

X-ray Rietveld and ^{57}Fe Mössbauer study of babingtonite from Kouragahana, Shimane Peninsula, Japan

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Babingtonite from Kouragahana, Shimane Peninsula, Japan, was investigated using electron microprobe, X-ray Rietveld, and ^{57}Fe Mössbauer spectral analyses to characterize its chemical compositions, crystal structure, oxidation state of Fe, and distribution of Fe between two crystallographically independent octahedral Fe1 and Fe2 sites.

The Kouragahana babingtonite occurs as single parallelohedrons with {100}, {001}, {001}, {111}, $\{\bar{1}10\}$, and $\{\bar{1}01\}$ and sometimes shows penetration twinning. Both normal and sector-zoned crystals occur. Babingtonite crystals with sector zoning consist of sectors relatively enriched in Fe and of sectors enriched in Mg, Mn, and Al. Babingtonite also shows compositional zoning with higher Fe^{2+} and Al core and higher Fe^{3+} and Mn rim. The average Fe content of the babingtonite without sector zoning is similar to the Fe^{2+} -rich sector of the sector-zoned babingtonite. The chemical formula based on the average composition of all analytical data ($n = 193$) is $[\text{Na}_{0.01(2)}\text{Ca}_{2.01(2)}][\text{Mg}_{0.11(4)}\text{Mn}_{0.09(3)}\text{Fe}_{0.76(7)}^{2+}\text{Fe}_{0.93(5)}^{3+}\text{Ti}_{0.01(1)}\text{Al}_{0.06(5)}]\text{Si}_{5.01(4)}\text{O}_{14}(\text{OH})$. X-ray Rietveld refinement was carried out using a model of space group $P\bar{1}$. The result of the refinement is characterized by R -weighted pattern = 9.91, R -expected pattern = 6.37, and goodness-of-fit = 1.56. The unit cell parameters are $a = 7.4667(3)$, $b = 11.6253(6)$, $c = 6.6820(2)$ Å, $\alpha = 91.533(4)$, $\beta = 93.886(3)$, $\gamma = 104.203(4)^\circ$, and $V = 560.43(4)$ Å³.

The refined site occupancies of atoms in the Fe1 and Fe2 sites are $[\text{Fe}_{0.91(2)}\text{Mg}_{0.09}]$ and $[\text{Fe}_{0.91(2)}\text{Al}_{0.09}]$, respectively, if Mg is assumed to distribute in the Fe1 site and Al in the Fe2 site. By allocating Mn, 0.09 atoms per formula unit (a.p.f.u.), to the Fe1 site, the site populations in the Fe1 and Fe2 sites are determined as $[\text{Fe}_{0.82(2)}\text{Mn}_{0.09}\text{Mg}_{0.09}]$ and $[\text{Fe}_{0.91(2)}\text{Al}_{0.09}]$ a.p.f.u., respectively. The ^{57}Fe Mössbauer spectrum taken at room temperature consists of three peaks, which were resolved into two doublets assigned to Fe^{2+} and Fe^{3+} at the two octahedral sites. The $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio was determined as $\text{Fe}^{2+}:\text{Fe}^{3+} = 43.3(3):56.7(4)$ and $47.1(4):52.9(3)$ by applying two fitting models, and the average $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio was $45.2(4):54.8(4)$. The results of X-ray Rietveld analysis and Mössbauer spectroscopy indicate that Fe^{2+} and Fe^{3+} are ordered at the Fe1 and Fe2 sites, respectively, in the Kouragahana babingtonite.

Keywords: Babingtonite, Sector zoning, X-ray Rietveld, Mössbauer, Crystal chemistry, Kouragahana

INTRODUCTION

Babingtonite, $\text{Ca}_2(\text{Fe}^{2+}, \text{Mn}, \text{Mg})\text{Fe}^{3+}\text{Si}_5\text{O}_{14}(\text{OH})$, is a pyroxenoid group mineral. Araki and Zoltai (1972) determined the crystal structure of babingtonite as triclinic system of space group $P\bar{1}$. Tagai et al. (1990) and Armbruster (2000) confirmed the crystal structure of babingtonite with space group $P\bar{1}$, although Kosoi (1976) described the

babingtonite structure with space group $P1$. The crystal structure in space group $P\bar{1}$ consists of two crystallographically independent 8-coordination sites (referred to as Ca1 and Ca2), two octahedral sites (Fe1 and Fe2), and five tetrahedral sites (Si1, Si2, Si3, Si4, and Si5). The ordered arrangement of the divalent cations, including Fe^{2+} , Mg^{2+} , and Mn^{2+} at the Fe1 site and the trivalent cations of Fe^{3+} and Al^{3+} at the Fe2 site, has been repeatedly demonstrated by X-ray diffraction and Mössbauer spectroscopic studies (Araki and Zoltai, 1972; Amthauer, 1980; Amthauer and Rossman, 1984; Burns and Dyar, 1991).

Tagai et al. (1990) confirmed the cation distributions of Mn and Mg in the Fe1 site and Al in the Fe2 site by applying the differences of the scattering lengths of the atoms in neutron diffraction. However, Armbruster (2000) found significant Mg in the Fe2 site in an Arvigo babingtonite crystal and suggested significant Fe^{3+} in the Fe1 site.

Well-shaped babingtonite crystals have been reported from Kouragahana, Shimane Peninsula, Japan (Nomura et al., 1984). In this study, we characterize Kouragahana babingtonite by examining its chemical properties, crystal structure, and the oxidation state and distribution of Fe using electron microprobe, X-ray Rietveld, and ^{57}Fe Mössbauer spectral methods. Powder Rietveld methods were chosen for direct comparison with Mössbauer spectroscopy results on the same powder.

OCCURRENCE OF SAMPLE

Miocene dolerite occurs in the Shimane Peninsula, Japan (Kano and Yoshida, 1985; Organization Committee of New Geological Map of Shimane Prefecture, 1997). A part of the dolerite is coarse-grained as a result of hydro-

thermal alteration, and was thus described as 'altered gabbroic sill' by Kano et al. (1986). Secondary minerals, such as iron-rich pumpellyite and prehnite, replacing primary minerals or filling cavities have been reported from such altered rocks (Kano et al., 1986; Akasaka et al., 1997).

In the altered dolerite at Kouragahana, Mihonoseki-cho, Shimane Peninsula, prehnite (Nomura et al., 1984; Akasaka et al., 2003a) and Fe-rich pumpellyite (Nagashima et al., 2006) occur in cavities or veins. Veins from a few to tens of centimeters in width and cavities with diameters of about 15 cm occur. In our study, assemblages of Fe-rich pumpellyite + prehnite + laumontite + chlorite + quartz were observed in veins, and assemblages of babingtonite + prehnite + calcite + quartz $\pm$ epidote + pyrite and of prehnite + calcite + quartz + chlorite + pyrite occurred in cavities. The babingtonite, black in color, occurs as single parallelohedrons up to about 1 mm in size (Fig. 1A) and sometimes shows penetration twinning (Fig. 1B) and includes trace augite.

EXPERIMENTAL METHODS

Sample separation and chemical analysis

Babingtonite crystals for the Mössbauer spectroscopic and X-ray powder diffraction analyses were handpicked from the babingtonite-bearing assemblages under a stereoscopic microscope and treated using a dilute HCl solution to remove calcite. Purification of the babingtonite was attained by these treatments. The purified babing-

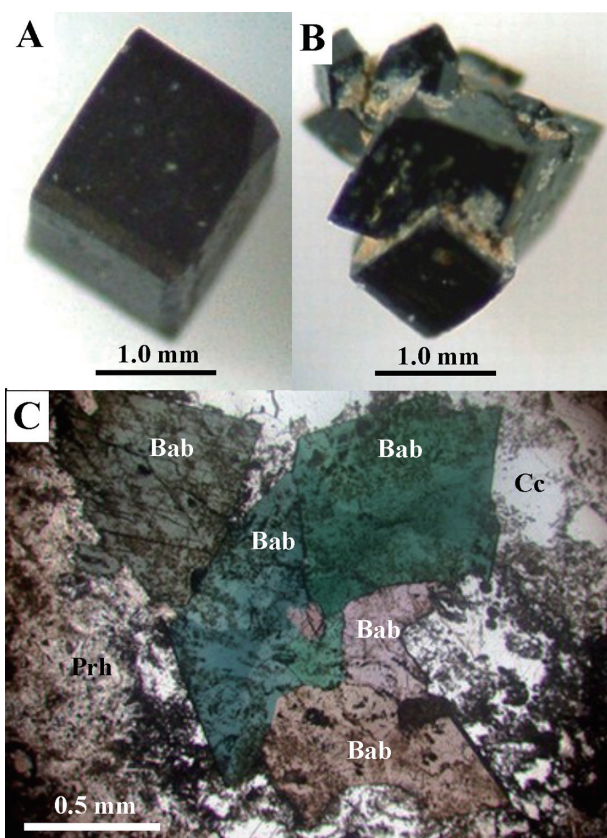


Figure 1. Kouragahana babingtonite single crystal (A), penetration twin (B), and microscopic photograph (C). Bab, Babingtonite; Cc, Calcite; Prh, Prehnite.

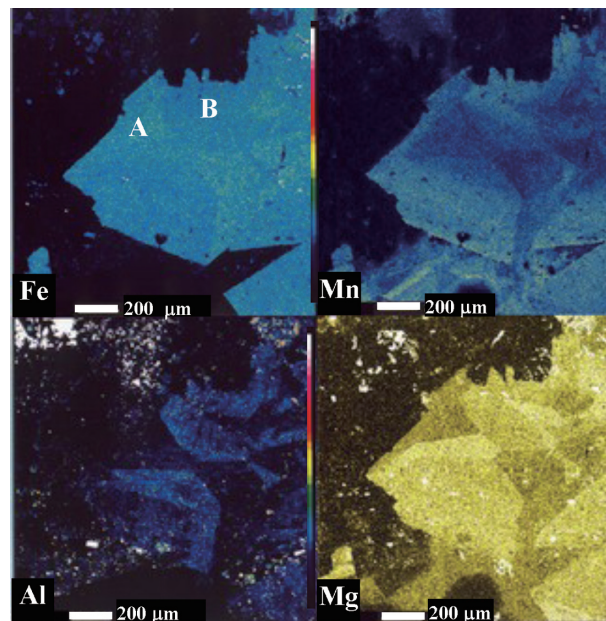


Figure 2. Fe, Mn, Al, and Mg concentration maps of babingtonite crystal with sector zoning. This is sample #2 in Table 1. A, Sector A in Table 1; B, Sector B in Table 1.

tonite sample was finely ground under alcohol for about 2 h. Particle sizes examined using an optical microscope were less than 10 μm .

Chemical compositions of babingtonite in thin sections were analyzed using a JEOL JXA-8800 microprobe analyzer (EMPA) operated at an accelerating voltage of 15 kV, with beam current of 20 nA, and beam diameter of 1 μm . The ZAF method was applied for data correction.

X-ray powder diffraction data collection and Rietveld analysis

The fine powder sample was mounted in a glass holder

with a $20 \times 18 \times 0.5$ mm cavity by loading the powder from the front of the holder.

Step-scan powder diffraction data were collected using a RIGAKU RINT diffractometer system equipped with 1° divergence and scatter slits, a 0.15 mm receiving slit, and a curved graphite diffracted-beam monochromator. The Cu X-ray tube generator was operated at 40 kV and 25 mA. The profile was taken between 5° and 150° in 2θ using a step interval of 0.04° and a step counting time of 8 s.

The crystal structure was refined using the Rietveld program RIETAN-FP (Izumi and Momma, 2007). Peaks were defined using the modified split pseudo-Voigt func-

Table 1. Chemical compositions of babingtonite with sector zoning and without sector zoning*

	Samples with sector zoning				No sector	All data
	Sample#1		Sample#2			
	Sector A Average ($n = 12$)	Sector B Average ($n = 16$)	Sector A Average ($n = 8$)	Sector B Average ($n = 13$)	Average ($n = 144$)	Average ($n = 193$)
SiO ₂	52.71(54)	52.84(43)	52.62(33)	53.15(47)	52.99(66)	52.95(63)
TiO ₂	0.04(4)	0.19(36)	0.07(9)	0.10(22)	0.07(14)	0.08(17)
Al ₂ O ₃	0.74(64)	0.77(50)	0.40(49)	0.95(57)	0.43(38)	0.51(46)
Fe ₂ O ₃ **	23.97(99)	22.95(77)	24.44(114)	22.49(101)	24.04(98)	23.86(106)
V ₂ O ₃	0.04(7)	0.04(5)	0.02(2)	0.03(4)	0.04(4)	0.04(4)
Cr ₂ O ₃	0.01(1)	0.02(3)	0.02(2)	0.01(3)	0.02(2)	0.02(2)
MnO	1.06(32)	1.46(43)	0.94(34)	1.67(45)	1.13(34)	1.18(39)
NiO	0.03(3)	0.02(3)	0.04(4)	0.01(1)	0.02(3)	0.02(3)
MgO	0.78(45)	0.86(32)	0.59(27)	0.78(12)	0.82(30)	0.80(30)
CaO	19.79(25)	19.62(37)	19.73(13)	19.86(15)	19.85(30)	19.81(31)
Na ₂ O	0.02(2)	0.02(3)	0.02(2)	0.02(2)	0.03(2)	0.03(11)
K ₂ O	0.04(1)	0.03(1)	0.04(1)	0.03(2)	0.03(1)	0.03(2)
Total	99.23	98.82	98.93	99.10	99.47	99.33
H ₂ O [†]	1.58	1.57	1.57	1.58	1.58	1.58
Total	100.81	100.39	100.50	100.68	101.05	100.91
Cations per $\Sigma\text{cations} = 9$ (O = 14.5)						
Si	4.99(4)	5.01(4)	5.00(4)	5.02(2)	5.01(4)	5.01(4)
Ti	0.00(0)	0.01(3)	0.01(1)	0.01(2)	0.00(1)	0.01(1)
Al	0.08(7)	0.09(6)	0.05(6)	0.09(6)	0.05(4)	0.06(5)
Fe ^{3+†}	0.91(7)	0.90(7)	0.94(6)	0.90(6)	0.94(4)	0.93(5)
Fe ^{2+†}	0.80(7)	0.74(6)	0.81(8)	0.71(7)	0.77(7)	0.76(7)
V	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)
Cr	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)
Mn	0.09(3)	0.12(3)	0.07(3)	0.13(4)	0.09(3)	0.09(3)
Ni	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)	0.00(0)
Mg	0.11(6)	0.12(4)	0.10(4)	0.11(2)	0.11(4)	0.11(4)
Ca	2.01(2)	1.99(3)	2.00(1)	2.01(1)	2.01(2)	2.01(2)
Na	0.00(0)	0.00(0)	0.00(0)	0.02(0)	0.01(0)	0.01(2)
K	0.00(0)	0.00(0)	0.00(0)	0.01(0)	0.00(0)	0.00(0)

* Standard deviations are shown in parentheses.

** Total Fe as Fe₂O₃.

† Recalculated values from stoichiometry (total cations = 9 per O = 14.5) and charge balance.

‡ Calculated based on the assumption of OH = 1.0 a.p.f.u.

tion in the RIETAN-FP program. The preferred orientation was corrected with the March-Dollase function (Dollase, 1986). A nonlinear least-squares calculation using the Marquardt method was followed by the conjugate-direction method to check the convergence at a local minimum (Izumi, 1993). The refined crystal structure was examined and drawn with the VESTA program by Momma and Izumi (2011).

⁵⁷Fe Mössbauer analysis

The Mössbauer spectrum of the Kouragahana babingtonite was measured at room temperature using 370 MBq ⁵⁷Co in Pd as the source. The absorber was about 20 mg of the finely ground sample. Mössbauer data were obtained using a constant acceleration spectrometer fitted with a 1024 channel analyzer. Isomer shift was referred to a metallic iron foil. Doppler velocity was calibrated using the same metallic iron foil. The spectrum was fitted to Lorentzians by the least-squares method. The QBMOSS program of Akasaka and Shinno (1992) was used for computer analysis. The quality of the fit was judged by the χ^2 value and standard deviations of Mössbauer parameters. The Fe²⁺ : Fe³⁺ ratio was determined from the area ratio of the doublets by Fe²⁺ and Fe³⁺, $[A(\text{Fe}^{2+})/A(\text{Fe}^{3+})]$, using the relation $\text{Fe}^{2+}/\text{Fe}^{3+} = C \times [A(\text{Fe}^{2+})/A(\text{Fe}^{3+})]$. In this study, C was assumed to be 1 as well as the studies by Amthauer (1980), Amthauer and Rossman (1984), and Burns and Dyar (1991).

RESULTS

Description and chemical compositions of Kouragahana babingtonite

Single crystals of the Kouragahana babingtonite are parallelohedrons with {100}, {001}, {001}, {111}, {110}, and {101} (Fig. 1A). Both normal and sector-zoned crystals occur (Fig. 1C). To the best of our knowledge, this is the first reporting of sector-zoned babingtonite. Chemical compositions of the babingtonite are listed in Table 1, in which Fe²⁺ and Fe³⁺ are recalculated from stoichiometry (total cations = 9 per O = 14.5) and charge balance. A correction of the intensity of the VK_α line by the TiK_β line was not made because of the very low contents of the elements. Babingtonite with sector zoning consists of sectors relatively enriched in Fe (sector A in Fig. 2 and Table 1) and sectors enriched in Mg, Mn, and Al (sector B in Fig. 2 and Table 1). In addition, the babingtonite has a zonal structure with higher Fe²⁺ and Al in the cores and higher Mn and Fe³⁺ in the rims (Figs. 2 and 3). Mn is assumed to be divalent in the oxidation state in Table 1 and Figure 3.

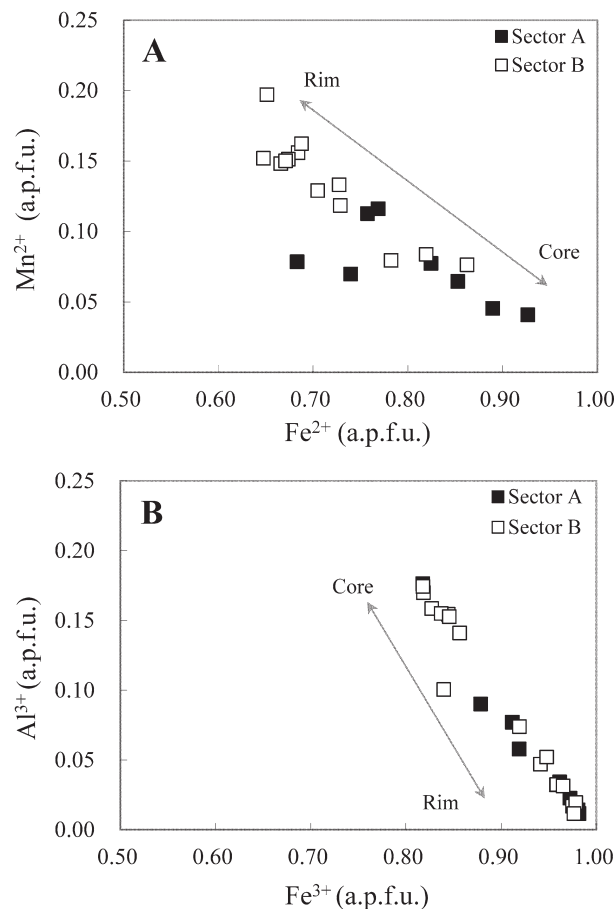


Figure 3. Fe²⁺–Mn²⁺ (A) and Fe³⁺–Al³⁺ (B) relations in sector-zoned babingtonite of sample #2 of Table 1.

The average total Fe₂O₃ of babingtonite without sector zoning is similar to the analyzed values for the sector A in the sector-zoned babingtonite (Table 1). The chemical formula based on the average composition of all the analytical data ($n = 193$) is $[\text{Na}_{0.01(2)}\text{Ca}_{2.01(2)}][\text{Mg}_{0.11(4)}\text{Mn}_{0.09(3)}\text{Fe}_{0.76(7)}^{2+}\text{Fe}_{0.93(5)}^{3+}\text{Ti}_{0.01(1)}\text{Al}_{0.06(5)}]\text{Si}_{5.01(4)}\text{O}_{14}(\text{OH})$ ($Z = 2$), and its Fe²⁺:Fe³⁺ ratio is evaluated as 45.0:55.0.

X-ray structural refinement

Details of the X-ray data collection are listed in Table 2. As indicated by the X-ray powder diffraction pattern in Figure 4, the powder sample consisted of single-phase babingtonite. The crystal structure of the Kouragahana babingtonite was refined assuming space group $P\bar{1}$ based on published X-ray single crystal data. X-ray single-crystal structural data of babingtonite from the Yakuki mine, Japan, from Araki and Zoltai (1972) were used as an initial structural model. In the structural refinement, Ca was fixed at the Ca1 and Ca2 sites and Si at the Si1, Si2, Si3, Si4, and Si5 sites, based on the EMPA data. Site occupancies of Fe in the Fe1 and Fe2 sites were refined us-

Table 2. Data collection and details of the structure refinement

2 θ scan range (°)	5 – 150
Step interval (°2 θ)	0.04
Integration time/step (s)	8
Max. intensity (counts)	5221
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	7.4667(3)
<i>b</i> (Å)	11.6253 (6)
<i>c</i> (Å)	6.6820(2)
α (°)	91.533 (4)
β (°)	93.886 (3)
γ (°)	104.203(4)
<i>V</i> (Å ³)	560.43 (4)
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ³)	3.359
<i>R</i> _p (%)	7.65
<i>R</i> _{wp} (%)	9.91
<i>R</i> _e (%)	6.37
<i>S</i>	1.56
<i>R</i> _B (%)	3.95
<i>R</i> _F (%)	1.81
D–W <i>d</i>	1.02

*R*_p, *R*-pattern; *R*_{wp}, *R*-weighted pattern; *R*_e, *R*-expected; *S*, Goodness-of-fit ($= R_{wp}/R_e$); *R*_B, *R*-Bragg factor; *R*_F, *R*-structure factor (Young, 1993); D–W *d*, Durbin-Watson *d* statistic (Hill and Flack, 1987).

ing the following constraints: Fe(Fe1) + Mg(Fe1) = 1.0; Fe(Fe2) + Al(Fe2) = 1.0, where Mg and Al are allocated to the Fe1 and Fe2 sites, respectively, based on the results of the neutron diffraction study of Tagai et al. (1990). The isotropic atomic displacement parameters of atoms at the octahedral sites and at the tetrahedral sites and those of oxygen atoms were constrained to be equal, respectively.

The refined unit cell parameters, *R*-factors, goodness-of-fit ($S = R_{wp}/R_e$), and the Durbin-Watson *d* statistic are shown in Table 2. The resulting site occupancies at the Fe1 and Fe2 sites, atomic positions, and isotropic atomic displacement parameters are listed in Table 3, and selected interatomic distances are given in Table 4. The resulting crystal structure (Fig. 5; color version of Figure 5 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120714>) and the mean interatomic distances (Table 4) are consistent with those of Araki and Zoltai (1972), Tagai et al. (1990), and Armbruster (2000).

The refined site occupancies of cations in the Fe1 and Fe2 sites are [Fe_{0.91}(2)Mg_{0.09}] and [Fe_{0.91}(2)Al_{0.09}], respectively, if Mg is assumed to distribute in the Fe1 site and Al in the Fe2 site (Table 3). The occupancies of Mg at the Fe1 site and Al at the Fe2 site are in agreement with those of the average chemical composition [Mg

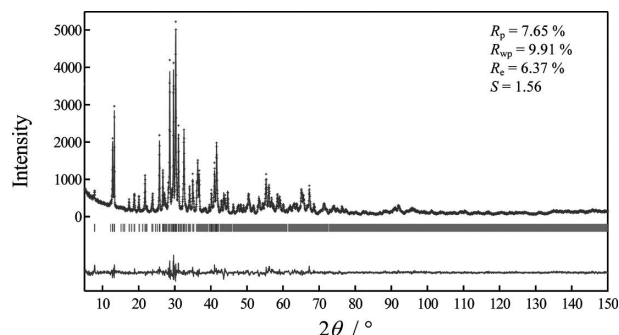


Figure 4. Observed and calculated X-ray powder diffraction patterns for Kouragahana babingtonite refined in space group $P\bar{1}$. The crosses are the observed data, the solid line is the calculated pattern, and the vertical bars mark all possible Bragg reflections ($K\alpha_1$ and $K\alpha_2$) for babingtonite. The difference between the observed and calculated pattern is shown at the bottom.

= 0.11(4); Al = 0.06(5)] within the experimental error. The refined Fe occupancy at the octahedral sites includes 0.09 Mn (Table 1). By allocating Mn, 0.09 atoms per formula unit (a.p.f.u.), to the Fe1 site based on the results of Tagai et al. (1990), the site populations in the Fe1 and Fe2 sites result in [Fe_{0.82}(2)Mn_{0.09}Mg_{0.09}] and [Fe_{0.91}(2)Al_{0.09}] (a.p.f.u.), respectively.

The consistency between the site populations and the refined atomic positions was examined in terms of the bond valence sum rule (Brown and Shannon, 1973):

$$V_i = \sum_j \exp\left(\frac{l_o - l_{ij}}{0.37}\right),$$

where V_i is the valence of cation *i*, l_o is the bond valence parameter (Brown and Altermatt, 1985; Brese and O'Keeffe, 1991) and l_{ij} is the bond length between cation *i* and anion *j*. As shown in Table 5, the bond valence sums of cation sites [$\sum V(A)$] approximately correspond to the oxidation state of the sites. The bond valences of Fe1 and Fe2 [2.01 and 2.91 valence units (v.u.), respectively] imply an ordering of divalent and trivalent cations at the Fe1 and Fe2 sites, respectively. Thus, the assignment of Mg to Fe1 and Al to Fe2 in the refinement is regarded to be appropriate. The bond valence sum of O1 (1.32 v.u.) suggests (OH)[−] at this position. The O atom at O1 acts as a donor and that at O11 (1.68 v.u.) as an acceptor for a hydrogen bond, which is consistent with the results of single crystal structural analyses using neutron diffraction by Tagai et al. (1990) and X-ray diffraction by Armbruster (2000).

⁵⁷Fe Mössbauer analysis

The ⁵⁷Fe Mössbauer spectrum of the Kouragahana ba-

Table 3. Refined atomic positions, site occupancies, and atomic displacement parameters*

	n_{eq}	g	x	y	z	B ($\text{\AA}^2$)**	U ($= B/8\pi_2$) ($\text{\AA}^2$)
Ca1	2	1	0.778(1)	0.942(1)	0.145(1)	0.9(2)	0.011(3)
Ca2	2	1	0.238(1)	0.523(1)	0.299(1)	0.7(2)	0.009(3)
Fe1	2	Fe0.908(19)Mg0.092	0.594(1)	0.6453(8)	0.060(1)	0.6(1)	0.008(1)
Fe2	2	Fe0.914(24)Al0.086	0.0449(9)	0.2349(7)	0.184(1)	0.6	0.0080
Si1	2	1	0.286(2)	0.051(1)	0.338(2)	0.5(1)	0.006(1)
Si2	2	1	0.465(2)	0.312(1)	0.422(2)	0.5	0.006
Si3	2	1	0.802(2)	0.446(1)	0.212(2)	0.5	0.006
Si4	2	1	0.988(2)	0.717(1)	0.313(2)	0.5	0.006
Si5	2	1	0.328(2)	0.839(1)	0.108(2)	0.5	0.006
O1	2	1	0.191(3)	0.983(2)	0.539(3)	0.5(1)	0.006(2)
O2	2	1	0.137(3)	0.079(2)	0.185(3)	0.5	0.006
O3	2	1	0.432(3)	0.1778(3)	0.433(3)	0.5	0.006
O4	2	1	0.312(3)	0.339(3)	0.244(4)	0.5	0.006
O5	2	1	0.548(3)	0.621(3)	0.362(3)	0.5	0.006
O6	2	1	0.675(3)	0.372(3)	0.378(3)	0.5	0.006
O7	2	1	0.973(3)	0.385(3)	0.162(3)	0.5	0.006
O8	2	1	0.681(3)	0.473(3)	0.025(4)	0.5	0.006
O9	2	1	0.919(3)	0.572(3)	0.329(3)	0.5	0.006
O10	2	1	0.869(3)	0.753(2)	0.128(3)	0.5	0.006
O11	2	1	0.018(3)	0.219(3)	0.481(3)	0.5	0.006
O12	2	1	0.194(3)	0.740(3)	0.259(4)	0.5	0.006
O13	2	1	0.517(3)	0.797(3)	0.052(4)	0.5	0.006
O14	2	1	0.809(3)	0.141(3)	0.097(3)	0.5	0.006
O15	2	1	0.396(3)	0.963(2)	0.225(3)	0.5	0.006

* Estimated standard deviations are in parentheses (1σ).** Isotropic atomic displacement parameters (B) of atoms at the octahedral sites, of silicon at the tetrahedral sites, and of oxygen were constrained to be equal, respectively. n_{eq} , Multiplicity of the Wyckoff position (number of equivalent points per unit cell); g , Site occupancy.

bingtonite taken at room temperature (Fig. 6; color version of Figure 6 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120714>) consists of three peaks that can be resolved into two doublets assigned to Fe^{2+} and Fe^{3+} at the octahedral sites. However, as indicated by Amthauer (1980), Amthauer and Rossman (1984), and Burns and Dyar (1991), the low-Doppler velocity components of each doublet in the Mössbauer spectrum of babingtonite measured at room temperature strongly overlap. Amthauer (1980) applied two fitting modes for analysis: (1) three peaks were fit without constraint and (2) two doublets were fit with the Fe^{2+} doublet consisting of the outermost peaks and the Fe^{3+} doublet positioned between them. On the other hand, Amthauer and Rossman (1984) employed a third fitting model where the low-velocity peak of the Fe^{3+} doublet located at a position of lower Doppler velocity than that of Fe^{2+} . 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 Fe^{3+} and Fe^{2+} 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 $\text{Fe}^{2+}:\text{Fe}^{3+}$ ra-

tio.

Generally, the peak widths and the intensities of component peaks in a doublet are constrained to be equal for a successful fit of Mössbauer spectra consisting of multiple doublets. In fact, such a constraint was applied for the Mössbauer spectral analyses of babingtonite by Amthauer (1980), Amthauer and Rossman (1984), and Burns and Dyar (1991). However, the fit of the Kouragahana babingtonite with constraints on both peak widths and intensities of doublet components resulted in high χ^2 values. By examining the influence of the constraints on the fitting procedure, we found that a fit with only the constraint on the intensities of component peaks of a doublet resulted in reasonable Mössbauer hyperfine parameters (peak widths, $I.S.$, and $Q.S.$) and improved χ^2 -values. Table 6 shows the results of two doublets fit based on the fitting modes of Amthauer (1980) [labeled Fit (1) in Table 6] and Amthauer and Rossman (1984) [Fit (2) in Table 6]. The $I.S.$ and $Q.S.$ values of the Kouragahana babingtonite are consistent with published values (Amthauer, 1980; Amthauer and Rossman, 1984; Burns and Dyar, 1991).

The $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratios determined from the area ratios of the Fe^{2+} and Fe^{3+} doublets are 43.3(3):56.7(4) and

Table 4. Interatomic distances (Å)*

Ca1– O1	2.24(2)	Si1– O1	1.69(2)
O2	2.36(2)	O2	1.56(2)
O2'	2.75(2)	O3	1.68(3)
O10	2.46(2)	O15	1.67(2)
O13	2.28(2)	Mean	1.65
O14	2.31(3)	Si2– O3	1.52(3)
O15	3.00(2)	O4	1.69(2)
O15'	3.08(2)	O5	1.65(2)
Mean	2.56	O6	1.60(2)
Ca2– O4	2.36(3)	Mean	1.61
O5	2.32(2)	Si3– O6	1.63(2)
O6	2.42(3)	O7	1.65(2)
O7	2.33(2)	O8	1.58(2)
O8	2.29(3)	O9	1.65(3)
O9	2.60(2)	Mean	1.63
O9'	2.95(2)	Si4– O9	1.64(3)
O12	2.64(3)	O10	1.59(2)
Mean	2.49	O11	1.56(2)
Fe1– O4	2.19(2)	O12	1.57(2)
O5	2.09(2)	Mean	1.59
O8	2.20(2)	Si5– O12	1.73(2)
O8'	2.26(2)	O13	1.66(2)
O10	2.14(2)	O14	1.70(2)
O13	1.99(2)	O15	1.57(3)
Mean	2.14	Mean	1.67
Fe2– O2	2.09(2)		
O4	2.07(2)		
O7	1.95(3)		
O10	2.22(2)		
O11	2.02(2)		
O14	1.88(2)		
Mean	2.04		

* Estimated standard deviations are in parentheses (1 σ).

47.1(4):52.9(3) for fit (1) and fit (2), respectively. The average is $\text{Fe}^{2+}:\text{Fe}^{3+} = 45.2(4):54.8(4)$.

DISCUSSION

Crystallization of babingtonite under low-temperature conditions has been reported repeatedly from zeolitic veins and cavities in basic igneous rocks and granites, low-grade assemblages in metabasites, skarn deposits, pegmatites, and calcareous volcanic rocks (Burns and Dyar, 1991; Armbruster et al., 2000). The crystallization conditions of babingtonite have been estimated at about 0.5 kbar and 100–150 °C for babingtonite from Harcourt (Birch, 1983) and at 0.5 kbar and 150–200 °C for that from cavities of the Deccan basalt, India (Wise and Moller, 1990).

The hydrothermal alteration of the Kouragahana dolerite is characterized by the mineral assemblages of Fe-rich pumpellyite + prehnite and of prehnite + babingtonite in veins and cavities. The former assemblage indicates

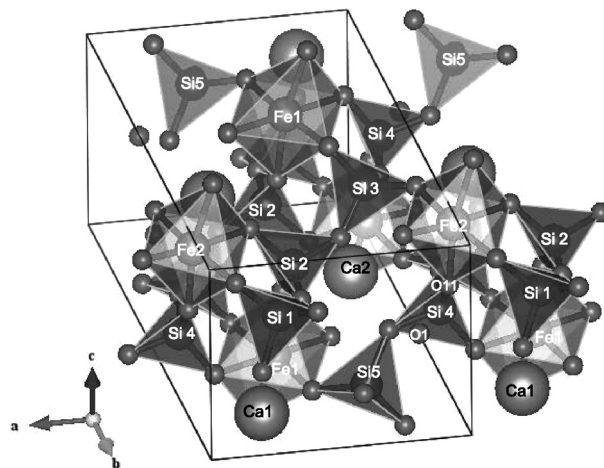


Figure 5. Projection of Kouragahana babingtonite. The crystal structure was drawn using the VESTA program (Momma and Izumi, 2011). Color version of Figure 5 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120714>.

low-temperature alteration conditions of the zeolite to prehnite-pumpellyite facies (Kano et al., 1986; Akasaka et al., 1997; Nagashima et al., 2006). In this assemblage, prehnite occurs as an overgrowth phase on the Fe-rich pumpellyite (Kano et al., 1986; Akasaka et al., 1997), indicating later crystallization of prehnite than Fe-rich pumpellyite with decreasing fluid temperature. Babingtonite in association with prehnite does not coexist with Fe-rich pumpellyite, and, as well as prehnite, is regarded to have crystallized at temperatures lower than that of Fe-rich pumpellyite. Pumpellyite crystallizes at temperatures below about 400 °C (Akasaka et al., 2003b) or 300 °C (Liou, 1973; Schiffman and Liou, 1983; Akasaka et al., 1988). Thus, the crystallization temperatures for babingtonite occurring in cavities (below 200 °C) proposed by Birch (1983) and Wise and Moller (1990) seem to hold for the Kouragahana babingtonite. The existence of hour-glass structure and the well-developed morphology of the Kouragahana babingtonite indicate rapid crystallization of the mineral in open space under supersaturated conditions. Birch (1983) considered the formation of a babingtonite-bearing assemblage from late-stage volatiles entrapped in cavities during the cooling process of the igneous body.

The distribution of Fe^{2+} and Fe^{3+} between the Fe1 and Fe2 sites is of additional interest. The X-ray Rietveld analysis of the present study resulted in the site populations of $^{\text{Fe1}}[\text{Fe}0.82(2)\text{Mn}0.09\text{Mg}0.09]$ and $^{\text{Fe2}}[\text{Fe}0.91(2)\text{Al}0.09]$, corresponding to an $\text{Fe}(\text{Fe1}):\text{Fe}(\text{Fe2})$ ratio of 47.4(14):52.6(14). On the other hand, the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratios determined by the Mössbauer analysis are 43.3(3):56.7(4) in fit (1), 47.1(4):52.9(3) in fit (2), and 45.2(4):54.8(4) on average. We therefore conclude that in the Kouragahana

Table 5. Calculated bond valence (v. u.)

Anion	Cation									$\Sigma V(C)^{**}$	Anion chemistry
	Ca1	Ca2	Fe1	Fe2	Si1	Si2	Si3	Si4	Si5		
O1	0.48				0.85					1.32	OH ⁻
O2	0.35			0.40	1.19					2.06	O ²⁻
O2'	0.12										
O3					0.86	1.33				2.18	O ²⁻
O4		0.35	0.29	0.43		0.84				1.90	O ²⁻
O5		0.39	0.38			0.93				1.70	O ²⁻
O6		0.29				1.04	0.98			2.32	O ²⁻
O7		0.38		0.59			0.93			1.90	O ²⁻
O8		0.42	0.28				1.13				
O8'			0.24							2.06	O ²⁻
O9		0.18					0.93	0.96		2.14	
O9'		0.07									O ²⁻
O10	0.26		0.33	0.28				1.10		1.97	O ²⁻
O11				0.49				1.19		1.68	O ²⁻
O12		0.16						1.16	0.81	2.13	O ²⁻
O13	0.43		0.50						0.91	1.83	O ²⁻
O14	0.36			0.71					0.75	1.82	O ²⁻
O15	0.06				0.88				1.16		
O15'	0.05									2.15	O ²⁻
$\Sigma V(A)^*$	2.11	2.23	2.01	2.91	3.78	4.13	3.97	4.40	3.63		

* $\Sigma V(A)$ is the valence of bonds emanating from cations summed over the bounded anions.

** $\Sigma V(C)$ is the valence of bonds reaching anions.

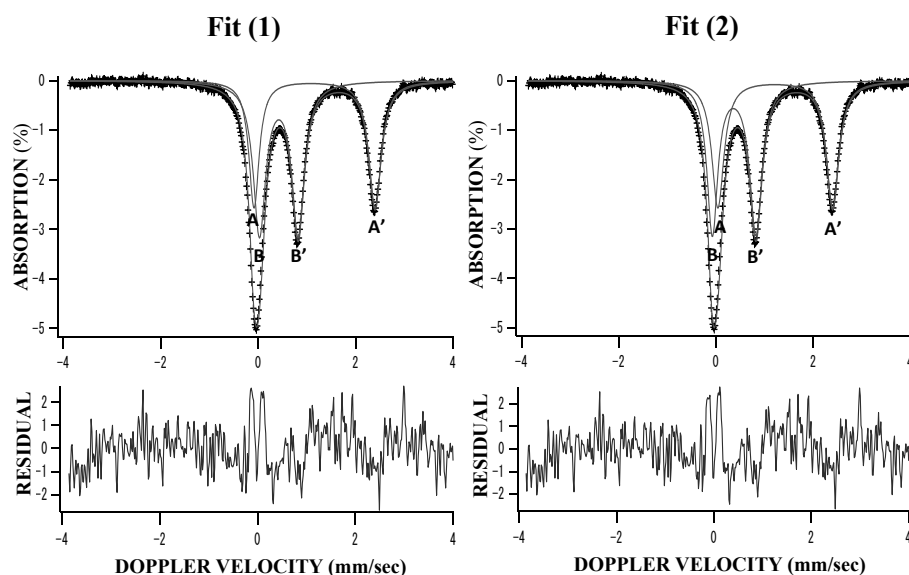


Figure 6. ⁵⁷Fe Mössbauer spectrum of Kouragahana babingtonite and two fitting results. Mössbauer hyperfine parameters and the assignments are shown in Table 6. Color version of Figure 6 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120714>.

babingtonite Fe²⁺ and Fe³⁺ are ordered at the Fe1 and Fe2 sites, respectively. This result confirms previous findings (Araki and Zoltai, 1972; Amthauer, 1980; Amthauer and Rossman, 1984; Tagai et al., 1990; Burns and Dyar, 1991) of order of M²⁺ cations at Fe1 and M³⁺ cations at Fe2 sites. In fact, the Fe²⁺:Fe³⁺ ratio calculated from the average chemical formula based on charge balance, that is Fe²⁺:Fe³⁺ = 45.0:55.0, agrees with the Mössbauer and X-ray diffraction data. However, Armbruster (2000) reported

a babingtonite with significant Fe³⁺ in the Fe1 site and Mg in the Fe2 site from Arvigo, Switzerland, that formed in Alpine fissures at less than 200 °C. Therefore, distributions of cations between the Fe1 and Fe2 sites in babingtonite should be examined carefully in each sample.

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Table 6. ^{57}Fe Mössbauer hyperfine parameters* of Kouragahana babingtonite

Doublets	<i>I.S.</i> (mm/s)	<i>Q.S.</i> (mm/s)	<i>Γ</i> (mm/s)	Area Ratio (%)	Assignments	$\chi^2/\text{Freedom}$
Fit (1)						
AA'	1.159(1)	2.484(2)	Peak A: 0.252(3); Peak A': 0.308(3)	43.3(3)	$^{\text{VI}}\text{Fe}^{2+}$	1.42
BB'	0.425(1)	0.794(1)	Peak B: 0.306(3); Peak B': 0.307(2)	56.7(4)	$^{\text{VI}}\text{Fe}^{3+}$	
Fit (2)						
AA'	1.220(1)	2.361(2)	Peak A: 0.301(4); Peak A': 0.308(3)	47.1(4)	$^{\text{VI}}\text{Fe}^{2+}$	1.42
BB'	0.375(1)	0.896(1)	Peak B: 0.265(3); Peak B': 0.307(3)	52.9(3)	$^{\text{VI}}\text{Fe}^{3+}$	

* Standard deviations, 1σ , are given in parentheses.

I.S., Isomer shift referred to a metallic iron absorber; *Q.S.*, Quadrupole splitting; *Γ*, Full width at half height.

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SUPPLEMENTARY MATERIALS

Color version of Figures 5 and 6 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120714>.

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