

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band: 80 (2000)
Heft: 3

Artikel: Cation distribution in Mg, Mn-bearing babingtonite from Arvigo, Val Calanca, Grisons, Switzerland
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DOI: <https://doi.org/10.5169/seals-60966>

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Cation distribution in Mg, Mn-bearing babingtonite from Arvigo, Val Calanca, Grisons, Switzerland

by Thomas Armbruster¹

Abstract

The crystal structures of three babingtonites, space group $P\bar{1}$, of simplified $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}\text{OH}]$ composition were refined from X-ray single-crystal data. Two samples originated from low-temperature Alpine fissures at Arvigo (Switzerland) and one from a skarn at Westfield (Mass.). Both Arvigo samples were enriched in Mg (0.21–0.28 p.f.u.) and Mn (0.21–0.26 p.f.u.) yielding the following cell dimensions, Arvigo 1: $a = 7.468(1)$, $b = 12.161(4)$, $c = 6.675(2)$ Å, $\alpha = 86.09(3)$, $\beta = 93.94(2)$, $\gamma = 112.21(2)^\circ$, and Arvigo 2: $a = 7.480(1)$, $b = 12.159(1)$, $c = 6.678(2)$ Å, $\alpha = 86.10(2)$, $\beta = 93.92(1)$, $\gamma = 112.08(2)^\circ$. Site population refinements for the Arvigo babingtonite crystal (Arvigo 2) that displayed epitaxially hedenbergite whiskers yielded significant Mg on the Fe2 site, commonly occupied by ferric iron and minor Al. For stoichiometry reasons significant Fe^{3+} must be assumed on Fe1, commonly occupied by ferrous iron, Mn^{2+} , and Mg. Only a very low degree of $\text{Fe}^{2+}/\text{Fe}^{3+}$ disorder could be derived for the skarn babingtonite from Westfield confirming published Mössbauer data.

Keywords: babingtonite, crystal structure, cation distribution.

Introduction

Babingtonite is a triclinic pyroxenoid mineral with Fünfer-einfachketten of simplified $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}\text{OH}]$ composition. ARAKI and ZOLTAI (1972) and KOSOI (1976) assumed the above ideal stoichiometry in their crystal-structure refinements. These previous studies were mainly performed to elucidate the structural principles (Fig. 1). Furthermore, all reported Mössbauer spectroscopic data (AMTHAUER, 1980; CZANK, 1981; AMTHAUER and ROSSMAN, 1984; BURNS and DYAR, 1991) could be fitted with one Fe^{2+} and one Fe^{3+} doublet indicating separation of ferrous and ferric iron onto two distinct crystallographic sites, designated Fe1 and Fe2, respectively. ARAKI and ZOLTAI (1972) studied a babingtonite (Yakukui Mine, Japan) with the additional 0.30 Mn, 0.13 Mg, and 0.09 Al per formula unit (p.f.u.), leading to a unit cell volume of 570 Å³ and average Fe1–O and Fe2–O distances of 2.169 and 2.048 Å, respectively. A crystal from the same locality was restudied by TAGAI et al. (1990) by neutron diffraction at 80 K to resolve the exact hydro-

gen-bonding scheme. In addition, neutron scattering-lengths confirmed occupation of Mg and Mn on Fe1 and Al on Fe2. Unfortunately, room temperature cell dimensions were mixed with 80 K positional parameters, thus making bond distances not very reliable within given standard deviations. KOSOI (1976) investigated a babingtonite without specifying its exact chemical composition and determined average Fe1–O and Fe2–O distances of 2.154 and 2.041 Å, respectively.

Recent chemical analyses of babingtonites formed in low-temperature Alpine fissures (ARMBRUSTER et al., 2000) indicated up to 0.28 Mg and 0.26 Mn p.f.u. The significant amount of Mg can be easily located from single-crystal X-ray data due to the lower scattering power of Mg compared to Fe. In contrast, Mn and Fe have too similar scattering power to allow discrimination. Thus the goal of the present study is a structural reinvestigation of babingtonite in order to analyze the distribution of light elements on the octahedral sites. Furthermore, two genetic types of babingtonite are studied, those formed below 200 °C in Alpine fissures (Arvigo, Grisons) and one sample

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Tab. 1 Experimental parameters for X-ray data collection and refinement on babingtonites.

sample	Arvigo 1 NMBE 34973	Arvigo 2 NMBE 34974	Westfield
space group	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2
a (Å)	7.468(1)	7.480(1)	7.458(1)
b (Å)	12.161(4)	12.159(2)	12.168(2)
c (Å)	6.675(2)	6.678(2)	6.675(1)
α (°)	86.09(3)	86.10(2)	86.12(1)
β (°)	93.94(2)	93.92(1)	93.86(1)
γ (°)	112.21(2)	112.08(1)	112.27(1)
V (Å ³)	559.3(3)	560.9(2)	558.7(2)
X-radiation	MoK α	MoK α	MoK α
machine	CAD4	SMART	CAD4
upper θ limit	30°	27.77°	30°
reflections measured	3523	3215	3494
unique reflections	3262	2347	3233
reflections > 4 σ (F)	2541	2009	2652
absorption corr.	empirical: Ψ	empirical: Ψ	empirical: Ψ
R_{σ} (%)	2.4	2.8	2.4
number of parameters	223	223	223
$R1$ (on F) %	3.53	2.52	3.21
wR (on F ²) %	10.34	9.11	6.95

Electron microprobe analyses (ARMBRUSTER et al., 2000):

Arvigo 1: $(\text{Ca}_{1.99}\text{Na}_{0.01})(\text{Fe}_{1.49}\text{Mn}_{0.21}\text{Mg}_{0.22}\text{Al}_{0.08})[\text{Si}_{5.01}\text{O}_{14}(\text{OH})]$

Arvigo 2 (composite): $(\text{Ca}_{1.99}\text{Na}_{0.01})(\text{Fe}_{1.41}\text{Mn}_{0.26}\text{Mg}_{0.28}\text{Al}_{0.03})[\text{Si}_{5.02}\text{O}_{14}(\text{OH})]$

Westfield: $\text{Ca}_{2.00}(\text{Fe}_{1.70}\text{Mn}_{0.06}\text{Mg}_{0.18}\text{Al}_{0.05})[\text{Si}_{5.01}\text{O}_{14}(\text{OH})]$

from a skarn (Westfield, Mass.) formed at considerably higher temperature. The Westfield sample was selected because Mössbauer data of a sample from the same locality were presented by AMTHAUER (1980) and BURNS and DYAR (1991).

Experimental

The samples investigated are the same crystals as described by ARMBRUSTER et al. (2000). For sample Arvigo 1 (NMBE 34973), one single crystal, ca. 0.5 mm in maximum dimension, was separated from a small hand specimen. This crystal was split into two parts, one was used for electron-microprobe analysis (ARMBRUSTER et al., 2000), the other was applied for X-ray data collection. The same procedure was used for the Westfield babingtonite. Crystal Arvigo 2 (NMBE 34974) is the babingtonite with epitaxial hedenbergite whiskers where the whiskers were mechanically removed before data collection (ARMBRUSTER et al., 2000). The chemical composition (Tab. 1) was not determined on the same crystal submitted to structure analysis but was taken from other composite crystals separated close to the crystal supplied for X-ray study.

All cell dimension were determined from high-angle data on an Enraf Nonius CAD4 single-crystal X-ray diffractometer. Details of data collection and X-ray refinement are summarized in table 1. The unit cell dimensions given in table 1 were transformed from standard setting ($a \approx 7.5$, $b \approx 11.6$, $c \approx 6.7$ Å, $\alpha \approx 91.6$, $\beta \approx 93.9$, $\gamma \approx 104.5^\circ$) by the matrix $[1\ 0\ 0; 1\ 1\ 0; 0\ 0\ -1]$ to obtain a setting where the tetrahedral chains run parallel to the b -axis. Structure solution and refinement was carried out with the SHELX-97 program package (SHELDRICK, 1997) applying neutral-atom scattering factors. The atom labeling of TAGAI et al. (1990) was adopted. The hydrogen position was extracted from difference Fourier maps and also refined. All atoms except H were refined with anisotropic displacement parameters. Due to the significant Mg concentration determined by electron-microprobe analyses, the population of the octahedral sites Fe1 and Fe2 were allowed to vary. Fe and Mg were assigned to Fe1 and Fe2. Notice that the scattering power for X-rays of Fe and Mn on one hand and Mg and Al on the other hand is too similar to be distinguished. Test refinements yielded that both Ca sites (Ca1 and Ca2) were completely occupied by Ca.

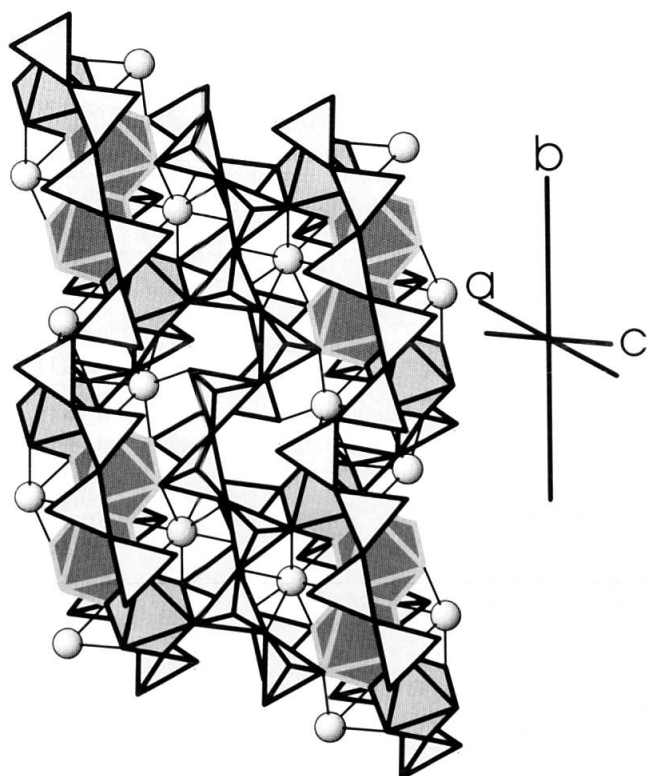


Fig. 1 Polyhedral drawing of the babingtonite structure displaying corrugated Fünfer-einfachketten extending parallel to the *b*-axis. Fe1 octahedra, predominantly occupied by divalent atoms (Fe, Mn, Mg), are dark gray with light rims and form edge-sharing doublets. Fe2 octahedra, predominantly occupied by trivalent atoms (Fe, Al), are light gray with black rims. Ca polyhedra are shown as spheres with bonds.

Results and discussion

Atomic coordinates are given in table 2, and bond lengths in table 3. A list of anisotropic displacement parameters may be obtained from the author upon request. For the two samples (Arvigo 1 and Westfield) for which X-ray data collection and electron-microprobe analysis were performed on the same crystal there is a good correspondence between the amount of (Mg + Al) refined from X-ray data and chemically analyzed. Only for the Arvigo 2 crystal X-ray data converged at 0.37 (Mg + Al) pro formula unit whereas average microprobe analyses yielded only 0.31 (Mg + Al) p.f.u. All three structure refinements accompanied by site occupation determinations for the octahedral Fe1 (Fe²⁺) and Fe2 (Fe³⁺) sites show a common trend. The concentration of light elements (Mg + Al) on the Fe2 site is significantly higher than the amount of Al determined by electron microprobe analyses. Thus the substitution on Fe2 is more complex than just Al³⁺ → Fe³⁺. In line with this result is the observation that the Mg

Tab. 2a Atomic coordinates and B_{eq} values, with standard deviations in parentheses, for babingtonite Arvigo 1 (NMBE 34973). Cell setting: $a = 7.468(1)$, $b = 12.161(4)$, $c = 6.675(2)$ Å, $\alpha = 86.09(3)$, $\beta = 93.94(2)$, $\gamma = 112.21(2)^\circ$.

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$B_{eq}(\text{\AA}^2)$
Ca1	0.1606(1)	0.94195(6)	0.8573(1)	0.84(1)
Ca2	0.28242(9)	0.52011(5)	0.6957(1)	0.718(9)
Fe1 ^a	0.05007(7)	0.64372(4)	0.93914(7)	0.530(9)
Fe2 ^b	0.18824(7)	0.23542(4)	0.81574(7)	0.437(8)
Si1	0.7656(1)	0.05311(7)	0.6594(1)	0.53(1)
Si2	0.8529(1)	0.31325(7)	0.5752(1)	0.47(1)
Si3	0.6386(1)	0.44490(7)	0.7906(1)	0.46(1)
Si4	0.7263(1)	0.71334(7)	0.6897(1)	0.46(1)
Si5	0.5087(1)	0.83531(7)	0.8941(1)	0.53(1)
H1	0.796(9)	0.922(5)	0.486(9)	3.2(13)*
O1	0.7888(4)	0.9869(2)	0.4659(4)	1.00(4)
O2	0.9506(3)	0.0805(2)	0.8158(3)	0.70(3)
O3	0.7374(3)	0.1710(2)	0.5624(3)	0.78(4)
O4	0.0213(3)	0.3380(2)	0.7544(3)	0.67(3)
O5	0.0707(3)	0.6206(2)	0.6352(3)	0.75(3)
O6	0.6922(3)	0.3704(2)	0.6266(3)	0.70(3)
O7	0.4154(3)	0.3843(2)	0.8434(3)	0.70(4)
O8	0.7971(3)	0.4749(2)	0.9735(3)	0.68(3)
O9	0.6427(3)	0.5684(2)	0.6617(3)	0.66(3)
O10	0.8835(3)	0.7550(2)	0.8758(3)	0.70(3)
O11	0.1992(3)	0.2213(2)	0.5221(3)	0.82(3)
O12	0.5332(3)	0.7369(2)	0.7495(3)	0.73(3)
O13	0.2891(3)	0.7985(2)	0.9448(4)	0.81(4)
O14	0.3367(3)	0.1429(2)	0.9172(3)	0.79(3)
O15	0.5736(3)	0.9678(2)	0.7757(4)	0.84(4)

Note: * Starred atoms were refined isotropically;

^a population 0.849(5) Fe, Mn and 0.151 Mg

^b population 0.874(5) Fe and 0.126 Mg, Al

concentration on Fe1 is always significantly lower than the concentration of chemically determined Mg. The data strongly suggest that there is pronounced disorder between di- and trivalent elements on Fe1 and Fe2. Inspection of table 3 indicates that the average Fe1–O distance (ca. 2.15 Å) is significantly longer than the average Fe2–O distance (ca. 2.03 Å) which indicates that Fe³⁺ (octahedral ionic radius according to SHANNON (1976): 0.645 Å) is concentrated on Fe2 whereas Fe²⁺ (octahedral ionic radius according to SHANNON (1976): 0.78 Å) is concentrated on Fe1. This is in qualitative agreement with previous crystal structure and Mössbauer studies. If the bond lengths of the three data sets are compared (Tab. 3) it is striking that crystal Arvigo 2 shows the longest average Fe1–O distance of 2.154 Å which is in agreement with the electron microprobe analyses where sample Arvigo 2 also exhibited the highest Mn²⁺ concentration (ionic radius 0.82 Å) and confirms the Mn assignment by TAGAI et al. (1990). In contrast, the Westfield crystal with the lowest Mn concentration exhibits a shorter average Fe1–O

Tab. 2b Atomic coordinates and B_{eq} values, with standard deviations in parentheses, for babingtonite Arvigo 2 (NMBE 34974). Cell setting:

$a = 7.480(1)$, $b = 12.159(1)$, $c = 6.678(2)$ Å, $\alpha = 86.10(2)$, $\beta = 93.92(1)$, $\gamma = 112.08(2)^\circ$.

atom	x/a	y/b	z/c	$B_{eq}(\text{\AA}^2)$
Ca1	0.1570(1)	0.94142(6)	0.85701(9)	1.20(1)
Ca2	0.28326(9)	0.52021(5)	0.69645(9)	0.96(1)
Fe1 ^a	0.05046(7)	0.64393(4)	0.93885(7)	0.760(9)
Fe2 ^b	0.18873(6)	0.23571(4)	0.81487(7)	0.658(8)
Si1	0.7667(1)	0.05336(7)	0.6593(1)	0.80(1)
Si2	0.8535(1)	0.31377(7)	0.5750(1)	0.69(1)
Si3	0.6385(1)	0.44492(7)	0.7903(1)	0.63(1)
Si4	0.7260(1)	0.71363(7)	0.6906(1)	0.70(1)
Si5	0.5078(1)	0.83622(7)	0.8934(1)	0.79(1)
H1	0.786(6)	0.928(4)	0.472(7)	3.9(13)*
O1	0.7893(3)	0.9878(2)	0.4654(3)	1.28(4)
O2	0.9513(3)	0.0798(2)	0.8158(3)	1.00(3)
O3	0.7384(3)	0.1711(2)	0.5648(3)	0.97(4)
O4	0.0215(3)	0.3392(2)	0.7536(3)	0.88(3)
O5	0.0711(3)	0.6210(2)	0.6352(3)	0.94(3)
O6	0.6923(3)	0.3704(2)	0.6260(3)	0.91(3)
O7	0.4155(3)	0.3846(2)	0.8419(3)	0.93(3)
O8	0.7958(3)	0.4737(2)	0.9740(3)	0.89(3)
O9	0.6435(3)	0.5689(2)	0.6627(3)	0.81(3)
O10	0.8832(3)	0.7548(2)	0.8760(3)	0.94(3)
O11	0.2000(3)	0.2209(2)	0.5203(3)	1.01(4)
O12	0.5330(3)	0.7374(2)	0.7505(3)	0.92(3)
O13	0.2889(3)	0.7999(2)	0.9441(3)	1.10(4)
O14	0.3386(3)	0.1423(2)	0.9160(3)	1.19(4)
O15	0.5747(3)	0.9676(2)	0.7753(3)	1.09(4)

Note: * Starred atoms were refined isotropically;

^a population 0.785(4) Fe, Mn and 0.215 Mg

^b population 0.841(3) Fe and 0.159 Mg, Al

distance of 2.145 Å. The crystal Arvigo 2 with the highest Mg concentration (microprobe data) and also the highest refined population (X-ray data) of light elements on Fe2 has the longest Fe2–O distance of 2.039 Å (compared to 2.031 Å for the Westfield crystal). This is additional evidence that Mg^{2+} (ionic radius 0.72 Å) partly occupies the Fe2 site. The consequence is that there is no complete separation between ferrous and ferric iron on Fe1 and Fe2 as hitherto assumed based on Mössbauer data of Fe-rich samples. A combination of single-crystal X-ray structure refinement and electron microprobe analysis does not allow for a precise estimate of the cation distribution on the octahedral sites in babingtonite. There are several reasons: (1) Mg and Al have similar scattering factors for X-rays and their position selectivity can only ambiguously be explored; (2) Major Fe^{2+} , Fe^{3+} ordering can be evaluated based on the Fe–O distances, however, minor disorder can not be resolved; (3) Mn distribution and valence can only be assumed. The small crystal size and the limited amount of Arvigo babingtonites did not enable collection of supporting neutron diffraction and Mössbauer data. Therefore, a rough estimate (based on stoichiometry considerations and al-

Tab. 2c Atomic coordinates and B_{eq} values, with standard deviations in parentheses, for Westfield, Mass. babingtonite. Cell setting:

$a = 7.458(1)$, $b = 12.168(1)$, $c = 6.675(1)$ Å, $\alpha = 86.12(1)$, $\beta = 93.86(1)$, $\gamma = 112.27(1)^\circ$.

atom	x/a	y/b	z/c	$B_{eq}(\text{\AA}^2)$
Ca1	0.16143(8)	0.94182(5)	0.85694(8)	0.917(9)
Ca2	0.28265(8)	0.52040(5)	0.69610(8)	0.789(8)
Fe1 ^a	0.05001(6)	0.64361(3)	0.93937(6)	0.596(7)
Fe2 ^b	0.18815(5)	0.23539(3)	0.81613(6)	0.510(7)
Si1	0.7648(1)	0.05306(6)	0.6596(1)	0.61(1)
Si2	0.8528(1)	0.31327(6)	0.5749(1)	0.56(1)
Si3	0.6391(1)	0.44505(6)	0.7904(1)	0.51(1)
Si4	0.7266(1)	0.71326(6)	0.6896(1)	0.55(1)
Si5	0.5087(1)	0.83522(6)	0.8941(1)	0.58(1)
H1	0.803(7)	0.920(4)	0.487(7)	3.5(11)*
O1	0.7892(3)	0.9872(2)	0.4663(3)	1.07(3)
O2	0.9502(3)	0.0803(2)	0.8167(3)	0.74(3)
O3	0.7372(3)	0.1708(2)	0.5635(3)	0.91(3)
O4	0.0210(3)	0.3382(2)	0.7544(3)	0.70(3)
O5	0.0706(3)	0.6205(2)	0.6348(3)	0.83(3)
O6	0.6925(3)	0.3703(2)	0.6271(3)	0.73(3)
O7	0.4149(3)	0.3845(2)	0.8431(3)	0.75(3)
O8	0.7978(3)	0.4751(2)	0.9734(3)	0.77(3)
O9	0.6436(3)	0.5685(2)	0.6611(3)	0.69(3)
O10	0.8840(3)	0.7548(2)	0.8757(3)	0.72(3)
O11	0.1986(3)	0.2211(2)	0.5222(3)	0.83(3)
O12	0.5330(3)	0.7369(2)	0.7493(3)	0.73(3)
O13	0.2879(3)	0.7975(2)	0.9448(3)	0.89(3)
O14	0.3367(3)	0.1427(2)	0.9177(3)	0.82(3)
O15	0.5718(3)	0.9674(2)	0.7759(3)	0.91(3)

Note: * Starred atoms were refined isotropically;

^a population 0.838(4) Fe, Mn and 0.162 Mg

^b population 0.925(4) Fe and 0.075 Mg, Al

lowing for the ambiguities discussed above) yields the following octahedral cation distributions:

Arvigo 1; Fe1: (0.59 Fe^{2+} , 0.05 Fe^{3+} , 0.15 Mg, 0.21 Mn^{2+}); Fe2: (0.87 Fe^{3+} , 0.08 Al, 0.05 Mg).

Arvigo 2; Fe1: (0.40 Fe^{2+} , 0.13 Fe^{3+} , 0.21 Mg^{2+} , 0.26 Mn^{2+}); Fe2: (0.84 Fe^{3+} , 0.03 Al, 0.13 Mg).

Westfield; Fe1: (0.76 Fe^{2+} , 0.02 Fe^{3+} , 0.16 Mg, 0.06 Mn^{2+}); Fe2: (0.93 Fe^{3+} , 0.05 Al, 0.02 Mg).

This latter composition is within the resolution of the Mössbauer method and within the variability of a larger sample identical to the formula postulated by AMTHAUER (1980) for Westfield babingtonite.

CZANK (1981) has demonstrated that silicate-chain periodicity faults (CPF's) frequently occur in babingtonite but the two Mn-poor samples from Massachusetts showed considerably less CPF's than a Mn-rich sample from Arendal (Norway). He further concludes that the frequency of faults is controlled not only by the different chemical composition, but also by the pressure and thermal history of the crystals, and possibly by a

Tab. 3 Selected interatomic distances (Å) of babingtonites.

		Arvigo 1	Arvigo 2	Westfield			Arvigo 1	Arvigo 2	Westfield
Ca1	O1	2.271(2)	2.268	2.270	Ca2	O8	2.336(2)	2.331	2.334
	O13	2.314(2)	2.310	2.315		O5	2.338(2)	2.344	2.337
	O2	2.350(2)	2.347	2.347		O7	2.360(2)	2.349	2.357
	O14	2.344(2)	2.352	2.343		O4	2.363(2)	2.360	2.362
	O10	2.430(2)	2.421	2.429		O6	2.432(2)	2.433	2.437
	O2	2.693(2)	2.664	2.700		O9	2.551(2)	2.555	2.552
	mean	2.400	2.394	2.401		O12	2.625(2)	2.631	2.619
						O9	2.853(2)	2.845	2.856
							mean	2.482	2.481
Fe1	O13	2.047(2)	2.058	2.034	Fe2	O14	1.921(2)	1.937	1.924
	O5	2.091(2)	2.090	2.095		O7	1.968(2)	1.970	1.965
	O10	2.164(2)	2.163	2.161		O11	1.989(2)	1.997	1.991
	O8	2.182(2)	2.177	2.181		O2	2.042(2)	2.054	2.043
	O4	2.195(2)	2.200	2.192		O4	2.077(2)	2.088	2.082
	O8	2.214(2)	2.236	2.205		O10	2.184(2)	2.190	2.183
	mean	2.149	2.154	2.145		mean	2.030	2.039	2.031
Si1	O3	1.613(2)	1.606	1.609	Si2	O5	1.598(2)	1.593	1.594
	O1	1.616(2)	1.616	1.619		O3	1.620(2)	1.625	1.622
	O2	1.620(2)	1.618	1.620		O4	1.631(2)	1.628	1.631
	O15	1.629(2)	1.633	1.633		O6	1.661(2)	1.660	1.658
	mean	1.620	1.618	1.620		mean	1.628	1.627	1.626
Si3	O8	1.600(2)	1.601	1.602	Si4	O11	1.600(2)	1.596	1.601
	O7	1.600(2)	1.602	1.604		O10	1.616(2)	1.616	1.617
	O6	1.628(2)	1.630	1.624		O9	1.651(2)	1.651	1.650
	O9	1.671(2)	1.670	1.671		O12	1.652(2)	1.654	1.653
	mean	1.625	1.626	1.625		mean	1.630	1.629	1.630
Si5	O13	1.583(2)	1.581	1.587					
	O14	1.613(2)	1.621	1.611					
	O15	1.656(2)	1.646	1.655					
	O12	1.657(2)	1.656	1.657					
	mean	1.627	1.626	1.628					

difference in the cation distribution. X-ray structure refinements are not very sensitive on the concentration of CPF's but it is striking that the Arvigo 2 crystal displays the largest atomic displacement parameters of all three crystals investigated. All B_{eq} values (Tab. 2) of the Arvigo 2 crystal are ca. 20% larger than corresponding B_{eq} values of the Westfield crystal. In addition, the Arvigo 2 crystal displayed epitaxial hedenbergite whiskers (ARMBRUSTER et al., 2000) and it could well be that the transition from babingtonite to hedenbergite is not as abrupt as assumed from the change of morphology. In other words, cation ordering and CPF's may be variable between the core and the rim of the crystals that could explain the unusual cation distribution and the increased displacement parameters.

It is striking that the low temperature (< 200 °C) babingtonites from Arvigo have a low-

er degree of Fe^{2+} - Fe^{3+} ordering than the high-temperature babingtonites from skarn deposits (e.g., Westfield). This is certainly caused by the size and charge of additional Mg^{2+} and Al in the Arvigo babingtonites rather than by the influence of temperature. In babingtonite Fe1 and Fe2 octahedra have common edges (Fig. 1). Thus any size effect of one octahedron influences the adjacent one. Before the exact cation distribution has been resolved it can not be predicted how the size and charge balancing order mechanism operates.

Acknowledgement

The author thanks H.A. Stalder (Bern) for introducing him to the chemical problems in low-temperature babingtonites. The constructive reviews of S. Graeser (Basel) and G. Amthauer (Salzburg) are highly acknowledged.

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Manuscript received April 28, 2000; revision accepted August 22, 2000.