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KULANITE, A NEW BARIUM IRON ALUMINUM PHOSPHATE FROM THE YUKON TERRITORY, CANADA

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ABSTRACT

Kulanite occurs as blue to green plates and rosette-like aggregates in a sideritic iron-formation in the Big Fish River-Blow River area in the northeastern part of the Yukon Territory. The mineral is triclinic (pseudo-monoclinic) with space group $P\bar{1}$, a 9.032, b 12.119, c 4.936Å, $\alpha \sim 90°$, $\beta = 100°23'$, $\gamma \sim 90°$, $Z = 2$. The plates are tabular parallel to $\{\bar{1}01\}$. Hardness is 4. The mineral has two fair to good cleavages parallel to {010} and {100}. The density is 3.91 ± 0.03 g/cm³ (meas) and 3.92 g/cm³ (calc). Kulanite is biaxial (+), $\alpha = 1.703$, $\beta = 1.705$, $\gamma = 1.723$, $2V$(meas) = 32°, $2V$(calc) = 38°; the unsymmetrical dispersion is very strong $r \gg v$; pleochroism α brownish green, β green, γ very pale brown; orientation, $b \backsimeq \beta$, $c \wedge \gamma = -8°$. Chemical analysis gave the formula:

$Ba_{1.00}\,(Fe^{2+}{}_{0.94}Mn^{2+}{}_{0.57}Mg_{0.49}Ca_{0.09})_{\Sigma=2.09}\,(Al_{1.81}Fe^{3+}{}_{0.17})_{\Sigma=1.98}\,(PO_4)_{3.02}\,(OH)_{2.74}$, or $Ba(Fe,Mn,Mg,Ca)_2(Al,Fe)_2(PO_4)_3(OH)_3$. Strongest spacings in the X-ray powder pattern are: 8.84(6)(100), 3.108(10)(031,$\bar{2}21$), 3.044(7)($\bar{1}31$), 2.927(8)(211), and 2.659Å(7)(311,320).

SOMMAIRE

La kulanite se présente sous forme de plaquettes ou de rosettes, allant du bleu au vert, dans une formation de fer sidéritique; elle provient de la région des rivières Big Fish et Blow située dans le Nord-Est du Territoire du Yukon. Le minéral est triclinique (pseudo-monoclinique) avec groupe spatial $P\bar{1}$, a 9.032, b 12.119, c 4.936Å, $\alpha \sim 90°$, β 100°23', $\gamma \sim 90°$, $Z = 2$. Les plaques sont tabulaires suivant $\{\bar{1}01\}$. La dureté est de 4. Le minéral possède deux clivages, {010} et {100}, d'assez bonne qualité. Le poids spécifique est de 3.91 ± 0.03 g/cm³ (mes.) et 3.92 g/cm³ (calc). La kulanite est biaxiale (+), $\alpha = 1.703$, $\beta = 1.705$, $\gamma = 1.723$, $2V$(mes.) = 32°, $2V$ (calc.) = 38°; la dispersion asymétrique est très prononcée $r \gg v$; le préochroïsme, α vert brunâtre, β vert, γ brun très pâle; l'orientation, $b \backsimeq \beta$, $c \wedge \gamma = -8°$. L'analyse chimique donne la formule:

$Ba_{1.00}\,(Fe^{+2}{}_{0.94}Mn^{+2}{}_{0.57}Mg_{0.49}Ca_{0.09})_{\Sigma=2.09}\,(Al_{1.81}Fe_{0.17})_{\Sigma=1.98}\,(PO_4)_{3.02}\,(OH)_{2.74}$, soit $Ba(Fe,Mn,Mg,Ca)_2\,(Al, Fe)_2\,(PO_4)_3(OH)_3$. Les raies les plus intenses du diagramme de poudre sont celles des es, pacements suivants: 8.84(6) (100), 3.108(10) (031-$\bar{2}21$), 3.044(7) ($\bar{1}31$), 2.927(8) (211), et 2.659Å 7(311.320).

(Traduit par le journal)

INTRODUCTION

In the spring of 1974, several mineral specimens were submitted to the Department of Mineralogy (now Department of Mineralogy and Geology), Royal Ontario Museum by Mr. Alan Kulan and Mr. Gunar Penikis, both of Ross River, Yukon Territory. The specimens proved to be exceptionally fine crystals of lazulite and wardite. Additional specimens were submitted and it soon became apparent that the locality contained a major new find of phosphate species. The authors visited Ross River in September, 1974 to select more specimens for research from the material which Messrs. Kulan and Penikis had collected in the spring and summer. One of us (B.D.S.) stayed on and visited the locality with Messrs. Kulan and Penikis. In July, 1975, the authors spent about two weeks at the locality.

Among the various minerals found at the locality are several as yet unidentified species. Studies completed on one of these prove that the mineral is a new species — kulanite. The mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. The name is in honor of Mr. Alan Kulan and is pronounced KŪ̆ LǍ•N AIT. Type material is preserved in the collections of the Royal Ontario Museum (ROM No. M 34170).

OCCURRENCE

The type locality of kulanite is a rock exposure at 68°34'N 136°50'W, on a small stream called Cross-cut Creek which flows into Rapid Creek. The exposure is about 1.5 km upstream from the juncture of the two streams. Rapid

TABLE 1. COMPARISON OF UNIT CELL DATA FOR KULANITE AND BJAREBYITE.

	bjarebyite (Moore *et al.* 1973)	kulanite (this study)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/m$	$P\bar{1}$
a	8.930	9.032 Å
b	12.073	12.119
c	4.917	4.936
α	---	90°
β	100.15°	100°23'
γ	---	90°
Z	2	2
$a : b : c$	0.7397:1:0.4073	0.7453:1:0.4073
V	521.8 Å^3	531.44 Å^3

TABLE 2. X-RAY POWDER DATA FOR KULANITE AND BJAREBYITE

Kulanite				Bjarebyite*		Kulanite		Bjarebyite	
I	d_{obs}	d_{calc}	hkl	I	d_{obs}	I	d_{obs}	I	d_{obs}
60	8.84	8.88	100	7	8.81	2	2.007	-	-
5	6.05	6.06	020	-	-	2	1.982	-	-
40	5.01	5.01	120	4	4.97	15	1.956	2	1.956
30	4.62	4.63	$\bar{1}01$	2	4.59	1	1.912	-	-
50	4.51	4.51	011	4	4.47	7	1.883	2	1.880
5	4.322	4.322	$\bar{1}11$	-	-	5	1.852	-	-
5	4.175	4.171	210	1	4.124	2	1.840	-	-
50	3.583	3.583	220	2	3.562	1	1.821	-	-
20	3.475	3.467	$\bar{2}11$	1	3.447	1	1.810	-	-
5	3.324	3.321	121	1	3.295	1	1.797	-	-
100	3.108	3.107	$\bar{2}21$	10	3.090	5	1.788	1	1.786
		3.105	031			2	1.776	-	-
70	3.044	3.043	$\bar{1}31$	3	3.024	1	1.765	-	-
20	2.988	2.989	230	-	-	1	1.758	1	1.759
80	2.927	2.928	211	4	2.910	2	1.729	1	1.733
30	2.883	2.877	310	2	2.852	2	1.710	1	1.702
20	2.868	2.868	140	-	-	5	1.684	1	1.681
40	2.829	2.831	131	2	2.811	5	1.672	-	-
50	2.698	2.695	231	-	-	2	1.660	1	1.659
60	2.690	2.690	$\bar{3}11$	7	2.681	1	1.641	-	-
70	2.659	2.661	320	3	2.643	15	1.629	2	1.624
5	2.531	2.534	$\bar{1}41$	1	2.514	1	1.617	-	-
5	2.515	2.511	321	2	2.495	7	1.604	2	1.600
1	2.503	2.503	240	-	-	10	1.578	2	1.578
30	2.458	2.457	$\bar{1}02$	2	2.444	15	1.561	3	1.556
40	2.428	2.428	002	1	2.413	1	1.553	-	-
5	2.409	2.408	141		-	15	1.529	3	1.528
		2.408	$\bar{1}12$			2	1.522	-	-
10	2.389	2.388	330	1	2.377	40	1.501	-	-
				1	2.310	30	1.495	5	1.495
15	2.271	2.272	$\bar{2}12$	1	2.261	25	1.468	-	-
15	2.186	2.185	410	2	2.177	1	1.439	-	-
30	2.146	2.146	$\bar{1}51$	3	2.137	7	1.429	-	-
10	2.100	2.100	$\bar{1}32$	1	2.090	2	1.415	-	-
5	2.045	2.046	$\bar{4}21$	-	-	5	1.400	-	-
10	2.040	2.040	$\bar{3}41$	2	2.039	2	1.376	-	-
		2.040	$\bar{3}12$						
30	2.020	2.020	060	2	2.010	-	-	-	-

*Bjarebyite data from Moore *et al.* (1973); 114.6 mm diameter camera, Fe/Mn radiation.
Kulanite: Guiner camera, Cu$K\alpha_1$ radiation.

Creek flows northward into the Beaufort Sea about 32 km north of the juncture of the two streams. Access to the locality is by helicopter and takes about one hour from the town of Inuvik in the Northwest Territories.

The area is gently rolling tundra with deeply incised rivers and streams. Interbedded shales and "ironstone" are exposed on the steep sides of the canyons. The rocks are Upper Cretaceous and have undergone a fair amount of folding and faulting. Fractures in the "ironstone" beds (a sideritic iron-formation) have been mineralized in many places. Preliminary studies indicate that mineral deposition was local in nature, the phosphates probably having been derived from the phosphorus-rich siderite beds. A detailed study of the paragenesis of the occurrence is being undertaken and will be published after work on the individual species has been completed. At this point it is apparent that the suite of phosphate minerals formed at relatively low temperatures. Minerals identified from the area are: quartz, siderite, "apatite", lazulite, wardite, vivianite, childrenite, ludlamite, metavivianite, arrojadite, augelite, brazilianite, and several other new species. Kulanite has been found in association only with quartz, siderite, and "apatite".

PHYSICAL PROPERTIES

Kulanite is green to blue and has a very pale green streak. The mineral occurs as thin plates, tabular parallel to $\{\bar{1}01\}$. The plates are commonly arranged in rosette-like aggregates. Individual plates measure up to 3x3x0.5 mm. The lustre is vitreous and the plates are transparent to translucent. The mineral shows no fluorescence under short-wave or long-wave ultraviolet light. The hardness is about 4. Measurement with the Berman balance gave a density of 3.91±0.03 g/cm^3. The calculated density of the analyzed material is 3.92 g/cm^3. Two fair to good cleavages are parallel to {010} and {100}.

CRYSTALLOGRAPHY

Single-crystal X-ray diffraction studies indicated that kulanite has unit cell parameters very similar to those given by Moore *et al.* (1973) for bjarebyite, monoclinic $Ba(Mn,Fe)_2Al_2(PO_4)_3(OH)_3$. Subsequent optical study showed that kulanite is triclinic (pseudo-monoclinic) rather than monoclinic. The unit cell data for kulanite are compared to Moore's data for bjarebyite in Table 1.

The X-ray powder diffraction data of kulanite are given in Table 2 where they are compared to those of bjarebyite. Incorrect intensities given by Moore *et al.* (1973) for lines at 3.090 and 2.010Å in the bjarebyite pattern (Moore, pers. comm. 1976) have been corrected in Table 2.

Measurements of several crystals on the optical goniometer provided the identification of the following forms: {001}, {100}, {120}, {110}, {011}, {031}, $\{\bar{1}01\}$, $\{\bar{3}01\}$, {111}, {121}, {131}, and {161}. Data in the angle table for kulanite (Table 3) were calculated from the unit cell parameters. A drawing of a typical crystal of kulanite is shown in Figure 1. Figure 2 shows the same crystal rotated such that $(10\bar{1})$ is vertical.

TABLE 3. ANGLE TABLE FOR KULANITE.

Triclinic $P\bar{1}$, pseudo-monoclinic $P2_1/m$

$a : b : c$ = 0.7453 : 1: 0.4073, β 100°23'

$p_0 : q_0 : r_0$ = 0.5465 : 0.4006 : 1

$r_2 : p_2 : q_2$ = 2.4961 : 1.3641 : 1 μ 79°37'

p_0' q_0' x_0' = 0.5556 : 0.4073 : 0.1832

Forms	ϕ	ρ	ϕ_2	$\rho_2 = B$	C	A
001	90°00'	10°23'	79°37'	90°00'	0°00'	79°37'
100	90°00'	90°00'	0°00'	90°00'	79°37'	0°00'
120	34°18'	90°00'	0°00'	34°18'	84°10'	55°42'
110	53°45'	90°00'	0°00'	53°45'	81°39'	36°15'
011	24°13'	24°04'	79°37'	68°10'	21°50'	80°22'
031	8°32'	51°00'	79°37'	39°47'	50°13'	83°23'
$\bar{1}01$	-90°00'	20°26'	110°26'	90°00'	30°49'	110°26'
$\bar{3}01$	-90°00'	56°01'	146°01'	90°00'	66°24'	146°01'
111	61°08'	40°09'	53°33'	71°52'	31°23'	55°37'
121	42°12'	47°43'	53°33'	56°46'	41°18'	60°12'
131	31°10'	54°59'	53°33'	45°31'	50°09'	64°55'
161	16°49'	68°37'	53°33'	26°57'	65°59'	74°22'

Note: Although the mineral is triclinic the data are given here in the form used for monoclinic crystals.

OPTICAL DATA

Kulanite is optically biaxial (+) with α= 1.703, β = 1.705, γ = 1.723, $2V$ (meas) = 32°. $2V$ (calc)=38°, birefringence=0.020. The dispersion is very strong with $r >> v$. The mineral shows unsymmetrical dispersion indicating that kulanite is triclinic. The optical orientation is $b \cong \beta$, $c \wedge \gamma = -8°$. One optic axis is almost normal to $\{\bar{1}01\}$. The mineral is pleochroic with α = brownish green, β = green, and γ = very pale brown; absorption $\alpha \cong \beta >> \gamma$.

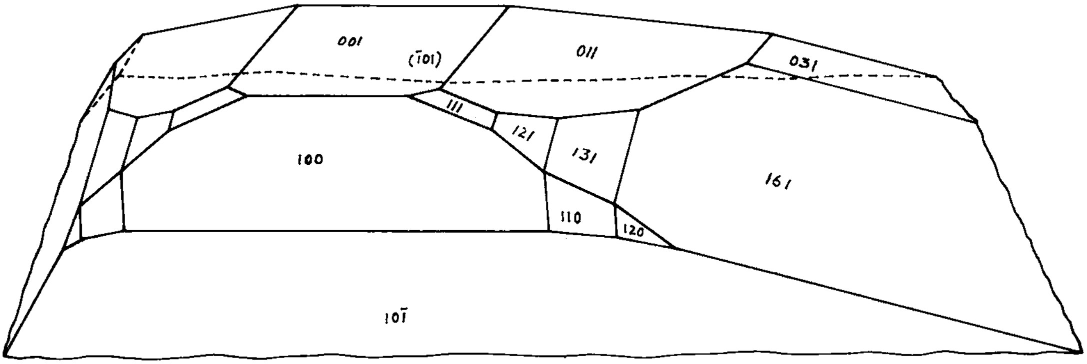

FIG. 1. Crystal of kulanite.

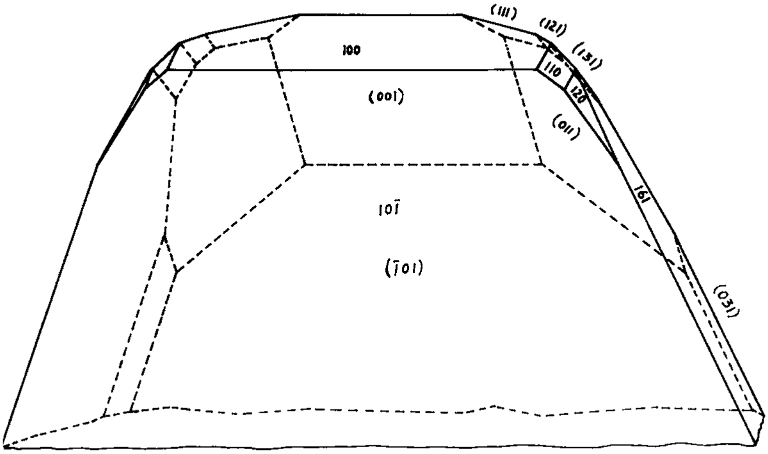

FIG. 2. Crystal of kulanite rotated so that $(\bar{1}01)$ face is vertical.

TABLE 4. CHEMICAL ANALYSIS AND DERIVATION OF THE CHEMICAL FORMULA OF KULANITE

	A	B	C	D		E (x 12.90)		F		G	
Na_2O	0.02	0.02	0.0003	Na	0.0006	Na	0.01	Na_2O	0.02		--
K_2O	nil	--									
MgO	3.16	3.08	0.0764	Mg	0.0764	Mg	0.99	MgO	3.08	MgO	3.02
CaO	0.79	0.77	0.0137	Ca	0.0137	Ca	0.18	CaO	0.77	CaO	0.76
MnO	6.49	6.32	0.0891	Mn	0.0891	Mn	1.15	MnO	6.32	MnO	6.16
FeO				Fe^{+2}	0.1462	Fe^{+2}	1.89	FeO	10.50	FeO	10.31
BaO	24.3	23.66	0.1543	Ba	0.1543	Ba	1.99	BaO	23.66	BaO	24.44
Al_2O_3	14.7	14.31	0.1403	Al	0.2806	Al	3.62	Al_2O_3	14.30	Al_2O_3	14.83
Fe_2O_3	14.2	13.82	0.0865	Fe^{+3}	0.0268	Fe^{+3}	0.35	Fe_2O_3	2.14	Fe_2O_3	2.23
P_2O_5	34.2	33.29	0.2345	P	0.4690	P	6.05	P_2O_5	33.28	P_2O_5	33.94
H_2O (+)		3.83	0.2125	H	0.4250	H	5.48	H_2O	3.83	H_2O	4.31
F	nil	--	--			O	30.00		97.90		100.00
Cl	nil	--	--					SiO_2	0.19		
SiO_2	0.2	0.19							98.09		
Total	98.06	99.29									
Wt. loss (N_2)	3.83			O	2.3992						
Wt. loss (O_2)	2.66	*1.17	0.0731	-	0.0731						
Diff. in wt. loss	1.17	98.12		O =	2.3261						

* less added oxygen

A. Figures in column A are the analytical results obtained for the oxidized residue. The wt. loss in N_2 is equivalent to the H_2O content. The difference between the wt. loss in N_2 and the wt. loss in O_2 is the wt. of oxygen added to the residue during oxidation of the ferrous iron to ferric iron.

B. In Column B, the figures from Column A have been multiplied by 0.9734 as the oxidized residue represents 97.34% (i.e. 100 minus 2.66) of the original mineral. The H_2O content (3.83%) has been added and 1.17 has been subtracted from the new sub-total to give a total of 98.12 wt. %.

C. Molecular proportions (wt.% of Column B divided by the appropriate molecular weights). Note that the excess oxygen is divided by 16.00 (atomic wt. of oxygen).

D. Atomic proportions. Total iron has been apportioned as follows: (1) the ferrous iron atomic proportion is made equal to twice the excess oxygen atomic proportion (0.0731x2=0.1462); (2) the ferrous iron atomic proportion is subtracted from the original atomic proportion of ferric iron (2x0.0865=0.1730) to obtain the new ferric iron atomic proportion (0.1730-0.1462=0.0268); (3) the oxygen atomic proportion is calculated from the figures in Column C and reduced by the atomic proportion of excess oxygen to obtain the total oxygen atomic proportion (2.3992-0.0731=2.3261); (4) the number of oxygen ions in the unit cell (in this case, 30) is divided by the oxygen atomic proportion to obtain the factor 12.90 (30÷2.3261=12.90).

E. Column D figures are multiplied by the factor 12.90 to obtain formula subscripts. The derived formula is: $Ba_{1.99}(Fe^{+2}_{1.89}Mn_{1.15}Mg_{0.99}Ca_{0.18})_{4.21}(Al_{3.62}Fe^{+3}_{0.35})_{3.97}(PO_4)_{6.05}(OH)_{5.48}$ or, ideally, $Ba_2(Fe^{+2}_{1.80}Mn_{1.09}Mg_{0.94}Ca_{0.17})_{4.00}(Al_{3.65}Fe^{+3}_{0.35})_{4.00}(PO_4)_6(OH)_6$.

F. For comparison to the figures in Column B, oxide wt. percentages have been calculated by multiplying the figures in Column D by the appropriate molecular weights (and dividing by 2 in the case of Na_2O, Al_2O_3, Fe_2O_3, P_2O_5 and H_2O). The FeO (10.50%) is equivalent to 11.67% Fe_2O_3. This figure added to the Fe_2O_3 in this column gives 13.81% which compares to 13.82% in Column B.

G. Theoretical oxide wt. percentages for the ideal formula (see E above).

THERMAL DATA

Simultaneous DTA-TGA analysis of two samples of kulanite were carried out by Mr. Donald R. McKinnon of the Department of Mineralogy and Geology, Royal Ontario Museum. The instrument used was a Mettler Thermal-analyzer. The following conditions apply to both analyses: reference substance, Al_2O_3; heating rate 8°C/minute; temperature range 25°C to 850°C. One sample (118.1 mg) was analyzed in an oxygen atmosphere and the other (28.7 mg) was analyzed in a nitrogen atmosphere. Both gave an endothermic peak at 710°C associated with the evolution of H_2O. The sample run in oxygen showed an exothermic peak at 749°C which corresponds to oxidation of the ferrous iron. Both TGA curves showed simple one-stage weight losses to 3.83 wt % in N_2 and 2.66 wt. % in O_2.

CHEMICAL DATA

The residue from the DTA-TGA sample run in oxygen was submitted to Dr. E. J. Brooker of X-ray Assay Laboratories, Ltd., Toronto. The analytical data from this oxidized residue together with the weight loss data in oxygen and in nitrogen permit the calculation of the ferrous and ferric iron contents. Details of the method are given by Mandarino (in prep.).

Table 4 gives the analysis of the oxidized residue and a step-by-step calculation leading to the derivation of the chemical formula of kulanite. The formula derived in Table 4 is, ideally:

$Ba_2(Fe^{2+}_{1.80}Mn_{1.09}Mg_{0.94}Ca_{0.17})_{\Sigma=4}(Al_{3.65}Fe^{3+}_{0.35})_{\Sigma=4}(PO_4)_6(OH)_6$. Kulanite is the triclinic, ferrous iron-dominant analogue of bjarebyite. Type kulanite is the manganoan, magnesian variety.

The *K* value calculated from the data in Column F of Table 4 using the revised Gladstone-Dale constants of Mandarino (1976) is 0.182. The value calculated from the refractive indices and the measured density is 0.182.

ACKNOWLEDGMENTS

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REFERENCES

MANDARINO, J. A. (1976): The Gladstone-Dale relationship. Part I: Derivation of new constants. (In press).

MOORE, P. B., LUND, D. H. & KEESTER, K. L. (1973): Bjarebyite, $(Ba,Sr)(Mn,Fe,Mg)_2Al_2(OH)_3(PO_4)_3$, a new species. *Mineral. Record* **4**, 282-285.

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