

THE OCCURRENCE OF VLASOVITE IN CANADA

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ABSTRACT

Vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) was originally described from the Kola Peninsula, U.S.S.R. as a metasomatic replacement of eudialyte. It was subsequently found in ejected blocks of peralkaline granite on Ascension Island. It has now been found in Villedieu Township, Temiskaming County, Quebec, in large crystals (up to 15 cm in length) in pegmatitic portions of an alkalic rock complex that has been regionally metamorphosed. It coexists with potash feldspar, eudialyte, mosandrite and alkalic amphibole and is not an alteration product of any other mineral. Rather, the vlasovite itself contains minute tufts of an alteration product which is a new mineral with the composition $\text{CaZrSi}_2\text{O}_7$. The grains are so small that as yet it has not been possible to determine sufficient physical properties to justify naming it. An analysis of the accompanying amphibole (potassian magnesio-kataphorite) is also presented.

Introduction and general geology

Vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) was first described by Tikhonenkova & Kazakova (1961) in rocks of the Lovozero alkalic massif, Kola Peninsula, USSR, where it occurs as irregular grains $0.5 \times 1 \times 1.5$ cm "in the contact zone of the massif among the albitized areas of the eudialyte — microcline fenites and pegmatoid nepheline syenites" (Gerasimovsky *et al.* 1966). It was subsequently discovered in ejected blocks of peralkaline granite on Ascension Island as an accessory mineral and described by Fleet & Cann (1967). What is probably the most abundant occurrence of the mineral has now been found in the agpaitic alkaline rock complex at Kipawa River, Villedieu Township, Temiskaming County, Quebec, Canada.

The Kipawa complex is poorly exposed in Villedieu Township, at $46^\circ 47' 49''\text{N } 78^\circ 29' 31''\text{W}$. It is essentially a regionally metamorphosed complex of agpaitic rocks which is in places intensely folded. The commonest rock type is a gneiss composed of albite, microcline and alkalic amphibole (magnesio-kataphorite, Table 4) with or without eudialyte. Within these gneisses are

lenses and pods of pyroxene, and amphibole-rich rocks of a more pegmatitic character that contain a wide variety of rare minerals such as eudialyte, agrellite, hiortdahlite and other members of the wöhlerite group, mosandrite, miserite and britholite. Pyroxene nepheline syenites outcrop within one mile of these gneisses and are probably part of the same complex.

Occurrence of vlasovite

The commonest occurrence of vlasovite is as sub-rounded grains from 1-2 cm across surrounded by red eudialyte in a rock composed of potash feldspar, eudialyte, vlasovite, mosandrite and alkalic amphibole. Less common are crystals up to 15 cm in length set in a matrix of potash feldspar and eudialyte. In large crystals vlasovite is pale brown but the smaller crystals always appear silvery owing to internal reflection from the excellent {010} cleavage planes.

Chemistry

Several specimens have been analyzed by electron microprobe at the University of Toronto and one by classical wet chemical methods at the Institute for the Mineralogy, Geochemistry and Crystal Chemistry of the Rare Elements (IMGRE) in Moscow. The results are set down in Table 1. The agreement with the accepted formula $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$ is very close. For comparison the analyses of the original Kola material and that from Ascension Island are also included.

Crystal symmetry

The original Kola mineral was described as monoclinic $C2/c$ but the Ascension Island mineral inverts to a triclinic form at 29°C . The Canadian specimens do not display any inversion, remaining monoclinic between the temperature of liquid nitrogen and 600°C . The crystallographic data are: $a = 11.1(1)$, $b = 10.1(1)$, $c = 8.6(1)\text{\AA}$, $\beta = 100.7(2)^\circ$. These may be compared with the data for the original Kola mineral which are: $a = 10.98$, $b = 10.00$, $c = 8.52$,

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$\beta = 100.24^\circ$. The space group (by single crystal methods) is a least *Cc* and there is almost certainly a centre of symmetry by analogy to the Kola mineral which would give it the symmetry *C2/c*.

In view of this peculiar inversion in the Ascension Island material it was decided to re-examine the type vlasovite from Lovozero. A few grains were kindly provided by R. Tikhonenkova through E.I. Semenov of the Institute for the Mineralogy, Geochemistry and Crystal Chemistry of the Rare Elements (IMGRE) of the Ministry of Geology, Moscow, U.S.S.R. The Lovozero vlasovite was found to remain monoclinic at all temperatures down to that of liquid nitrogen and so the inversion to a triclinic form at 29°C remains unique to the Ascension Island vlasovite.

Both the Lovozero and Kipawa vlasovite display thermally diffuse reflections indicating disorder which may arise in a framework unable to readjust into two twinned triclinic forms. There is, however, no obvious explanation of this behaviour as there is no significant chemical difference between any of the three occurrences. An indexed powder pattern of the Kipawa vlasovite is presented in Table 2 where it is com-

pared with the original Russian data that appear in the PDF file. *d*-spacings have been calculated from the cell constants for α -radiation of wavelength 1.5418\AA and are compared with the measured values. There are distinct differences between the indexing arrived at in this manner and that given in the PDF file. Further inspection of Table 2 shows that a number of the observed lines in the pattern of the Lovozero material do not agree with the calculated possible lines. This is probably to be attributed to the differences between the cell constants for the Kipawa mineral and those presented by Tikhonenkova & Kazakova (1961) for the original Kola mineral. A re-determination of the Kola mineral would be desirable.

Stability

A reconnaissance study of a preliminary nature in the system $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2$ has been reported

TABLE 1. CHEMICAL COMPOSITION OF VLASOVITE

	1	2	3	4	5
SiO_2	55.1	55.67	55.57	55.76	56.47
Al_2O_3	0.0	0.00	-	0.20	-
FeO	0.1	0.60*	-	0.10*	-
MgO	0.1	0.00	0.23	0.06	-
CaO	0.0	0.50	0.41	0.49	-
Na_2O	14.6	14.07	14.38	14.03	14.57
K_2O	0.0	0.00	0.15	0.68	-
ZrO_2	30.4	29.40	28.14	28.11**	28.96
	100.3	100.24	99.99+	100.29++	100.00

1. vlasovite from Kipawa River, Villedieu Township, Temiscaming Co., Quebec, Canada, analyzed by microprobe. (Average of 4 analyses)

2. vlasovite from Kipawa River analyzed by classical wet chemistry, analyst M. Kazakova, IMGRE, Moscow, USSR, by courtesy of E. Semenov (IMGRE)

3. vlasovite from Ascension Island, analyzed by classical wet chemistry, analyst J.H. Scoon. (Fleet & Cann 1967)

4. vlasovite from Lovozero massif, Kola Peninsula, USSR, analyzed by classical wet chemistry, analyst M. Kazakova (Tikhonenkova & Kazakova 1962)

5. Ideal vlasovite composition

Formula calculated as cations to 11 oxygens:

1. $\text{Na}_{2.02}\text{Zr}_{1.06}\text{Si}_{3.94}\text{O}_{11}$ 2. $(\text{Na,Ca})_{1.91}\text{Zr}_{1.19}\text{Si}_{3.81}\text{O}_{11}$

3. $(\text{Na,K,Ca})_{2.02}\text{Zr}_{.97}\text{Si}_{4.01}\text{O}_{11}$

4. $(\text{Na,K,Ca})_{2.00}\text{Zr}_{.96}\text{Si}_{3.91}\text{O}_{11}$ 5. $\text{Na}_2\text{ZrSi}_4\text{O}_{11}$

* Fe_2O_3 **includes HfO_2 1.7 †includes loss on ignition 0.11 ††includes Nb_2O_5 0.33, H_2O 0.41, F 0.20

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR VLASOVITE

KIPAWA, QUEBEC				LOVOZERO, USSR				
<i>hkl</i>	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å	<i>I</i> _{est}	<i>hkl</i>	<i>d</i> _{calc}	<i>d</i> _{obs} Å	<i>hkl</i> (PDF) <i>I</i> _o / <i>I</i>	
11 $\bar{1}$	5.953	5.957	12	011	6.423	5.94	111 25	
200	5.454	5.454	12	01 $\bar{1}$	6.423	5.48	200? 35	
111	5.252	5.253	20	101	6.108	5.26	111 40	
020	5.053	5.050	100	11 $\bar{1}$	5.890	5.02	020 70	
021 $\bar{1}$	4.333	4.335	9	200	5.400	4.23	201 30	
02 $\bar{1}$	4.220	4.225	12	111	5.213	3.88	211,121 30	
002	3.882	3.888	43	020	5.000	3.68	102,220 45	
11 $\bar{2}$	3.669	3.680	74	20 $\bar{1}$	4.966	3.57	301 20	
20 $\bar{2}$	3.548	3.563	26	210	4.751	3.50	221 14	
22 $\bar{1}$	3.483	3.486	5	120	4.537	3.37	310 60	
112	3.40	3.421	3	21 $\bar{1}$	4.447	3.26	201,022? 100	
310	3.363	3.367	33	021	4.294	3.058	202 18	
030	3.237	3.235	42	02 $\bar{1}$	4.294	2.966	311,122 95	
12 $\bar{2}$	2.988	2.994	14	201	4.207	2.909	212,320 10	
311	2.954	2.953	4	002	4.190	2.723	401,113 50	
131	2.903		20	10 $\bar{2}$	4.168	2.536	302? 30	
	2.719		10	12 $\bar{1}$	4.123	2.455	232 30	
	2.527		20	211	3.877	2.386	421 12	
	2.449		12	121	3.869	2.245	322,232 6	
	2.378		14	012	3.865	2.173	133,323 60	
	2.169		12	01 $\bar{2}$	3.865	2.117	510 8	
	1.984		7	11 $\bar{2}$	3.847	2.070	341,142 8	
	1.945		22	102	3.688	1.985	104,520 8	
	1.857		5	220	3.669	1.951	341,114 50	
	1.783		16	20 $\bar{2}$	3.644	1.860	521,043 20	
	1.685		11	300	3.600	1.819		8
	1.62		4	30 $\bar{1}$	3.548	1.781		20
	1.610		6	22 $\bar{1}$	3.523	1.734		8
	1.560		3	112	3.460	1.685		25
	1.533		2	21 $\bar{2}$	3.424	1.650		14
	1.450		7	310	3.387	1.628		18
	1.430		4	31 $\bar{1}$	3.344	1.606		12
	1.305		3	030	3.333	1.562		14
				221	3.219	1.536		8
				022	3.212	1.499		6
				02 $\bar{2}$	3.212	1.475		8
				12 $\bar{2}$	3.202	1.455		25
				130	3.185	1.433		18
				301	3.110	1.417		6
				031	3.097			
				202	3.054			
				131	3.031			
				302	3.013			
				311	2.970			
				122	2.968			
				22 $\bar{2}$	2.945			
				131	2.926			
				320	2.922			

Data obtained by Norelco diffractometer using diamond and synthetic CaF_2 (previously calibrated against diamond) as internal standards, nickel-filtered Cu radiation.

by Michel-Levy (1962), but the absence of a rigorously systematic study of the system precludes the drawing of any conclusions about the relative stabilities and relations between the various sodium zirconium silicates.

This is important because the original Lovozero vlasovite is described as an alteration product of eudialyte. "... it forms after eudialyte and metasomatically replaces it" (Gerasimovsky *et al.* 1968). This most assuredly is not the case in the Kipawa occurrence where vlasovite forms large clear crystals in sharp contact with eudialyte. Eudialyte is perfectly fresh and it is indeed the vlasovite that shows evidence of alteration. Not only has eudialyte not been metasomatically altered to vlasovite but the evidence of two regionally metamorphosed eudialyte-bearing alkalic complexes in Canada suggests that eudialyte is a mineral that is stable through a very wide range of metamorphic conditions.

The petrographic evidence at the Kipawa occurrence suggests that vlasovite, eudialyte and potash feldspar have crystallized together or in sequence; indeed vlasovite and eudialyte probably have adjoining primary phase volumes in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{ZrO}_2$ although to date eudialyte has proved to be extremely difficult to synthesize and vlasovite extremely easy.

A series of heating experiments at one atmosphere in platinum foil give the following results: 1200°C vlasovite; 1250°C vlasovite; 1300°C zircon + liquid; 1400°C baddeleyite + liquid. Vlasovite thus melts initially to zircon and a sodium silicate liquid of composition $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ and then to baddeleyite and a more siliceous liquid of composition $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$. The evidence from Kipawa strongly suggests that vlasovite is a primary igneous mineral and not a metasomatic alteration product.

Alteration of vlasovite

Although vlasovite generally occurs in large clear crystals a number of grains display an alteration along cleavages. The alteration forms radiating sheaves of prismatic crystals 0.1-0.3 mm long. These are far too small to permit the determination of optical or physical properties except that they have very low birefringence. The chemical composition determined by electron microprobe is shown in Table 3. It is apparent that the mineral has the ideal composition $\text{CaZrSi}_2\text{O}_7$ and is a new mineral. Indeed, no chemical compound of this composition is known. In view of the lack of physical or optical data it is not possible to name the mineral formally.

Apparently its formation is due to the penetration of calcium-rich solutions along the cleavages

either during the late igneous history of the complex or during its subsequent regional metamorphism. There is much to suggest that some melting of the rocks occurred during regional metamorphism and the fact that lime-rich liquids were present is indicated by interstitial intergrowths of calcite and fluorite that strongly resemble the synthetic products of eutectic crystallization. The alteration is a simple one requiring the substitution of one calcium ion for two sodium ions and the removal of two molecules of silica.

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TABLE 3. ALTERATION PRODUCT OF VLASOVITE (Av. of 2 analyses)

Cations to 7 oxygens		
SiO_2	40.3	2.00
FeO	0.3	.01
MgO	0.1	.01
CaO	18.0	.96
Na_2O	0.4	.02
K_2O	0.1	.00
ZrO_2	41.3	1.00
	100.5	
		(Ca, etc) _{1.00} Zr _{1.00} Si _{2.00} O ₇

TABLE 4. POTASSIAN MAGNESIO-KATAPHORITE ACCOMPANYING VLASOVITE

	wt. %	Cations to 24 (O,OH,F)
SiO_2	54.95	7.731
Al_2O_3	0.70	0.117
TiO_2	0.05	0.005
ZrO_2	0.19	0.013
Nb_2O_5	0.01	-
Fe_2O_3	7.68	0.813
FeO	3.24	0.381
MnO	0.84	0.100
MgO	16.52	3.463
Li_2O	0.32	0.181
Cs_2O	0.01	-
CaO	5.10	0.768
Na_2O	7.26	1.980
K_2O	2.06	0.370
H_2O^+	0.35	0.328
F	2.17	0.965

(Na,K)_{2.35}Ca_{.77}(Mg,Fe²⁺,etc)_{4.5}Fe³⁺_{.81}(Si,Al)_{7.85}O₂₂OH_{.33}F_{.97}

Analyzed at Institute for Mineralogy, Geochemistry and Crystal Chemistry of the Rare Elements (IMGRE), Moscow, USSR.
Analyst: Z.T. Kataeva

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