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REFINEMENT OF THE CRYSTAL STRUCTURE OF KULANITE

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ABSTRACT

The crystal structure of kulanite, $Ba(Fe^{2+}_{1.19}Mg_{0.61}Mn^{2+}_{0.08})(Al_{1.87}Fe^{3+}_{0.13})(PO_4)_3(OH)_3$, monoclinic $P2_1/m$, a 9.014(1), b 12.074(1), c 4.926(1) Å, β 100.48(1)°, V 527.1(1) Å^3, $Z = 2$, has been refined to an R index of 2.1% for 1584 observed (5σ) reflections measured with Mo$K\alpha$ X-radiation. Kulanite is isostructural with bjarebyite, ideally $BaMn^{2+}_2Al_2(PO_4)_3(OH)_3$. The hydrogen positions were located and refined at the final stages of the refinement. The H(1) atom is disordered off its ideal position on the mirror plane, and has a weak hydrogen-bond to a [3]-coordinated O^{2-} anion. The H(2) atom occupies the general position, and is strongly hydrogen-bonded to a [2]-coordinated O^{2-} anion. Both hydrogen bonds promote cross-linkage of the prominent chains of octahedra in this structure type.

Keywords: kulanite, crystal-structure refinement, phosphate, hydrogen bond.

SOMMAIRE

La structure cristalline de la kulanite, $Ba(Fe^{2+}_{1.19}Mg_{0.61}Mn^{2+}_{0.08})(Al_{1.87}Fe^{3+}_{0.13})(PO_4)_3(OH)_3$, monoclinique $P2_1/m$, a 9.014(1), b 12.074(1), c 4.926(1) Å, β 100.48(1)°, V 527.1(1) Å^3, $Z = 2$, a été affinée jusqu'à un résidu R de 2.1%; nous avons utilisé 1584 réflexions observées (5σ), mesurées avec rayonnement Mo$K\alpha$. La kulanite possède la même structure que la bjarebyite, dont la composition idéale est $BaMn^{2+}_2Al_2(PO_4)_3(OH)_3$. La position des atomes d'hydrogène a été déterminée et affinée au dernier stade de l'ébauche de la structure. L'atome H(1) est déplacé de sa position idéale sur le plan mirroir, et montre une faible liaison hydrogène envers un anion O^{2-} à coordinence [3]. L'atome H(2) occupe une position générale, et se trouve fortement impliqué dans une liaison hydrogène avec un anion O^{2-} à coordinence [2]. Les deux liaisons hydrogène renforcissent l'articulation perpendiculaire aux chaînes d'octaèdres, élément important de ce type de structure.

(Traduit par la Rédaction)

Mots-clés: kulanite, affinement de la structure cristalline, phosphate, liaison hydrogène.

INTRODUCTION

The minerals of the bjarebyite group have the general formula $XY_2Z_2(PO_4)_3(OH)_3$ with X = Ba; Y = Mg, Fe^{2+}, Mn^{2+}, and Z = Al, Fe^{3+}. The following species are currently known: penikisite (Mandarino *et al.* 1977), ideally $BaMg_2Al_2(PO_4)_3(OH)_3$, kulanite (Mandarino & Sturman 1976), ideally $BaFe^{2+}_2Al_2(PO_4)_3(OH)_3$, and bjarebyite (Moore *et al.* 1973), ideally $BaMn^{2+}_2Al_2(PO_4)_3(OH)_3$. Penikisite and kulanite are found at the Yukon phosphate locality near Rapid Creek, occurring in fractures in a sideritic iron-formation (Robertson 1982, Robinson *et al.* 1992); the temperature of crystallization has been estimated as less than 200°C. Bjarebyite occurs in the Palermo No. 1 pegmatite, North Groton, New Hampshire (Moore *et al.* 1973); Moore & Araki (1974) solved the crystal structure of bjarebyite, showing it to have an intriguing atomic arrangement with an unusual hydrogen-bond.

EXPERIMENTAL

X-ray data collection

The crystal used in this work was removed from the cotype specimen of rapidcreekite (Roberts *et al.* 1986) during an exhaustive but unsuccessful attempt to find a crystal of this latter species adequate for single-crystal work. The kulanite crystal was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Cell dimensions (Table 1) and diffraction-intensity data were collected according to the experimental procedure of Hawthorne & Groat (1985). Both kulanite and penikisite are listed as being triclinic in their original descriptions, whereas bjarebyite was reported as

TABLE 1. MISCELLANEOUS DATA COLLECTION AND STRUCTURE REFINEMENT INFORMATION: KULANITE

a(Å)	9.014(1)
b	12.074(1)
c	4.926(1)
β(°)	100.48(1)
V(Å^3)	527.1(1)
Z	2
Space group	$P2_1/m$
Crystal size (mm)	0.20 x 0.20 x 0.32
Rad/mono	MoKα/Graphite
Total |I|	3419
R(azimuthal)	7.9 → 2.3%
R(sym)	2.2%
Total $\|F_o\|$	1611
$\|F_o\| > 5\sigma$	1584
Final R(obs)	2.1%
Final R_w(obs)	2.1%
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	
$wR = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$, w=1	

TABLE 2. ELECTRON-MICROPROBE DATA* AND UNIT FORMULA+ OF KULANITE

P_2O_5	33.80	P	3.016
Al_2O_3	15.06		
Fe_2O_3	1.61	Al	1.871
FeO	13.47	Fe^{3+}	0.129
MnO	0.95		2.000
MgO	3.89		
CaO	0.42	Fe^{2+}	1.187
BaO	24.99	Mn^{2+}	0.085
H_2O	(4.27)	Mg	0.611
Total	98.46	Ca	0.047
			1.930
		Ba	1.032

* mean of 10 analyses;
+ calculated on the basis of 15 oxygens assuming 3 OH pfu and Al + Fe^{3+} = 2 apfu.

being monoclinic. The cell obtained for kulanite was initially refined as triclinic, but the deviations from a metrically monoclinic cell (0.006 and 0.010° for α and γ, respectively) were found not to be significant; this result was confirmed by centering on a set of high-angle reflections. Intensity data were collected for $\pm h$, k, $\pm l$ (*i.e.*, one asymmetric unit in the Laue group $\bar{1}$, and two asymmetric units in $2/m$). A psi-scan absorption correction reduced the R(azimuthal) index from 7.9 to 2.3%, and the merging R index for the Laue group $2/m$ was found to be 2.2%. There were two observed reflections apparently violating the extinction criterion for the 2_1 screw axis, but psi-scans

TABLE 3. FINAL REFINED PARAMETERS AND ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS FOR KULANITE

Site	x	y	z	$^+U_{eq}$	$^*U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
X	0.54695(3)	3/4	0.74102(5)	0.82(1)	81(1)	90(1)	75(1)	0	11(1)	0
M(1)	0.29518(6)	-0.11021(5)	0.2092(1)	0.78(2)	78(3)	74(3)	80(3)	1(2)	6(2)	-6(2)
M(2)	0.0914(1)	0.40046(8)	0.1287(2)	0.61(3)	62(4)	63(4)	56(4)	-4(3)	4(3)	0(3)
P(1)	0.1559(1)	3/4	0.6860(2)	0.62(3)	66(4)	63(5)	53(4)	0	7(4)	0
P(2)	0.33261(8)	0.44177(7)	0.7046(2)	0.64(2)	67(3)	66(3)	56(3)	4(3)	6(2)	6(3)
O(1)	0.2781(4)	3/4	0.9471(7)	0.94(8)	89(14)	125(15)	61(14)	0	-7(11)	0
O(2)	0.2313(4)	3/4	0.4325(7)	0.90(8)	109(14)	98(14)	66(14)	0	26(11)	0
O(3)	0.0595(3)	0.6453(2)	0.6865(5)	0.96(6)	107(10)	88(10)	98(10)	-37(8)	30(8)	-13(8)
O(4)	0.3679(3)	0.5565(2)	0.6099(5)	1.04(6)	132(10)	82(10)	98(10)	-10(8)	21(8)	24(8)
O(5)	0.2581(3)	0.4521(2)	0.9668(5)	1.03(6)	116(10)	141(11)	59(9)	-9(8)	34(8)	-9(8)
O(6)	0.2266(3)	0.3810(2)	0.4700(5)	1.15(6)	132(10)	115(10)	82(10)	-8(9)	-26(8)	11(8)
O(7)	0.4737(2)	0.3700(2)	0.7881(5)	1.09(6)	80(9)	115(11)	129(10)	38(9)	12(8)	28(8)
O(8)	0.1236(4)	1/4	0.0067(7)	0.98(9)	125(15)	114(15)	49(13)	0	1(11)	0
O(9)	0.0593(3)	0.5572(2)	0.1907(5)	0.93(6)	111(10)	102(10)	63(9)	-7(8)	6(7)	-31(8)
H(1)	0.117(8)	0.228(7)	-0.186(5)	1.0**						
H(2)	0.034(5)	0.599(3)	0.346(6)	1.0**						

$^+U_{eq} = U_{eq} \times 10^2$; $^*U_{ij} = U_{ij} \times 10^4$; ** fixed

showed that these are due to double diffraction. Thus there was no diffraction evidence for triclinic symmetry, and the space group $P2_1/m$ was adopted, following the work of Moore & Araki (1974).

Subsequent to the crystallographic work, the crystal used in the collection of the intensity data was analyzed by electron microprobe (Cameca SX–50) in the wavelength-dispersion mode. The unit formula was calculated assuming that all Fe at the *Z* site is trivalent, and Fe at the *Y* site is divalent (Table 2).

Crystal-structure refinement

The SHELXTL PC Plus system of programs was used for the computational aspects of this work. Using the structural parameters of Moore & Araki (1974) as a starting model, full-matrix least-squares refinement of all parameters converged to an *R* index of 4.2% for an isotropic displacement model. A difference-Fourier map was calculated at this stage and revealed the two hydrogen positions. Inclusion of these positions in the refinement, together with conversion to an anisotropic displacement model, resulted in convergence at an *R* index of 2.1%. We released the constraint that H(1) lie on the mirror plane, and the H(1) atom moved off the mirror plane. Although there was no reduction in *R* index, the physical aspects of this model are more persuasive, and this disordered model was adopted. Final positional and equivalent isotropic displacement parameters are given in Table 3, selected interatomic distances and angles are listed in Table 4, and the refined site-scattering values and assigned site-populations are given in Table 5. Observed and calculated structure-factors and anisotropic displacement coefficients may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 5. SITE SCATTERING* AND ASSIGNED SITE POPULATIONS**

	Site scattering (epfu)		Site populations (apfu)
	SREF	EMPA	
M(1)	26.8(2)	27.7	1.871 Al + 0.129 Fe^{3+}
M(2)	41.8(4)	42.8	1.187 Fe^{2+} + 0.085 Mn^{2+} + 0.611 Mg

* in epfu (electrons per formula unit)
** in apfu (atoms per formula unit)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN KULANITE

M1-O(1)c	2.114(2)	X-O(1)	2.793(4)	
M1-O(2)b	2.150(2)	X-O(2)	2.872(3)	
M1-O(4)d	2.068(2)	X-O(4),f	2.846(2)	x2
M1-O(5)e	2.245(2)	X-O(6)i,l	2.919(3)	x2
M1-O(7)k	2.095(2)	X-O(7)j,m	2.770(2)	x2
M1-O(9)d	2.206(2)	X-O(7)i,l	2.958(2)	x2
<M1-O>	2.146	X-O(8)l	3.003(3)	
		<X-O>	2.887	
M2-O(3)h	1.863(3)	P1-O(1)	1.533(3)	
M2-O(5)a	1.928(3)	P1-O(2)	1.526(4)	
M2-O(6)	1.903(2)	P1-O(3),f	1.534(2)	x2
M2-O(8)	1.951(2)	<P1-O>	1.532	
M2-O(9)	1.947(3)			
M2-O(9)g	1.950(2)	P2-O(4)	1.514(3)	
<M2-O>	1.922	P2-O(5)	1.566(3)	
		P2-O(6)	1.544(2)	
		P2-O(7)	1.532(2)	
		<P2-O>	1.539	

a: x,y,z-1; b: x,y-1,z; c: x,y-½,z-1; d: x,ȳ + ½,z; e: x,ȳ + ½,z-1; f: x,ȳ+3/2,z; g: x̄,ȳ+1,z̄; h: x̄,ȳ+1,z̄+1; i: x̄+1,y+½,z+1; j: x̄+1,y+½,z+2; k: x̄+1, y-½,z+1; l: x̄+1,ȳ+1, z̄+1; m: x̄+1,ȳ+1,z̄+2

DISCUSSION

This work confirms the isostructural relation between kulanite and bjarebyite, and the structural details of kulanite are all in accord with the structure of bjarebyite reported by Moore & Araki (1974).

Hydrogen bonding

Moore & Araki (1974) assigned the O(8) and O(9) anions as OH groups, and the H atoms located in the current study are in accord with this model. The observed O–H distances, 0.82(4) Å, are somewhat shorter than the ideal value of ~1.0 Å, but this is a common feature of X-ray-determined H positions, as the X-ray density is somewhat polarized along the O–H bond and does not correspond to the position of the nucleus.

In its ideal position, the H(1) atom lies on a mirror plane and is 2.69(4) Å from the O(6) anion. This value of 2.69 Å is actually longer than the true distance because of the apparent shortening of the O–H bond discussed above; allowing for this produces an H(1)–O(6) distance of ~2.5 Å. This is a long distance for a hydrogen bond to the O(6) anion. In addition, if H(1) were on the mirror plane, it would have two O(6) neighbors, forming a *bifurcated* hydrogen-bond to two O(6) anions, and further weakening the possible H(1)...O(6) interaction. With H(1) disordered off the mirror plane, the H(1)...O(6) distance is 2.49 Å, indicating a stronger H(1)...O(6) hydrogen-bond than is possible when H(1) occupies an ordered position on the mirror plane.

The H(2) atom lies 1.90(4) Å from the O(3) anion, and the O(9)–H(2)...O(3) angle is 154(4)°; both of these values are typical for moderately strong hydrogen-bonds, and the bond-valence sum at the O(3) anion (Table 6) is in accord with this assignment. A view of the assigned hydrogen-bond scheme is shown in Figure 1. In this structure type, chains of

TABLE 6. BOND-VALENCE ARRANGEMENTS IN KULANITE AND BJAREBYITE

KULANITE								
	X	M(1)	M(2)	P(1)	P(2)	H(1)	H(2)	Σ
O(1)	0.254	$0.352^{\times 2}\rightarrow$		1.273				2.231
O(2)	0.165	$0.322^{\times 2}\rightarrow$		1.298				2.107
O(3)			0.584	$1.270^{\times 2}\downarrow$			0.20	2.054
O(4)	$0.223^{\times 2}\downarrow$	0.396			1.342			1.971
O(5)		0.254	0.478		1.162			1.894
O(6)	$0.187^{\times 2}\downarrow$		0.511		1.235	$^{+}0.05^{\times 2}\downarrow$		1.983
O(7)	$0.270^{\times 2}\downarrow$	0.370			1.277			2.087
	$0.170^{\times 2}\downarrow$							
O(8)	0.153		$0.450^{\times 2}\rightarrow$			0.90		1.953
O(9)		0.270	0.455				0.80	1.977
			0.452					
Σ	2.272	1.964	2.930	5.111	5.016	1.00	1.00	
BJAREBYITE								
	X	M(1)	M(2)	P(1)	P(2)	H(1)	H(2)	Σ
O(1)	0.294	$0.368^{\times 2}\rightarrow$		1.295				2.325
O(2)	0.160	$0.327^{\times 2}\rightarrow$		1.350				2.164
O(3)			0.615	$1.291^{\times 2}\downarrow$			0.20	2.106
O(4)	$0.226^{\times 2}\downarrow$	0.384			1.361			1.971
O(5)		0.268	0.510		1.191			1.969
O(6)	$0.193^{\times 2}\downarrow$		0.526		1.245	$^{+}0.05^{\times 2}\downarrow$		2.014
O(7)	$0.279^{\times 2}\downarrow$	0.403			1.346			2.204
	$0.176^{\times 2}\downarrow$							
O(8)	0.168		$0.452^{\times 2}\rightarrow$			0.90		1.962
O(9)		0.294	0.454				0.80	2.022
			0.474					
Σ	2.355	2.044	3.031	5.027	5.143	1.00	1.00	

* bond-valences in v.u., calculated with the curves of Brown (1981);
+ H(1) is disordered off the ideal position on the mirror plane, forming one hydrogen bond of ~0.10 v.u. instead of two hydrogen bonds of ~0.05 v.u. as it would if it occupied the position on the mirror plane.

edge- and corner-sharing octahedra of the form $[Al_2\phi_9]$ (ϕ = unspecified ligand) extend along the *Y* axis (see Moore & Araki 1974, Fig. 1) and are cross-linked through $\{(Fe^{2+}, Mn^{2+}, Mg)\phi_6\}$ octahedra, $Ba\phi$ polyhedra and (PO_4) tetrahedra. The hydrogen bonds (Fig. 1) provide further cross-linking of these chains, particularly in the *Z* direction. This view shows the weak bifurcated hydrogen-bond formed by H(1) and the O(6) anions, and the stronger hydrogen-bond between H(2) and O(3).

Bond-valence arrangement

Table 6 shows the bond-valence arrangements in both kulanite and bjarebyite, calculated with the parameters of Brown (1981); note that the hydrogen-bonding scheme proposed above works well, with satisfactory bond-valence sums around both the donor and acceptor anions. There are some fairly large deviations from ideality at the *X*(1) cation and at the O(1) anion. However, these are present in *both* structural arrangements, indicating that these deviations are a character of the structural arrangement, rather than an indication of a problem with the structural data. The reason for the two hydrogen-bonds of different strengths is readily apparent in Table 6: O(3) is coordinated by only two cations (apart from hydrogen) and requires a relatively strong hydrogen-bond, whereas O(6) is coordinated by three cations and requires only a weak hydrogen-bond to satisfy its requirements.

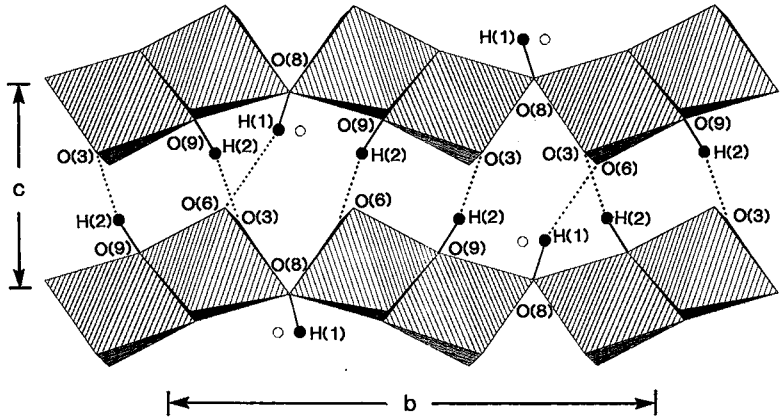

FIG. 1. Part of the structure of kulanite projected down [100]; hydrogen bonds are shown as dotted lines, and hydrogen atoms as full circles, the octahedra are line-shaded. The H(1) atoms are disordered, and the alternate positions are shown by hollow circles.

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