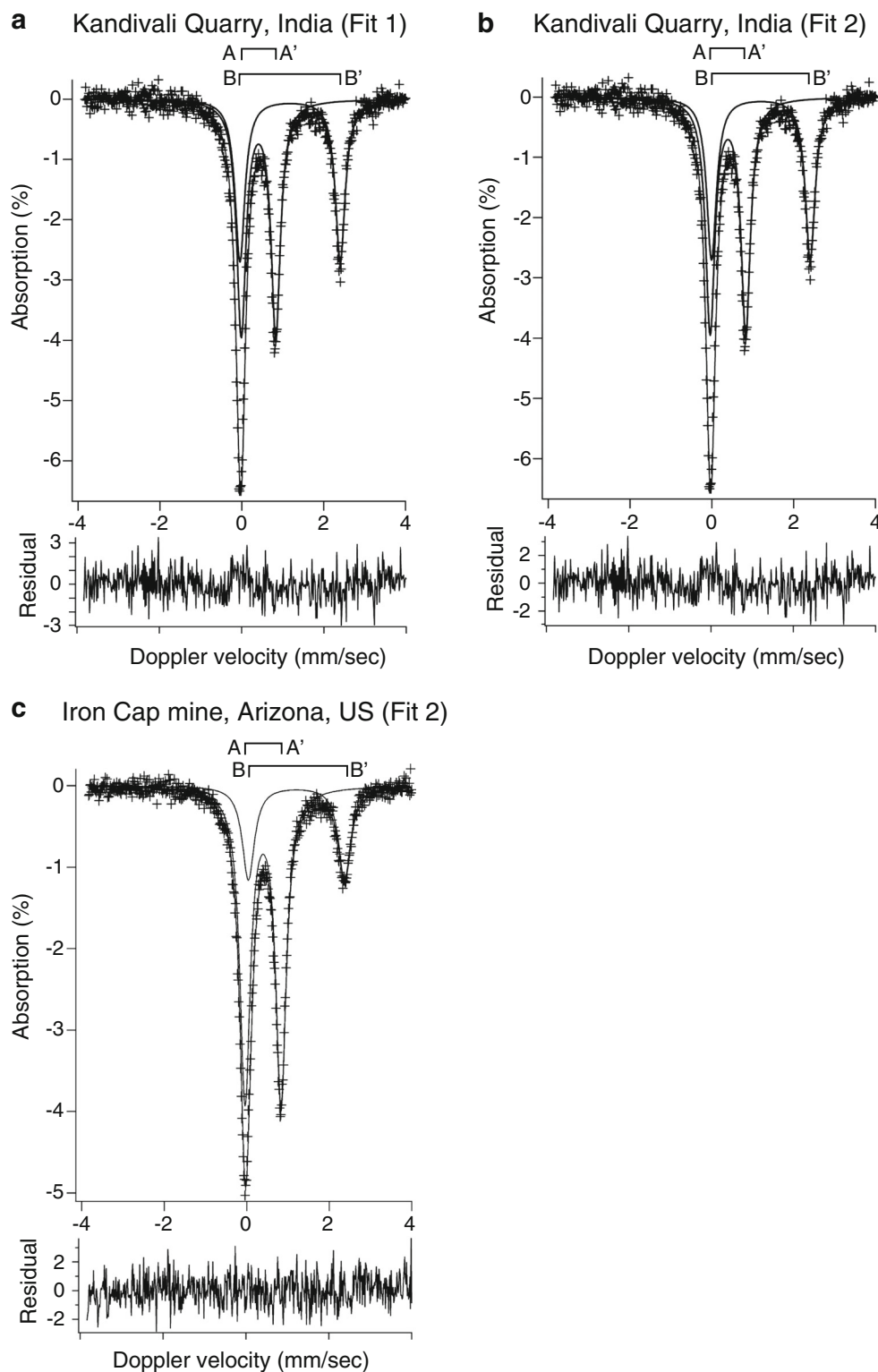
	1 Yakuki mine, Fukushima, Japan		2 Grönsjöberget, Borlänge, Sweden		3 Kandivali Quarry, Mumbai, India		4 Baveno Quarry, Lago Maggiore, Italy		5 Bråstad mine, Arendal, Norway		6 Iron Cap mine, Arizona, USA ^b			7 Kouragahana, Shimane, Japan (Akasaka et al. 2013)	
	Ave. <i>n</i> =34	Std.	Ave. <i>n</i> =62	Std.	Ave. <i>n</i> =51	Std.	Ave. <i>n</i> =18	Std.	Ave. <i>n</i> =23	Std.	Ave. <i>n</i> =14	Std.	Max. Mn content	Ave. <i>n</i> =186	Std.
SiO ₂	52.20	0.32	53.13	0.28	52.06	0.35	52.08	0.35	52.14	0.32	52.23	0.36	51.96	53.03	0.54
TiO ₂	0.02	0.03	0.05	0.05	0.03	0.04	0.01	0.02	0.04	0.07	0.03	0.04	0.07	0.09	0.20
Al ₂ O ₃	0.12	0.11	0.20	0.13	0.40	0.24	0.41	0.49	0.18	0.13	0.27	0.08	0.14	0.52	0.46
Cr ₂ O ₃ ^a	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.00	0.02	0.02
V ₂ O ₃ ^a	0.01	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.03	0.00	0.00	0.00	0.04	0.04
Fe ₂ O ₃ ^a	22.36	1.27	20.70	1.80	23.75	0.85	23.61	1.22	20.58	0.74	16.82	0.99	15.97	23.83	1.08
MnO ^a	4.02	1.06	3.42	1.47	1.42	0.42	2.29	0.81	4.24	0.91	9.26	1.07	14.12	1.20	0.39
MgO	0.52	0.14	1.46	0.37	0.90	0.11	0.19	0.11	0.93	0.29	0.20	0.06	0.31	0.79	0.280
CaO	19.33	0.21	19.81	0.17	19.70	0.19	19.48	0.12	19.44	0.19	19.46	0.16	16.09	19.83	0.29
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	
BaO	0.03	0.03	0.03	0.04	0.02	0.03	0.00	0.01	0.01	0.02	0.03	0.03	0.00	n.a.	
Na ₂ O	0.02	0.02	0.02	0.02	0.05	0.04	0.05	0.03	0.07	0.05	0.03	0.02	0.02	0.03	0.11
K ₂ O	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.03	0.02
NiO	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.00	0.02	0.03
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.00	0.00	0.00	n.a.	
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.04	0.04	0.00	0.00	0.00	n.a.	
P ₂ O ₅	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	n.a.	
Total	98.67		98.89		98.39		98.21		97.73		98.43		98.68	99.43	
Total cations = 9															
Si	4.99	0.03	5.01	0.02	4.97	0.04	5.01	0.01	5.00	0.02	4.98	0.01	4.98	5.03	0.03
Ti	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01
Al	0.01	0.01	0.02	0.01	0.04	0.03	0.05	0.05	0.02	0.01	0.03	0.01	0.02	0.06	0.05
Cr ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ³⁺	1.61	0.09	1.47	0.13	1.71	0.06	1.71	0.10	1.49	0.05	1.21	0.07	1.15	1.66	0.07
Mn ²⁺	0.33	0.09	0.27	0.47	0.11	0.03	0.18	0.07	0.35	0.07	0.75	0.08	1.15	0.10	0.03
Mg	0.07	0.02	0.21	0.21	0.13	0.02	0.03	0.02	0.13	0.04	0.03	0.01	0.04	0.11	0.04
Ca	1.98	0.02	2.00	1.08	2.02	0.01	2.01	0.02	2.00	0.02	1.99	0.02	1.65	2.02	0.02
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	—	
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	—	
Na	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	—	
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	—	
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	—	
Total	9.00		9.00		9.00		9.00		9.00		9.00		9.00	9.00	
Recalculated values from stoichiometry (total cations = 9 per 14.5 oxygens) and charge balance															
Fe ²⁺	0.61		0.53		0.80		0.77		0.50		0.21		0.13	0.79	
Fe ³⁺	1.00		0.94		0.91		0.94		0.99		1.00		1.02	0.87	

^a Total Cr as Cr₂O₃, V as V₂O₃, Fe as Fe₂O₃ and Mn as MnO^b The average composition of manganbabingtonite was obtained from the crystal used for the structural analysis. The data showing the highest Mn content among all analytical points is also shown in the Table, which is not used for the structural analysis

chemical formula of the analytical data with high Mn content in this study can be written as $(\text{Ca}_{1.65}\text{Mn}_{0.35})_{\Sigma 2.00}(\text{Mn}_{0.80}\text{Mg}_{0.04}\text{Fe}^{2+}_{0.13})_{\Sigma 0.97}(\text{Fe}^{3+}_{1.02}\text{Ti}_{0.01})_{\Sigma 1.03}(\text{Si}_{4.98}\text{Al}_{0.02})_{\Sigma 5.00}\text{O}_{14}(\text{OH})$, with the total number of cations, except H ion,

normalized to 9 for $\text{O}_{14}(\text{OH})$. The manganbabingtonite from the Mitani mine, Japan also showed Mn-poor and Mn-rich zonation (Matsubara and Kato 1989), and its composition is very similar to that from the Iron Cap mine (this study).

Fig. 1 ^{57}Fe Mössbauer spectra of babingtonite specimens from the Kandivali Quarry (a for fit 1, and b for fit 2) and the Iron Cap mine (c for fit 2). The outer most peak is assigned to Fe^{2+} for fit 1. The low-velocity peak of the Fe^{3+} doublet located at a position of lower Doppler velocity than that of Fe^{2+} in fit 2. Fit 1 and fit 2 correspond to fit B and fit C described in Burns and Dyar (1991)



⁵⁷Fe Mössbauer spectroscopic analysis

The ⁵⁷Fe Mössbauer spectra of babingtonite samples are shown in Fig. 1 and the hyperfine parameters are listed in Table 2. Mössbauer spectra of babingtonite consist of two doublets with isomer shift (*I.S.*)=1.16–1.223 mm/s and quadrupole splitting (*Q.S.*)=2.331–2.499 mm/s and with *I.S.*=0.3829–0.4202 mm/s and *Q.S.*=0.822–0.896 mm/s. The former and latter are assigned to Fe²⁺ and Fe³⁺ at the octahedral sites, respectively. As indicated by Amthauer (1980), Amthauer and Rossman (1984), and Burns and Dyar (1991), the peak fitting calculation of the Mössbauer spectra of babingtonite measured at room temperature has some difficulty, because the low-Doppler velocity components of Fe²⁺ and Fe³⁺ doublets strongly overlap. Amthauer (1980) applied two fitting modes for analysis: (1) three peaks were fitted without constraint and (2) two doublets were fitted with the Fe²⁺ doublet consisting of the outermost peaks and the Fe³⁺ doublet positioned between them. On the other hand, Amthauer and Rossman (1984) employed a third fitting model (3) where the low-velocity peak of the Fe³⁺ doublet located at a position of lower Doppler velocity than that of Fe²⁺. Burns and Dyar (1991) examined these three fitting models and concluded that there is no best spectrum-fitting model because the low-velocity peaks of Fe³⁺ and Fe²⁺ almost exactly superimpose. Fitting models (2) and (3) were employed in the present study for the fit of the Mössbauer spectrum with two doublets to determine the Fe²⁺:Fe³⁺ ratio. Table 2 shows the results of two doublets fit based on the fitting modes of Amthauer (1980) [labeled Fit 1 in Table 2] and Amthauer and Rossman (1984) [Fit 2 in Table 2] for babingtonite from Yakuki mine (Japan), Grönsjöberget (Sweden), Kandivali Quarry (India), Baveno Quarry (Italy), Bråstad Mine (Norway). However, Arizona manganbabingtonite was successfully fitted with Fit 2 fitting mode only (Table 2, Fig. 1c).

In fit of the spectra of Yakuki, Grönsjöberget, Kandivali Quarry, and Baveno Quarry babingtonites and of Arizona manganbabingtonite, peak widths and intensities of component peaks in a doublet were constrained to be equal for a successful fit, as in the studies by Amthauer (1980), Amthauer and Rossman (1984), and Burns and Dyar (1991). However, for the spectrum of Bråstad babingtonite (Fig. 1a and b), only intensities of component peaks of a doublet were constrained, which resulted in reasonable Mössbauer hyperfine parameters (*I*, *I.S.*, and *Q.S.*) and improved χ^2 values, as well as the study by Akasaka et al. (2013).

The resulting *I.S.* and *Q.S.* values are similar to those reported in previous studies (Amthauer 1980; Amthauer and Rossman 1984; Burns and Dyar 1991; Akasaka et al. 2013). The Fe²⁺:Fe³⁺ ratio derived from Fits 1 and 2 are almost consistent within standard deviation.

The ratio of Fe²⁺/total Fe in Arizona manganbabingtonite (0.26) was smaller than that in the others (0.35–0.44) because

of high Mn²⁺ content instead of Fe²⁺ (Table 2, Fig. 1c). The peak width of BB' doublet of manganbabingtonite is larger than that of the others. This may be attributed to the chemical heterogeneity (especially for Fe, Mn and Ca) among different crystals of this specimen.

Crystal structure solution and refinements

Crystallographic data and refinement parameters are summarized in Table 3. The refined atomic positions and anisotropic displacement parameters are listed in Supplementary Materials Tables SM1 and SM2. The interatomic distances and distortions of octahedral sites are presented in Table 4, and the selected angles in Supplementary Material Table SM3. The site occupancies are listed in Table 5. The crystal structure of babingtonite is shown in Fig. 2.

The unit-cell parameters of babingtonite are *a*=7.4664(1)–7.4780(1), *b*=11.6235(3)–11.6418(1), *c*=6.6813(1)–6.6897(1) Å, α =91.530(1)–91.594(1), β =93.861(1)–93.937(1), γ =104.203(1)–104.337(1)°, *V*=560.21(2)–562.31(1) Å³ and those of manganbabingtonite are *a*=7.4967(3), *b*=11.6632(4), *c*=6.7014(2) Å, α =91.602(2), β =93.989(2), γ =104.574(3)°, and *V*=565.09(5) Å³. Structural refinements of babingtonite crystals converged to *R*₁=1.64–3.16 %. The Kouragahana babingtonite has the highest and deepest difference Fourier peaks among all specimens. The highest peak locates near to the hydrogen position (*c.* 1.34 Å from H1) and *c.* 1.57 Å from O1. The deepest hole is very close to M2 octahedron (*c.* 0.73 Å from M2) and is associated with the distinct chemical heterogeneity of this specimen.

The site-scattering value of M1 is lower than that of M2 in each specimen (Table 5). It is mainly due to the Mg concentration at M1. On the basis of chemical data and published neutron diffraction data (Tagai et al. 1990), all Mg and Mn²⁺ are assigned to M1, and Al to M2, respectively. In all babingtonites, iron is the predominant element at both M1 and M2. On the other hand, the predominant cation in manganbabingtonite from the Iron Cap mine is Mn at M1 and Fe at M2. The Fe ions at M1 and M2 were assumed to be ferrous and ferric, respectively (Table 5) based on the results of Mössbauer spectroscopic analysis.

Discussion

Cation distribution and structural variation

To examine the relationship between cation distribution and structural variation in babingtonite, accurate and precise cation populations at the M1 and M2 sites have to be determined. The difficulty for determination of the cation populations using X-ray structural refinement and electron microprobe analysis was summarized as follows by Armbruster

Table 2 Mössbauer hyperfine parameters^a of the babingtonite samples

	1 Yakui mine		2 Grönsjöberget		3 Kandivali Quarry		4 Baveno Quarry		5 Brästad mine		6 Iron Cap mine	
	Fit 1	Fit 2	Fit 1	Fit 2	Fit 1	Fit 2	Fit 1	Fit 2	Fit 1	Fit 2	Fit 1	Fit 2
<i>I.S.</i> (mm/s)	AA'	AA'	AA'	AA'	AA'	AA'	AA'	AA'	AA'	AA'	AA'	AA'
<i>Q.S.</i> (mm/s)	0.406(5)	0.388(6)	0.409(3)	0.390(3)	0.408(3)	0.395(3)	0.415(2)	0.384(2)	0.4202(9)	0.3829(9)	0.396(2)	0.396(2)
<i>Γ</i> (mm/s)	0.84(1)	0.87(1)	0.841(7)	0.879(7)	0.843(6)	0.870(6)	0.830(4)	0.892(4)	0.822(2)	0.896(2)	0.870(3)	0.870(3)
<i>I</i> (mm/s)	0.29(1)	0.29(1)	0.311(6)	0.311(7)	0.276(4)	0.276(4)	0.309(5)	0.304(5)	0.291(5)/0.304(3)	0.274(4)/0.305(3)	0.306(3)	0.306(3)
Area ratio (%)	64(3)	65(3)	68(2)	68(2)	58(1)	58(1)	57(1)	56(1)	63(1)	61(1)	74(1)	74(1)
Assignment	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}	νFe^{3+}
<i>I.S.</i> (mm/s)	BB'	BB'	BB'	BB'	BB'	BB'	BB'	BB'	BB'	BB'	BB'	BB'
<i>Q.S.</i> (mm/s)	1.16(1)	1.19(1)	1.167(6)	1.204(6)	1.179(4)	1.199(4)	1.170(3)	1.210(3)	1.163(2)	1.223(2)	1.206(4)	1.206(4)
<i>Γ</i> (mm/s)	2.45(2)	2.38(2)	2.47(1)	2.39(1)	2.452(9)	2.412(9)	2.483(5)	2.402(6)	2.499(3)	2.377(3)	2.331(8)	2.331(8)
<i>I</i> (mm/s)	0.30(2)	0.29(2)	0.29(1)	0.29(1)	0.290(6)	0.289(6)	0.299(7)	0.308(7)	0.252(7)/0.313(5)	0.278(7)/0.313(5)	0.36(1)	0.36(1)
Area ratio (%)	36(3)	35(3)	32(1)	32(1)	42(1)	42(1)	43(1)	44(1)	37(1)	39(1)	26(1)	26(1)
Assignment	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}	νFe^{2+}
$\chi^2/\text{Freedom}$	1.69	1.69	1.18	1.18	1.09	1.09	1.58	1.58	1.50	1.48	1.15	1.15

^a Standard deviations, 1σ , are given in parenthesis. *I.S.*, Isomer shift referred to a metallic iron absorber; *Q.S.*, Quadrupole splitting; *Γ* Full width at half height.

Table 3 Data collection and details of structure refinements

Locality	1 Yakuki mine	2 Grönsjöberget	3 Kandivali Quarry	4 Baveno Quarry	5 Brästad mine	6 Iron Cap mine	7 Kouragahana
Space group				$P\bar{1}$			
Crystal size (mm)	0.14×0.11×0.09	0.18×0.12×0.08	0.20×0.08×0.03	0.13×0.13×0.12	0.17×0.10×0.07	0.075×0.05×0.01	0.13×0.13×0.12
Cell parameters							
<i>a</i> (Å)	7.4753(1)	7.4771(2)	7.4664(1)	7.4692(1)	7.4780(1)	7.4967(3)	7.4672(2)
<i>b</i> (Å)	11.6397(1)	11.6376(3)	11.6276(2)	11.6315(1)	11.6418(1)	11.6632(4)	11.6235(3)
<i>c</i> (Å)	6.6897(1)	6.6841(2)	6.6813(1)	6.6865(1)	6.6892(1)	6.7014(2)	6.6805(2)
α (°)	91.594(1)	91.591(1)	91.564(1)	91.589(1)	91.564(1)	91.602(2)	91.530(1)
β (°)	93.934(1)	93.861(1)	93.889(1)	93.873(1)	93.937(1)	93.989(2)	93.880(1)
γ (°)	104.312(1)	104.337(1)	104.203(1)	104.208(1)	104.326(1)	104.574(3)	104.222(1)
<i>V</i> (Å ³)	562.07(2)	561.63(2)	560.44(2)	561.26(1)	562.31(1)	565.09(5)	560.21(2)
Dcalc (g/cm ³)	3.318	3.284	3.310	3.319	3.301	3.304	3.305
Absorption coefficient μ (mm ⁻¹)	4.13	4.13	4.14	4.13	4.13	4.11	4.14
Corrected reflections	18,050	14,335	16,157	16,117	17,555	8,051	17,114
Unique reflections	5,360	5,215	5,280	5,151	5,364	2,539	5,194
Criterion for observed reflections				$I > 2\sigma(I)$			
<i>R</i> _{int} (%)	2.34	2.02	2.12	1.31	1.70	3.16	2.69
<i>R</i> σ (%)	2.36	2.36	2.10	1.35	1.71	3.32	2.68
θ max (°)	36.3	36.3	36.4	36.3	36.3	27.5	36.3
Miller index limit	-12≤ <i>h</i> ≤12, -19≤ <i>k</i> ≤19 -10≤ <i>l</i> ≤11	-12≤ <i>h</i> ≤12, -19≤ <i>k</i> ≤18 -11≤ <i>l</i> ≤11	-12≤ <i>h</i> ≤12, -18≤ <i>k</i> ≤19 -11≤ <i>l</i> ≤11	-11≤ <i>h</i> ≤12, -19≤ <i>k</i> ≤17 -11≤ <i>l</i> ≤11	-12≤ <i>h</i> ≤12, -19≤ <i>k</i> ≤19 -11≤ <i>l</i> ≤11	-9≤ <i>h</i> ≤9, -13≤ <i>k</i> ≤15 -8≤ <i>l</i> ≤8	-12≤ <i>h</i> ≤12, -19≤ <i>k</i> ≤19 -10≤ <i>l</i> ≤10
<i>R</i> ₁ (%)	2.29	2.36	1.84	1.64	1.77	3.00	3.16
<i>wR</i> ₂ (%)	5.88	7.18	5.26	4.77	4.87	8.17	8.76
<i>S</i>	1.08	1.09	1.07	1.09	1.08	1.06	1.05
No. of parameters	222	222	222	222	222	222	222
Weighting scheme	$w = 1/(\sigma^2(F_o^2) + (0.0362P)^2 + 0.37P)$	$w = 1/(\sigma^2(F_o^2) + (0.0242P)^2 + 0.40P)$	$w = 1/(\sigma^2(F_o^2) + (0.0238P)^2 + 0.24P)$	$w = 1/(\sigma^2(F_o^2) + (0.0237P)^2 + 0.24P)$	$w = 1/(\sigma^2(F_o^2) + (0.0226P)^2 + 0.22P)$	$w = 1/(\sigma^2(F_o^2) + (0.0427P)^2 + 0.49P)$	$w = 1/(\sigma^2(F_o^2) + (0.0521P)^2 + 0.48P)$
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.59 (0.70 Å from O8)	0.64 (0.81 Å from Si4)	0.46 (0.80 Å from O5)	0.48 (0.65 Å from O12)	0.51 (0.70 Å from O11)	0.81 (0.91 Å from M2)	2.08 (1.34 Å from H1)
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.79 (0.72 Å from Ca1)	-0.67 (0.67 Å from M2)	-0.56 (0.63 Å from Ca1)	-0.43 (0.33 Å from Si4)	-0.48 (0.30 Å from Si4)	-0.57 (0.70 Å from Si3)	-1.01 (0.73 Å from M2)

X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer. Intensity data were measured at room temperature using graphite-monochromatized MoK α radiation ($\lambda=0.71069$ Å). Diffraction data were collected with φ - ω scan (Bruker 1999). Data were processed using SAINT (Bruker 1999). An empirical absorption correction using SADABS (Sheldrick 1996) was applied. Structural refinement was performed using SHELXL-97 (Sheldrick 2008). The function of the weighting scheme is $w=1/(\sigma^2(F_o^2)+(a\cdot P)^2+b\cdot P)$, where $P=(\text{Max}(F_o^2,0+2F^2))/3$, and the parameters *a* and *b* are chosen to minimize the differences in the variances for reflections in different ranges of intensity and diffraction angle

Table 4 Selected bond distances (Å), volumes of polyhedra (Å³) and deformation parameters for the octahedral sites ^a

	1 Yakuki mine	2 Grönsjöberget	3 Kandivali Quarry	4 Baveno Quarry	5 Bråstad mine	6 Iron Cap mine	7 Kouragahana
Ca1- O1	2.270(1)	2.276(1)	2.2730(8)	2.2730(8)	2.2728(8)	2.269(2)	2.275(1)
O13	2.308(1)	2.311(1)	2.3161(9)	2.3167(8)	2.3129(8)	2.296(3)	2.319(1)
O14	2.341(1)	2.340(1)	2.3429(8)	2.3420(7)	2.3431(8)	2.339(2)	2.342(1)
O2	2.348(1)	2.349(1)	2.3510(8)	2.3507(7)	2.3506(7)	2.348(2)	2.352(1)
O10	2.430(1)	2.434(1)	2.4318(8)	2.4294(8)	2.4301(8)	2.421(2)	2.430(1)
O2'	2.689(1)	2.694(1)	2.6997(8)	2.6936(8)	2.6833(8)	2.663(2)	2.703(1)
O15	3.048(1)	3.046(1)	3.0387(9)	3.0461(8)	3.0473(8)	3.064(2)	3.038(1)
O15'	3.082(1)	3.070(1)	3.0537(8)	3.2438(3)	3.0862(8)	3.137(3)	3.049(1)
Mean	2.564	2.565	2.5634	2.5869	2.5658	2.567	2.564
M1- O13	2.056(1)	2.051(1)	2.0430(8)	2.0450(7)	2.0550(8)	2.080(2)	2.041(1)
O5	2.099(1)	2.092(1)	2.0969(8)	2.0984(7)	2.0986(7)	2.107(2)	2.096(1)
O10	2.172(1)	2.164(1)	2.1664(8)	2.1693(8)	2.1704(8)	2.185(2)	2.162(1)
O8	2.190(1)	2.179(1)	2.1872(8)	2.1901(8)	2.1872(8)	2.219(2)	2.185(1)
O4	2.208(1)	2.202(1)	2.1982(8)	2.2019(7)	2.2063(7)	2.219(2)	2.196(1)
O8'	2.234(1)	2.234(1)	2.2126(8)	2.2136(7)	2.2318(8)	2.270(2)	2.206(1)
Mean	2.160	2.154	2.1507	2.1531	2.1582	2.180	2.148
V^{M1}	13.20	13.09	13.04	13.08	13.17	13.48	12.99
DI	0.025	0.025	0.025	0.025	0.025	0.025	0.025
$\langle\lambda_{oct}\rangle$	1.013	1.012	1.013	1.013	1.013	1.013	1.012
$\sigma_0 (oct)^2$	38.61	37.45	38.01	38.31	38.43	39.19	37.22
M2- O14	1.924(1)	1.925(1)	1.9227(8)	1.9269(7)	1.9269(8)	1.930(2)	1.927(1)
O7	1.966(1)	1.968(1)	1.9659(8)	1.9675(7)	1.9667(8)	1.967(2)	1.968(1)
O11	1.995(1)	1.995(1)	1.9938(8)	1.9955(7)	1.9950(7)	1.996(2)	1.995(1)
O2	2.048(1)	2.047(1)	2.0425(8)	2.0478(7)	2.0486(8)	2.055(2)	2.042(1)
O4	2.0830(9)	2.087(1)	2.0809(8)	2.0842(7)	2.0857(8)	2.092(2)	2.082(1)
O10	2.195(1)	2.195(1)	2.1867(8)	2.1897(7)	2.1939(7)	2.209(2)	2.185(1)
Mean	2.035	2.036	2.0321	2.0353	2.0361	2.042	2.033
V^{M2}	11.11	11.13	11.07	11.12	11.13	11.22	11.09
DI	0.036	0.036	0.035	0.035	0.036	0.038	0.034
$\langle\lambda_{oct}\rangle$	1.009	1.009	1.009	1.009	1.009	1.009	1.009
$\sigma_0 (oct)^2$	24.59	24.77	24.45	24.45	24.37	24.60	23.71
O1...O11	2.571(1)	2.565(1)	2.565(1)	2.5652(9)	2.563(1)	2.569(3)	2.563(1)
Ca2- O8	2.332(1)	2.334(1)	2.3355(8)	2.3351(7)	2.3365(7)	2.333(2)	2.337(1)
O5	2.339(1)	2.342(1)	2.3395(8)	2.3391(8)	2.3413(8)	2.342(2)	2.340(1)
O7	2.356(1)	2.355(1)	2.3600(8)	2.3589(8)	2.3555(8)	2.346(2)	2.360(1)
O4	2.363(1)	2.364(1)	2.3639(8)	2.3626(7)	2.3646(8)	2.366(2)	2.362(1)
O6	2.438(1)	2.437(1)	2.4356(8)	2.4382(7)	2.4369(7)	2.442(2)	2.440(1)
O9	2.554(1)	2.553(1)	2.5524(8)	2.5533(8)	2.5538(8)	2.556(2)	2.549(1)
O12	2.625(1)	2.629(1)	2.6231(8)	2.6235(7)	2.6282(8)	2.638(2)	2.624(1)
O9'	2.866(1)	2.862(1)	2.8568(8)	2.8625(8)	2.8636(8)	2.877(2)	2.855(1)
Mean	2.484	2.485	2.4834	2.4842	2.4851	2.488	2.483
Si1- O3	1.611(1)	1.612(1)	1.6111(8)	1.6113(8)	1.6121(8)	1.610(2)	1.614(1)
O2	1.620(1)	1.619(1)	1.6200(8)	1.6201(8)	1.6201(8)	1.620(2)	1.619(1)
O1	1.623(1)	1.622(1)	1.6202(9)	1.6214(8)	1.6220(8)	1.623(2)	1.620(1)
O15	1.629(1)	1.630(1)	1.6330(8)	1.6302(8)	1.6301(8)	1.626(2)	1.633(1)
Mean	1.621	1.621	1.6211	1.6208	1.6211	1.620	1.622
Si2- O5	1.597(1)	1.598(1)	1.5968(8)	1.5975(8)	1.5980(7)	1.595(2)	1.597(1)
O3	1.622(1)	1.621(1)	1.6215(8)	1.6232(8)	1.6224(8)	1.623(2)	1.623(1)
O4	1.632(1)	1.631(1)	1.6313(8)	1.6318(7)	1.6305(8)	1.630(2)	1.630(1)
O6	1.659(1)	1.663(1)	1.6591(8)	1.6583(8)	1.6591(8)	1.660(2)	1.659(1)

Table 4 (continued)

	1 Yakuki mine	2 Grönsjöberget	3 Kandivali Quarry	4 Baveno Quarry	5 Bråstad mine	6 Iron Cap mine	7 Kouragahana
Mean	1.628	1.628	1.6272	1.6277	1.6275	1.627	1.627
Si3- O8	1.600(1)	1.602(1)	1.6008(8)	1.6028(7)	1.6012(8)	1.600(2)	1.602(1)
O7	1.604(1)	1.605(1)	1.6042(8)	1.6039(8)	1.6040(8)	1.606(2)	1.602(1)
O6	1.629(1)	1.626(1)	1.6292(8)	1.6293(8)	1.6299(8)	1.630(2)	1.631(1)
O9	1.675(1)	1.674(1)	1.6731(8)	1.6725(8)	1.6748(8)	1.675(2)	1.674(1)
Mean	1.627	1.627	1.6268	1.6271	1.6275	1.628	1.627
Si4- O11	1.601(1)	1.600(1)	1.6011(8)	1.6013(8)	1.6013(8)	1.600(2)	1.602(1)
O10	1.616(1)	1.613(1)	1.6164(8)	1.6177(7)	1.6169(8)	1.618(2)	1.616(1)
O9	1.652(1)	1.654(1)	1.6530(8)	1.6523(7)	1.6531(8)	1.650(2)	1.653(1)
O12	1.654(1)	1.660(1)	1.6543(8)	1.6539(8)	1.6539(8)	1.655(2)	1.656(1)
Mean	1.631	1.632	1.6312	1.6313	1.6313	1.631	1.632
Si5- O13	1.585(1)	1.589(1)	1.5855(8)	1.5849(8)	1.5857(8)	1.584(2)	1.586(1)
O14	1.617(1)	1.616(1)	1.6139(8)	1.6145(8)	1.6165(8)	1.619(2)	1.614(1)
O15	1.653(1)	1.654(1)	1.6529(8)	1.6543(8)	1.6525(8)	1.652(2)	1.654(1)
O12	1.661(1)	1.660(1)	1.6589(8)	1.6589(8)	1.6593(8)	1.661(2)	1.657(1)
Mean	1.629	1.630	1.6278	1.6282	1.6285	1.629	1.628

^a $DI(\text{oct}) = 1/6 \sum |R_i - R_{\text{av}}|/R_{\text{av}}$ (R_i : each bond length, R_{av} : average distance for an octahedron) (Baur 1974), $\langle \lambda_{\text{oct}} \rangle = \sum_{i=1}^6 (l_i - l_0)^2 / 6$ (l_i : each bond length, l_0 : center-to-vertex distance for an octahedron with O_h symmetry, whose volume is equal to that of a distorted octahedron with bond lengths l_i) (Robinson et al. 1971), and $\sigma_{\theta}(\text{oct})^2 = \sum_{i=1}^{12} (\theta_i - 90^\circ)^2 / 11$ (θ_i : O–M–O angle) (Robinson et al. 1971)

(2000): (1) Mg and Al have similar X-ray scattering factors and their position selectivity can only be explored ambiguously; (2) Major Fe^{2+} - Fe^{3+} ordering can be evaluated based on the Fe–O distances, however, minor disorder cannot be resolved; (3) Mn distribution and valence can only be assumed. In addition, Armbruster (2000) pointed out the effect of temperature dependence of the Fe^{2+} - Fe^{3+} ordering: babingtonite with a lower degree of Fe^{2+} - Fe^{3+} order is formed at low temperatures ($< 200^\circ\text{C}$), whereas babingtonite with

higher Fe^{2+} - Fe^{3+} order occurs at high temperature conditions like in skarn deposits.

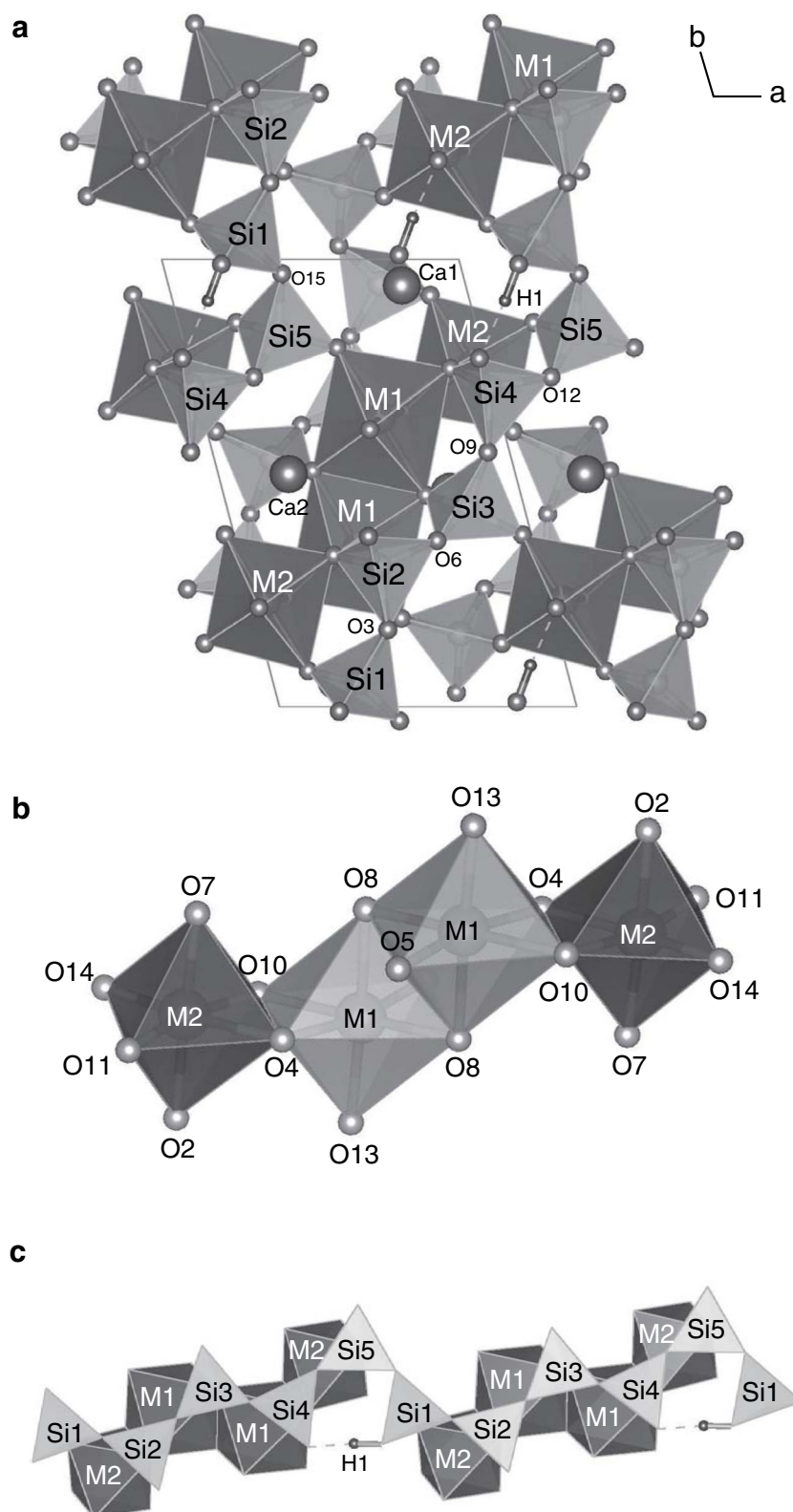
In our study, the oxidation state and site distribution of iron in babingtonite were directly determined using both X-ray diffraction and ^{57}Fe Mössbauer methods. Distribution of Fe^{2+} at M1 and Fe^{3+} at M2 were confirmed in all babingtonites in this study. As seen from the Mössbauer analysis, the Fe^{2+} -ratios against total iron in Kandivali and Baveno babingtonites, which are rich in Fe and poor in Mg and Mn^{2+} , are obviously higher

Table 5 Number of electrons and cation assignments

	Locality	Site	Site-scattering	Site occupancies	No. e [−]
1	Yakuki mine	M1	23.85(3)	$\text{Fe}^{2+}_{0.61}\text{Mn}^{2+}_{0.32}\text{Mg}_{0.07}$	24.70
		M2	25.14(3)	$\text{Fe}^{3+}_{0.99}\text{Al}_{0.01}$	25.87
2	Grönsjöberget	M1	22.26(4)	$\text{Fe}^{2+}_{0.51}\text{Mn}^{2+}_{0.28}\text{Mg}_{0.21}$	22.78
		M2	25.13(4)	$\text{Fe}^{3+}_{0.98}\text{Al}_{0.02}$	25.74
3	Kandivali Quarry	M1	24.00(3)	$\text{Fe}^{2+}_{0.76}\text{Mg}_{0.13}\text{Mn}^{2+}_{0.11}$	24.07
		M2	24.91(3)	$\text{Fe}^{3+}_{0.96}\text{Al}_{0.04}$	25.48
4	Baveno Quarry	M1	25.02(3)	$\text{Fe}^{2+}_{0.79}\text{Mn}^{2+}_{0.18}\text{Mg}_{0.03}$	25.40
		M2	25.27(2)	$\text{Fe}^{3+}_{0.95}\text{Al}_{0.05}$	25.35
5	Bråstad mine	M1	24.12(3)	$\text{Fe}^{2+}_{0.52}\text{Mn}^{2+}_{0.35}\text{Mg}_{0.13}$	23.83
		M2	24.78(3)	$\text{Fe}^{3+}_{0.98}\text{Al}_{0.02}$	25.74
6	Iron Cap mine	M1	24.38(6)	$\text{Mn}^{2+}_{0.74}\text{Mg}_{0.03}\text{Fe}^{2+}_{0.23}$	24.84
		M2	24.84(6)	$\text{Fe}^{3+}_{0.97}\text{Al}_{0.03}$	25.61
7	Kouragahana	M1	24.23(4)	$\text{Fe}^{2+}_{0.79}\text{Mg}_{0.11}\text{Mn}^{2+}_{0.10}$	24.36
		M2	24.53(4)	$\text{Fe}^{3+}_{0.94}\text{Al}_{0.06}$	25.22

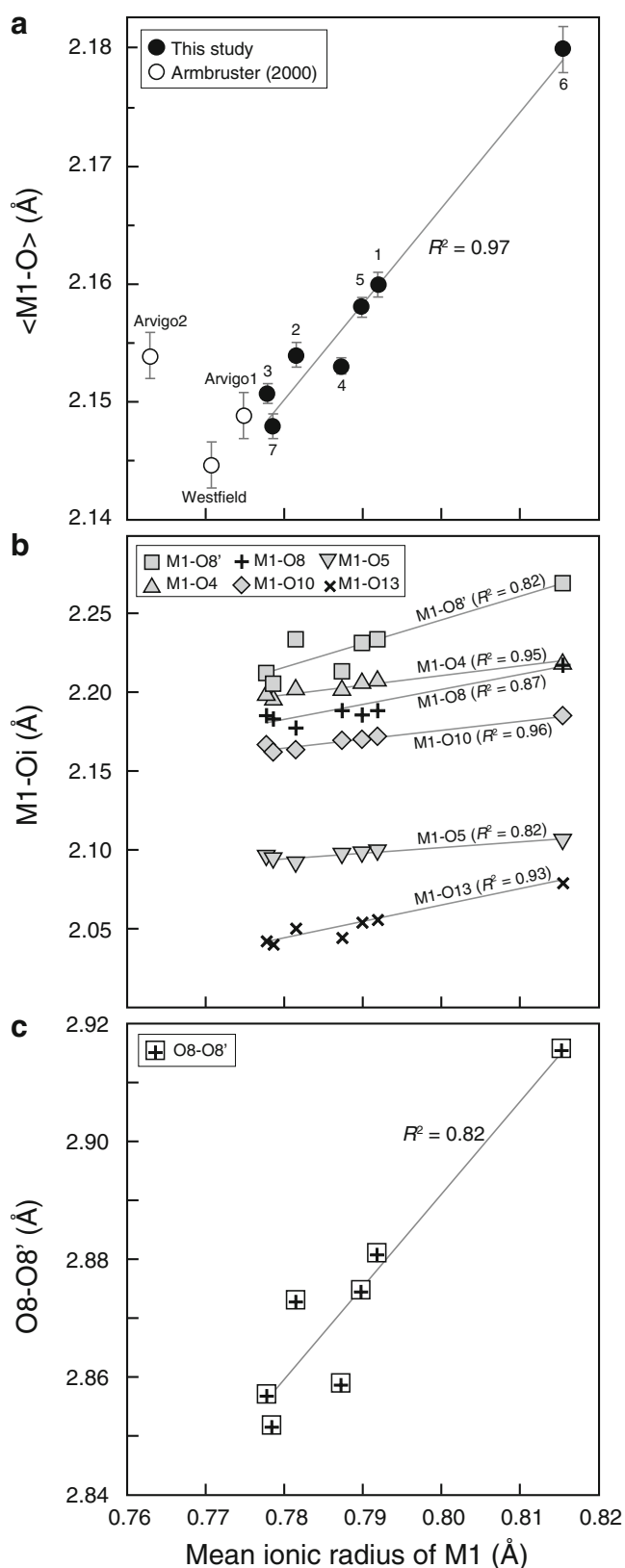
Mn^{2+} , Mg, Al and total Fe contents are fixed by EMPA data

Fig. 2 The crystal structure of babingtonite (**a**), and the topology of octahedra (**b**) and octahedra with silicate chains (**c**) drawn with VESTA (Momma and Izumi 2011)



than in the others. On the other hand, the Mg- and Mn^{2+} -rich babingtonites, especially manganbabingtonite from Arizona, show a lower ratio of Fe^{2+} against total Fe (Table 2 and Fig. 1). Thus, it makes sense that Mn^{2+} and Mg^{2+} ions are assigned to

M1. By allocation of divalent cations to the M1 site, Al^{3+} is assigned to the M2 site. After all, ordered distribution of divalent and trivalent cations at the M1 and M2 sites, respectively, is concluded in all babingtonite samples studied here.



According to the results of this study, the M1O_6 octahedra occupied by divalent cations tend to expand in an isotropic

Fig. 3 (a) Variation of $\langle \text{M1-O} \rangle$, (b) M1-Oi distances and (c) O8-O8' distances as a function of mean ionic radius of M1. Sample numbers in Fig. 3a correspond to those given in all Tables. Estimated standard deviations in Figs. 3a, b are smaller than the symbol sizes. Cation ionic radii according to Shannon (1976)

manner (Figs. 3a, b). The increase of the M1-O8, M1-O8' and M1-O13 lengths with mean ionic radii is slightly more pronounced than of the other M1-Oi lengths. The Mn-poor babingtonites tend to have shorter M1-O8' distances (*c.* 2.21 Å) than Mn-rich ones (2.23–2.27 Å). The mean $\langle \text{M1-O} \rangle$ distance shows a good positive correlation against the mean ionic radius ($R^2 = 0.96$ in Fig. 3a). The M1 site of Arizona manganbabingtonite is obviously larger than the others, which is due to high Mn^{2+} occupation (74 % of M1). Therefore, the volume of the M1O_6 octahedra is simply governed by the cation distribution at M1. The increase of the volume of M1O_6 octahedra with increasing the mean ionic radius at M1 is also indicated by the lengthened O8-O8' edge: in the babingtonite structure, the O8-O8' edge is shared by two M1O_6 octahedra (Fig. 2b) and thus, the O8-O8' edge becomes longer with increasing of the mean ionic radius at M1 (Fig. 3c). The deviation of the $\langle \text{M1-O} \rangle$ distance in Arvigo2 specimen from the general trend reported by Armbruster (2000) may imply more Fe^{2+} at M1 (Fig. 3a). If all iron at M1 is presumed as divalent, $\langle \text{M1-O} \rangle$ can be almost plotted on the regression line. On the other hand, the M2 site which has no significant substitution shows almost constant M2-Oi distances. Despite the fact that the M2 site of manganbabingtonite from Arizona is mostly occupied by Fe^{3+} as all the others, the $\langle \text{M2-O} \rangle$ distance is longer than the others. Especially the lengthened M2-O10 distance is significant. The octahedral M1 and M2 sites share the O4-O10 edge (Fig. 2b). Probably the slight expansion of the M2O_6 octahedra of Arizona manganbabingtonite is a consequence of the cation distribution at M1. This may indicate that the cation distribution at M1 promotes stereochemical distortion at M2. This kind of effect has been shown in other related structures before (e.g. Oberti et al. 1998, 1999). Nevertheless, it should also be noted that in scandiobabingtonite with 73 % Fe^{3+} + 27 % Sc^{3+} at M2 (Orlandi et al. 1998), the $\langle \text{M2-O} \rangle$ distance reaches 2.092 Å because of the increase of the mean ionic radius up to 0.672 Å.

The variation of T-O-T angles within the silicate chain is compiled in Table 6. As shown in Fig. 2, the M1O_6 and M2O_6 octahedra share oxygen atoms with TO_4 tetrahedra. The Si2-O6-Si3 and Si3-O9-Si4 angles of manganbabingtonite are larger than those in others. On the other hand, scandiobabingtonite studied by Orlandi et al. (1998) showed the largest Si1-O3-Si2 and Si4-O12-Si5 angles. An increase of Si1-O3-Si2 and Si4-O12-Si5 angles due to the increase of mean ionic radius of M2 was also observed in this study. After considering the topology of the babingtonite structure,

Table 6 T-O-T angles (°) of babingtonite group minerals

	Si1-O3-Si2	Si2-O6-Si3	Si3-O9-Si4	Si4-O12-Si5	Si5-O15-Si1
This study					
1 Yakuki mine	136.56(7)	144.00(7)	139.22(7)	131.12(6)	134.65(7)
2 Grönsjöberget	136.58(7)	143.73(7)	139.31(7)	131.36(7)	134.35(7)
3 Kandivali Quarry	136.54(5)	143.80(5)	139.03(5)	131.39(5)	134.12(5)
4 Baveno Quarry	136.55(5)	143.81(5)	139.11(5)	131.41(5)	134.18(5)
5 Bråstad mine	136.57(5)	143.91(5)	139.25(5)	131.31(5)	134.68(5)
6 Iron Cap mine (Manganbabingtonite)	136.7(1)	144.1(1)	139.8(1)	131.0(1)	135.5(2)
7 Kouragahana	136.48(8)	143.47(7)	138.84(7)	131.54(7)	133.87(8)
Armbruster (2000) ^a					
Arvigo1 (NMBE34973)	136.2(2)	143.5(2)	139.0(2)	131.6(2)	134.1(1)
Arvigo2 (NMBE34974)	136.8(2)	143.3(2)	139.5(2)	131.8(2)	135.0(2)
Westfield, Massachusetts	136.6(2)	143.8(2)	138.9(2)	131.5(2)	133.7(2)
Orlandi et al. (1998) ^a					
Scandiobabingtonite	138.8(3)	143.0(3)	139.7(3)	132.8(3)	133.8(3)

^a The T-O-T angles are calculated from the atomic parameters. Standard deviation was estimated by that of atomic position listed in each study

the variation of $M1O_6$ octahedra leads to the change of connected angles among the Si_2O_4 , Si_3O_4 and Si_4O_4 tetrahedra. Moreover, it is also clear that the connected angle between Si_1O_4 and Si_2O_4 tetrahedra and that between Si_4O_4 and Si_5O_4 tetrahedra are influenced by the variation of M_2O_6 octahedra. The lengthened M1-O13 distance mentioned before shifts the oxygen atom at O13 away from cation at M1. This leads to the positive correlation between Si5-O15-Si1 angle and M1-O13 distance (Fig. 4; $R^2=0.98$). Because the M1-O13 distance of scandiobabingtonite, in which “theoretically” Sc predominantly occupies M2, is out of this trend. Therefore, this regression is confined to babingtonite having Fe^{3+} at M2.

As a result of the cation distributions and structural variations of the octahedra, the unit-cell parameters of babingtonites except for manganbabingtonite vary in a very narrow range (Table 3), and are close to those reported in previous structural studies (e.g. Armbruster 2000). All the unit-cell parameters of manganbabingtonite from Arizona, $a=7.4967(3)$ Å, $b=11.6632(4)$ Å, $c=6.7014(2)$ Å, $\alpha=91.602(2)^\circ$, $\beta=93.989(2)^\circ$, $\gamma=104.574(3)^\circ$ and $V=565.09(5)$ Å³, are larger than those of the other babingtonites in this study, but smaller than scandiobabingtonite, $a=7.536(2)$ Å, $b=11.734(2)$ Å, $c=6.748(2)$ Å, $\alpha=91.70(2)^\circ$, $\beta=93.86(2)^\circ$, $\gamma=104.53(2)^\circ$ and $V=575.64$ Å³, reported by Orlandi et al. (1998). This is a result of the larger ionic radius of Sc^{3+} (0.745 Å) compared to Fe^{3+} . Thus, this study reveals that the variation of the unit-cell parameters of babingtonite is influenced by the cation distribution at both M1 and M2 sites. It is noted that the cell parameters of manganbabingtonite given by Vinogradova et al. (1966), $a=6.88$ Å, $b=11.80$ Å, $c=6.77$ Å, $\alpha=90.30^\circ$, $\beta=93.30^\circ$, $\gamma=104.54^\circ$ and $V=531.02$ Å³, are extremely much

smaller than those obtained in this study. We conclude that the unit cell parameters of manganbabingtonite in our study are reasonable in terms of the accuracy of the results and are coincident with the fact that the ionic radius of Mn^{2+} (0.83 Å after Shannon 1976) is greater than that of Mg^{2+} (0.72 Å) and Fe^{2+} (0.78 Å).

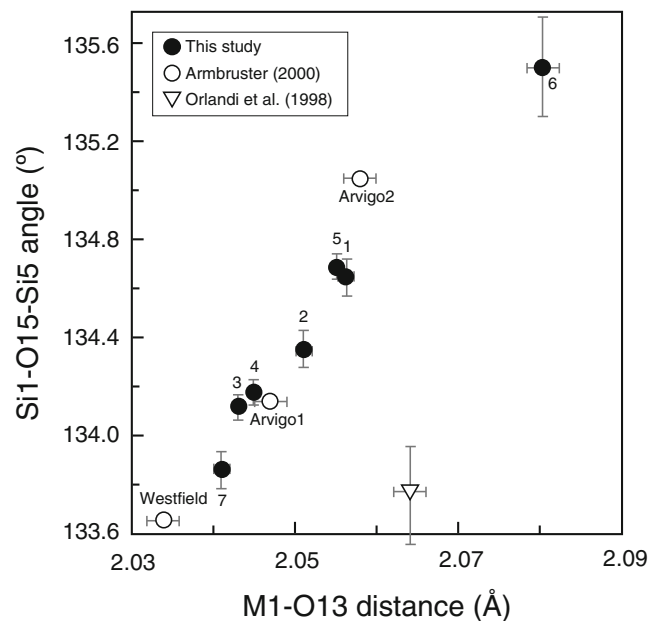


Fig. 4 Relationship between M1-O13 distance (Å) and Si1-O15-Si5 angle (°). Because the site occupancy at M1 is not clear, the structural data reported by Araki and Zoltai (1972) and Kosoi (1976) was not considered. Tagai et al. (1990) was not considered because the discrepancy between their unit-cell parameters and atomic coordination measured under different conditions

Hydrogen bond and structural characteristics as hydropyroxenoid

Bond-valence sums were calculated using the electrostatic strength function of Brown and Altermatt (1985) and the bond-valence parameters of Brese and O'Keeffe (1991). The results are given in Table 7. The calculated bond-valence sums and refined hydrogen positions indicate that one hydroxyl group is located at O1 (donor) with O11 acting as acceptor, which is consistent with the result of a neutron diffraction study by Tagai et al. (1990). The bond-valence sums of O1 and O11 are *c.* 1.49 and 1.63, respectively (Table 7). The over-bonded values of Si1-5 (> 4.1 v.u.) and O6 (2.25–2.26 v.u.), and the under-bonded value of O5 (1.87–1.88 v.u.) can be explained as a consequence of structural packing of pyroxenoids. Over-bonded silicon in the corner-linked single chains and over/under-bonded oxygen sites shared between a tetrahedron and an octahedron were also observed in other hydropyroxenoids having five-fold periodicity. The oxygen atoms at OC2 and OC3 (2.16 v.u.) and OB2 (1.84 v.u.) in santaclaraite (Ohashi and Finger 1981), and Si1-5 (4.07–4.23 v.u.), O4 (2.24–2.28 v.u.), and O18 (1.79–1.92 v.u.) in saneroite (Nagashima and Armbruster 2010) confirm this property as peculiarity of the structure type.

Babingtonite is characterized by a five-periodic single chain and a silanol group. The Si₅O₄ tetrahedron is defined as the center tetrahedron in the C-shaped tetrahedral triplet consisting of Si1, Si5 and Si4 sites (Fig. 2c). The oxygen at O14 is shared with the M₂O₆ octahedron and the Si₅O₄ tetrahedron. The upper triangular faces of the Si₅O₄ tetrahedron and the M₂O₆ octahedron are pointing in opposite directions (Fig. 2c). The hydrogen bond exists at the open side of the C-shaped triplet. The O11–H1...O1 separation, 2.56–2.57 Å, in this study is supported by that obtained in previous studies (Araki and Zoltai 1972; Kosoi 1976; Tagai et al. 1990; Armbruster 2000; Orlandi et al. 1998). As Nagashima and Armbruster (2010) summarized, the open side of the C-shaped triplet in hydrous pyroxenoids is much shorter than that in anhydrous pyroxenoid because of the presence of the strong hydrogen-bond. This feature is typically observed in hydrous pyroxenoids with 3- and 5-periodic chains such as cascandite (Mellini and Merlino 1982), pectolite (e.g. Ohashi and Finger 1978), serandite (e.g. Jacobsen et al. 2000), santaclaraite (Ohashi and Finger 1981) and saneroite (e.g. Nagashima and Armbruster 2010). Liebau (1980) pointed out that the hydrogen bonds within the tetrahedral chains lead to marked chain shrinkage due to

Table 7 Bond valence sum calculation of the babingtonite samples

	1 Yakuki mine	2 Grönsjö berget	3 Kandivali Quarry	4 Baveno Quarry	5 Bråstad mine	6 Iron Cap mine	7 Kouragahana
Ca1	2.09	2.01	2.07	2.06	2.08	2.07	2.07
Ca2	2.17	2.17	2.17	2.17	2.17	2.17	2.17
M1	2.01	2.00	1.98	2.01	2.01	1.99	1.99
M2	2.91	2.89	2.90	2.86	2.89	2.87	2.87
Si1	4.22	4.21	4.21	4.21	4.21	4.21	4.21
Si2	4.15	4.14	4.15	4.14	4.14	4.15	4.15
Si3	4.16	4.16	4.16	4.15	4.15	4.15	4.15
Si4	4.11	4.10	4.10	4.10	4.10	4.10	4.10
Si5	4.13	4.13	4.15	4.14	4.14	4.15	4.15
O1	1.49	1.48	1.49	1.49	1.49	1.49	1.49
O2	2.01	1.94	2.01	2.00	2.01	2.00	2.00
O3	2.13	2.13	2.13	2.13	2.13	2.12	2.12
O4	2.07	2.06	2.06	2.06	2.07	2.07	2.07
O5	1.88	1.87	1.87	1.87	1.87	1.87	1.87
O6	2.26	2.26	2.26	2.26	2.26	2.25	2.25
O7	2.02	2.01	2.01	2.01	2.02	2.01	2.01
O8	2.06	2.05	2.05	2.05	2.05	2.05	2.05
O9	2.17	2.17	2.18	2.18	2.17	2.18	2.18
O10	1.98	1.98	1.97	1.97	1.98	1.98	1.98
O11	1.64	1.64	1.63	1.63	1.63	1.62	1.62
O12	2.08	2.06	2.08	2.08	2.08	2.08	2.08
O13	1.99	1.98	1.98	1.99	1.99	1.98	1.98
O14	2.07	2.07	2.07	2.06	2.06	2.06	2.06
O15	2.10	2.10	2.09	2.07	2.10	2.09	2.09

kinking of the chains in the hydrous pyroxenoids. It implies that the distance of the open side of C-shaped triplet gives us the clue to identify pyroxenoid group minerals.

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