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Crystal structure of andremeyerite, $BaFe(Fe,Mn,Mg)Si_2O_7$

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ABSTRACT

The sorosilicate andremeyerite is monoclinic pseudo-orthorhombic, $a = 7.488$, $b = 13.785$, $c = 7.085$ Å, $\beta = 118.23°$, space group $P2_1/c$; it always shows multiple (100) twinning. The crystal structure was determined by Patterson and Fourier syntheses and refined by least-squares cycles with isotropic and anisotropic temperature factors. The final R values for 1430 observed reflections were 0.10 and 0.04 (0.06 for all the 1883 measured reflections), respectively, before and after the correction of the structure amplitudes for twinning. In the structure, Si_2O_7 groups bridge chains of flattened FeO_4 tetrahedra: Ba atoms fill cavities between four silicate groups. The atomic arrangement in Si_2O_7 is very near to an ideal arrangement in which the atoms are related by the symmetry *mm*2: the Si–O–Si angle is 127°, and the mean Si–O distances are 1.656 and 1.619 Å for bridging and nonbridging oxygens, respectively. Two independent Fe sites have four nearest neighbors with oxygens: mean Fe–O distances are 1.987 and 2.034 Å, respectively; the latter Fe site has a fifth neighbor at a greater distance (2.425 Å). The Ba polyhedron is a rough trigonal prism with a centered lateral face (mean Ba–O distance: 2.856 Å). The crystal-chemical formula unit of andremeyerite is $BaFe(Fe,Mn,Mg)Si_2O_7$, Z = 4.

INTRODUCTION

Andremeyerite from the Nyiragongo volcano in Zaire was first studied by Sahama et al. (1973). The mineral occurs in the vesicles of a melilite-leucite-nephelinite block carried up by later nephelinite lava. The crystals are intimately associated with a green, Fe-rich glass. Morphological, X-ray, physical, and chemical properties of andremeyerite were reported by Sahama et al. Some of these properties, which are relevant for the present paper, are as follows: the idealized chemical formula is $BaFe_2Si_2O_7$; minor amounts of K, Na, Ca, Al, Mg, and Mn were also detected by microprobe analysis. The emerald-green prismatic crystals are monoclinic pseudo-orthorhombic with unit-cell parameters $a = 7.464$, $b = 13.794$, $c = 7.093$ Å, $\beta = 118.25°$, Z = 4, space group $P2_1/c$, and the crystals show multiple (100) twinning.

EXPERIMENTAL DETAILS

The specimen of andremeyerite from Nyiragongo used in this study was obtained some years ago, thanks to the courtesy of Professor Th. G. Sahama.

Table 1 gives a summary of the X-ray and refinement data.

The resolution of the crystal structure was straightforward after the Ba coordinates were obtained from a preliminary Patterson synthesis. The positional parameters of the remaining atoms were identified in a Fourier synthesis, which was computed with the phases given by the

TABLE 1. X-ray crystal and refinement data

X-ray single-crystal diffractometer: Philips PW 1100
Radiation: Mo$K\alpha$ monochromatized on graphite
Formula unit: $BaFe(Fe_{0.85}Mn_{0.08}Mg_{0.07})Si_2O_7$

Unit-cell dimensions

	Monoclinic	Pseudo-orthorhombic*
a (Å)	7.488(1)	13.195(2)
b (Å)	13.785(1)	13.785(1)
c (Å)	7.085(1)	7.085(1)
β (°)	118.23(1)	89.99(1)
Volume (Å^3)	644.3	1288.7
Space group	$P2_1/c$	*Bmcb*
Z	4	8

Crystal dimensions (mm):	0.18 × 0.16 × 0.11
Scan: mode ω, width 1.8°, speed 0.06°/s	
θ range (°):	2–30
Mean variation in three standard reflections	1.7%
Measured reflections ($\pm h$, $\pm k$, l)	3771
Unique reflections ($\pm h$, k, l)	1883
R (sym) = $\Sigma\lvert I(hkl) - I(h\bar{k}l)\rvert / \Sigma\lvert I(hkl) + I(h\bar{k}l)\rvert$	0.033
Observed reflections ($I/\sigma(I) \geq 6$)	1430
Absorption correction after North et al. (1968)	
R (obs) before correction for twinning	0.10
R (obs) after correction for twinning	0.039
R (all)	0.060
Ratio between volumes of the twin individuals	3:2

* Transformation matrix: 201 / 010 / 001.

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TABLE 2. Site occupancies, atomic coordinates (×10⁴), equivalent isotropic temperature factors, and deviations (Δ*d*) from the mean "orthorhombic" positions

Atom	Site population		*x*	*y*	*z*	B_{eq}	Δ*d* (Å)
Ba	Ba 1.00		4893(1)	1434(0)	2940(1)	0.96(1)	0.071
Fe1	Fe 1.00		−24(2)	2439(1)	3058(2)	0.78(3)	0.086
Fe2	Fe 0.92	Mg 0.08*	−380(2)	5016(1)	2115(2)	0.86(4)	0.140
SiA			2765(3)	3908(2)	2023(4)	0.75(6)	0.146
SiB			7241(3)	3833(2)	3877(4)	0.65(6)	
O1A			2262(9)	5001(5)	1055(9)	1.04(16)	0.349
O1B			7251(10)	4833(5)	2737(11)	1.39(19)	
O2A			2573(9)	3118(5)	249(10)	1.17(17)	0.162
O2B			7270(9)	2903(5)	2481(11)	1.34(19)	
O3A			1229(9)	3714(4)	3016(11)	1.21(18)	0.258
O3B			9090(9)	3763(5)	6290(10)	1.24(17)	
O4			5104(8)	3784(4)	4021(9)	0.76(15)	0.068

Note: Numbers in parentheses are esd's referred to the last digit. Standard deviations in occupancies: 0.01 for Ba, and 0.02 for Fe sites. Atom pairs related by the orthorhombic pseudosymmetry have the same label plus an extra "A" and "B", respectively: their coordinates are roughly *x y z* and −*x y* (*z* − *x* + 0.5). In the pseudo-orthorhombic description, four atoms lie in special positions, i.e., Ba and O4 (point symmetry *m*), Fe1 and Fe2 (point symmetry 2).

* The site population in Fe2, corresponding to 24.9 electrons, could also be due to 0.07 Mg, 0.08 Mn, and 0.85 Fe, a composition that is more coherent with microprobe analysis.

Ba coordinates. Scattering factors for ionized Ba, K, Fe, and Mg were used for the calculation of the structure amplitudes and for the successive refinements; mixed scattering factors (Si/Si^{4+} and O/O^{2-}) were assumed for the silicate group in the fixed ratio 1:1. Cycles of least-squares refinements, using isotropic and then anisotropic temperature factors, and, furthermore, varying the occupancy of Ba against K and that of Fe against Mg, converged to a high *R* (0.10) for the observed reflections, because of the presence of the multiple (100) twinning.

This type of multiple twin is formed by individuals in two orientations: *hkl* reflections from one individual are perfectly superposed on −(*h* + *l*)*kl* reflections from the other, because of the virtually orthorhombic geometric properties of the andremeyerite lattice (Table 1). The presence of twinning was confirmed by comparison between observed and calculated structure factors for the *hkl* and −(*h* + *l*)*kl* reflection pairs, which had notably differing structure amplitudes: in each pair, the $F_{obs} - F_{calc}$ differences were systematically negative for the most in-

TABLE 3. Anisotropic temperature parameters (×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	61(1)	11(0)	67(1)	−2(0)	31(1)	−2(0)
Fe1	33(3)	10(1)	56(3)	1(1)	14(2)	0(1)
Fe2	40(3)	10(1)	65(3)	−2(1)	19(2)	−3(1)
SiA	30(4)	10(1)	52(5)	2(2)	12(4)	3(2)
SiB	32(4)	8(1)	46(5)	1(2)	16(4)	2(2)
O1A	49(12)	13(3)	56(13)	4(5)	6(10)	7(5)
O1B	72(14)	14(3)	132(17)	7(5)	58(13)	13(6)
O2A	37(12)	19(3)	74(14)	−6(5)	12(11)	−22(6)
O2B	49(12)	13(3)	143(18)	−3(5)	46(12)	−17(6)
O3A	63(12)	10(3)	136(17)	−2(5)	64(12)	6(6)
O3B	49(12)	13(3)	91(15)	−5(5)	10(11)	2(5)
O4	44(11)	14(3)	17(11)	−3(4)	7(9)	0(5)

Note: The anisotropic temperature parameters are defined by exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. Numbers in parentheses are esd's referred to the last digit.

TABLE 4. Bond distances (Å) and angles (°)

SiA–O1A	1.625(7)	SiB–O1B	1.600(7)
–O2A	1.618(6)	–O2B	1.626(7)
–O3A	1.630(6)	–O3B	1.615(7)
–O4	1.659(6)	–O4	1.653(6)
Mean	1.633	Mean	1.623
TQE	1.0042	TQE	1.0012
O1A–SiA–O2A	112.3(3)	O1B–SiB–O2B	111.6(4)
–O3A	105.3(3)	–O3B	112.3(4)
–O4	113.3(3)	–O4	107.6(3)
O2A–SiA–O3A	113.8(3)	O2B–SiB–O3B	110.2(4)
–O4	105.3(3)	–O4	107.3(3)
O3A–SiA–O4	106.9(3)	O3B–SiB–O4	107.6(3)
SiA–O4–SiB	127.2(4)		
Fe1–O2A*iv*	1.981(6)	Fe2–O1A*ii*	2.009(6)
–O2B*i*	1.975(6)	–O1B*i*	2.036(6)
–O3A	2.000(6)	–O3A	2.086(6)
–O3B*vi*	1.992(6)	–O3B*iii*	2.003(6)
Mean	1.987	–O1A	2.425(6)
TQE	1.199	Mean	2.112
		Mean*	2.034
		TQE	1.040
O2A*iv*–Fe1–O2B*i*	144.9(3)	O1A*ii*–Fe2–O1B*i*	91.0(3)
–O3A	93.3(3)	–O3A	109.3(3)
–O3B*vi*	94.7(3)	–O3B*iii*	122.5(3)
O2B*i*–Fe1–O3A	98.9(3)	O1B*i*–Fe2–O3A	105.3(2)
–O3B*vi*	97.8(3)	–O3B*iii*	102.6(3)
O3A–Fe1–O3B*vi*	137.8(3)	O3A–Fe2–O3B*iii*	119.7(3)
		O1A–Fe2–O1A*ii*	84.1(2)
		–O1B*i*	171.1(3)
		–O3A	69.5(2)
		–O3B*iii*	86.3(2)
Ba–O1A*vii*	2.741(6)	Code of equivalent sites	
–O1B*vii*	2.636(6)	*i*:	*x* − 1, *y*, *z*
–O2A	2.984(7)	*ii*:	−*x*, 1 − *y*, −*z*
–O2A*iv*	2.960(6)	*iii*:	1 − *x*, 1 − *y*, 1 − *z*
–O2B	2.814(6)	*iv*:	*x*, 0.5 − *y*, 0.5 + *z*
–O2B*iv*	2.990(6)	*v*:	*x*, 0.5 − *y*, *z* − 0.5
–O4*v*	2.870(6)	*vi*:	*x* − 1, 0.5 − *y*, *z* − 0.5
–O3A*v*	3.269(7)	*vii*:	1 − *x*, *y* − 0.5, 0.5 − *z*
–O4	3.315(6)		
Mean	2.953		
Mean**	2.856		

Note: Numbers in parentheses are esd's referred to the last digit. TQE = tetrahedral quadratic elongation after Robinson et al. (1971).

* Mean of the four shortest distances.

** Mean of the distances shorter than 3 Å.

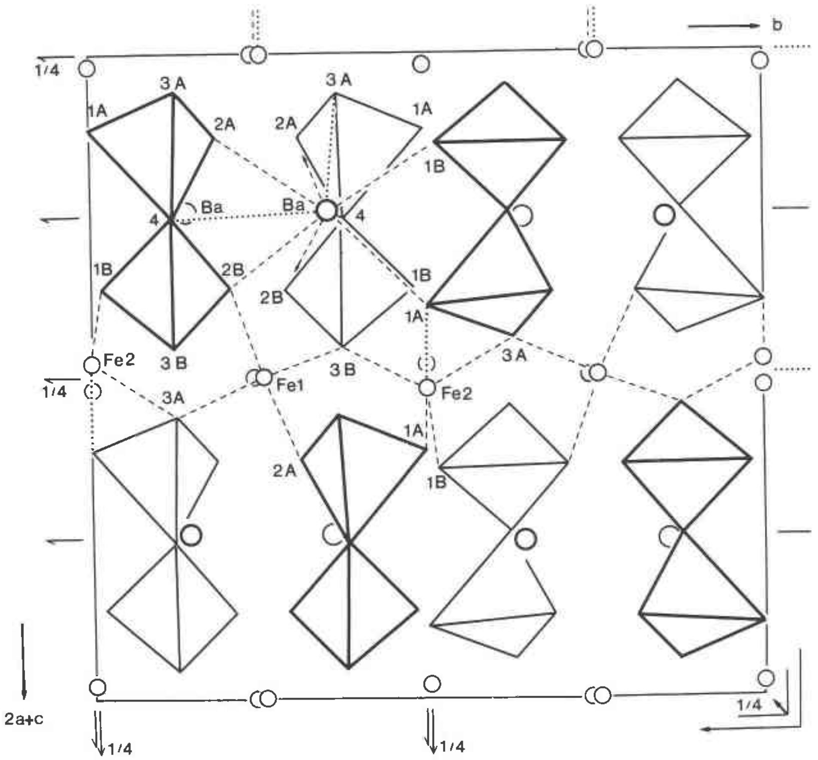

Fig. 1. Crystal structure of andremeyerite in the "orthorhombic" unit cell as seen along [001]. Dotted lines represent the greatest Ba–O and Fe2–O bond distances.

tense reflection and positive for the less intense reflection, just as would have happened in a twin of two individuals with differing sizes.

The structure amplitudes were accordingly corrected by using the following equations, in which $H = -(h + l)$, $A = F_{\mathrm{obs}}(hkl)$, $B = F_{\mathrm{obs}}(Hkl)$, and x is the fraction of one twin individual:

$$F^2(hkl) = [x(A^2 + B^2) - B^2]/(2x - 1)$$
$$F^2(Hkl) = [x(A^2 + B^2) - A^2]/(2x - 1).$$

The x fraction was obtained by carrying out several refinements with structure factors that had been corrected according to different x values and by assuming as real the x fraction used in the refinement that converged to the lowest R factor. The best result ($R = 0.039$ for the observed reflections) was obtained with $x = 0.6$ (actually $x = 0.595$); it corresponds to a ratio 3:2 between the twin individuals.

Tables 2 and 3 give positional and thermal parameters at the end of the refinement; bond distances and angles are in Table 4; observed and calculated structure factors are compared in Table 5.[1]

Description and discussion of the crystal structure

All atomic positions are related by a pseudosymmetry in the space group *Bmcb*, as is clearly shown by the [001] projection of the crystal structure (Fig. 1). Apart from the real monoclinic symmetry elements (i.e., the (010) *c* glide planes and the [010] screw axes, which separately relate the A and B sites of Si, O1, O2, and O3 atoms), Figure 1 shows the additional pseudo-elements of symmetry that relate A sites to B sites—in particular, the (100) mirror plane on which the Ba and O4 atoms lie and the two sets of diad axes, one parallel to **c** through the Fe1 sites and the other parallel to [201] (orthorhombic **a**) through the Fe2 sites. An indication of the departure from this pseudosymmetry in the real structure is given in the last column of Table 2.

In the crystal structure of andremeyerite, Si_2O_7 groups are held together by Fe and Ba cations; each of these is connected to the oxygens of four differing silicate radicals.

The atomic arrangement in Si_2O_7 is very near to an ideal arrangement in which the atoms of the paired tetrahedra are related by *mm*2 symmetry: accordingly, the bridging O4 oxygen and both the SiA–SiB and the O3A–O3B atoms lie approximately (±0.05 Å) on one of the mirror planes; the diad axis coincides with the bisectrix of the SiA–O4–SiB angle, and the second mirror plane relates the atoms of the two tetrahedra forming the Si_2O_7

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[1] A copy of Table 5 may be ordered as Document AM-88-372 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 6. Chemical composition of andremeyerite

	A	B		C	D	E	F
SiO_2	32.46	54.9	Si	2.08	2.60	2.00	2.00
Al_2O_3	1.00	3.9	Al	0.08	0.22	0.05	
FeO	31.55	23.2	Fe	1.69	0.91	1.82	1.85
MnO	1.33	0.6	Mn	0.07	0.02	0.08	0.08
MgO	0.75	0.4	Mg	0.07	0.03	0.08	0.07
TiO_2		1.1	Ti		0.04		
				1.91		2.03	2.00
CaO	0.52	3.5	Ca	0.04	0.18	0.02	
BaO	32.55	2.3	Ba	0.82	0.04	0.95	1.00
Na_2O	0.10	0.8	Na	0.01	0.07		
K_2O	0.65	7.8	K	0.05	0.47		
	100.91	98.5		0.92		0.97	1.00
			O	7.00	7.00	7.00	7.00

Note: Columns are A, chemical analysis of andremeyerite (Sahama et al., 1973); B, chemical analysis of glass (Sahama et al., 1973); C, andremeyerite—chemical composition based on 7 oxygens; D, glass—chemical composition based on 7 oxygens; E, andremeyerite—chemical composition after subtraction of glass (14%); F, andremeyerite—chemical composition from the refinement of the site occupancies (Table 2).

radical. These three symmetry elements are roughly parallel to (010), [001], and (100), respectively (Fig. 1). An examination of the crystal structures of different sorosilicates, reported in the literature, shows similar features for the Si_2O_7 groups in all cases. The most important differences are in the amplitudes of the Si–O–Si angle, which can range from nearly 124° to over 170°, and in the ratio between the mean Si–O distances that involve, respectively, the bridging oxygen and the nonbridging ones (from over 1.03 to 1). In general, these two quantities are inversely related. In andremeyerite, the SiA–O4–SiB angle is among the lowest (127°), the mean Si–O distances are 1.656 Å (with the O4 bridging oxygen) and 1.619 (with the remaining oxygens), and their ratio is 1.023.

The Fe atoms lie in two independent sites whose coordinations with oxygens from the Si_2O_7 groups show some differences. Fe1 is bonded to four oxygens, which are arranged at the vertices of a markedly flattened tetrahedron; the tetrahedral quadratic elongation (after Robinson et al., 1971) is 1.20 (Table 4). This polyhedron, similar to that present in pellyite, $Ba_2Ca(Fe,Mg)_2Si_6O_{17}$ (Meagher, 1976), may be considered as intermediate between a real tetrahedron and a square; in staurolite, $Al_{18}(Fe,Mg)Si_8O_{46}(OH)_2$ (Smith, 1968), the FeO_4 polyhedron is very near to a tetrahedron, whereas, for instance, Fe has a square coordination in gillespite, $BaFeSi_4O_{10}$ (Pabst, 1943), and eudialyte, $(Fe,Mn,Mg)_3Zr_{>3}(Ca,REE)_6Na_{12}[Si_9(O,OH)_{27}]_2[Si_3O_9]_2Cl_{\sim 1}$ (Giuseppetti et al., 1971).

If one neglects the fifth greatest bond distance (2.45 Å against 2.04, the mean of the four shortest distances), Fe2 shows a tetrahedral coordination as well, which is even more regular than that around Fe1 (tetrahedral quadratic elongation = 1.04); however, when also considering the fifth bond, the Fe2 polyhedron becomes a distorted trigonal dipyramid. This coordination is very similar to that found in phenaxite, $FeNaKSi_4O_{10}$ (Golovacev et al., 1970). According to the results of crystallographic refinement, some Mg (or, more probably, Mg plus Mn) replaces Fe in site Fe2 (Table 2), whereas only Fe is present in Fe1.

Alternate Fe1 and Fe2 polyhedra connected by O3A and O3B vertices form sets of chains running along [010]. Each Si_2O_7 group bridges four of these chains and shares all its oxygens but O4. In this way, a three-dimensional tetrahedral framework is formed, and Ba occupies its cavities between four Si_2O_7 groups (Fig. 1).

The Ba polyhedron approximates a trigonal prism with a centered lateral face. If one also considers the two greatest distances (Table 4), two other faces (lateral and basal, respectively) are also centered.

The electrostatic charge balance (after Donnay and Allmann, 1970) can be considered as satisfactory. The sums of the bond strengths on the oxygens range from 1.94 to 2.02, and only in the case of the bridging oxygen O4 does it rise to 2.18.

The crystal structure of andremeyerite resembles to some extent that of barylite, $BaBe_2Si_2O_7$ (Cannillo et al., 1970; Robinson and Fang, 1977). For instance, the scheme of the connections between the chains of Be tetrahedra and the Si_2O_7 groups is analogous to that between the chains of Fe tetrahedra and silicate radicals in andremeyerite; however, because of a different topological arrangement of its atoms, the space group and the cell dimensions of barylite are not comparable with those of andremeyerite.

A recalculation of the chemical composition of andremeyerite from the microprobe analysis by Sahama et al. (1973) is reported in Table 6. The chemical composition given in that paper shows an excess of Si, which the authors explained by the presence of glass "trapped in the andremeyerite structure during the crystallization process." As the same authors also reported a chemical analysis of this glass, it has been possible to recalculate the composition of the andremeyerite by subtracting 14% of glass. The result is coherent with the X-ray results and the real Si content.

The crystal-chemical formula of andremeyerite is therefore $BaFe(Fe,Mn,Mg)Si_2O_7$.

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