Vlasovite: a second occurrence and a triclinic to monoclinic inversion

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Summary. Vlasovite, $Na_2ZrSi_4O_{11}$, previously reported as monoclinic by Pyatenko and Voronkov from an occurrence in the Kola Peninsula, Russia, has been found in rocks from Ascension Island in a triclinic twinned modification. The obliquity is very slight (α and γ differ from 90° by less than 1°), and X-ray photographs show arrays of paired spots corresponding to diffraction by different parts of the crystal related by the twinning operation, reflexion across (010).

On heating, this vlasovite is found to transform to the monoclinic variety at 29° C. The phase change has been followed on a single-crystal X-ray heating camera, and the obliquity is found to have successively smaller values as the crystal is heated from temperatures below room temperature to 29° C. The obliquity is characteristic of the particular temperature over the transformation range and is not affected by thermal history.

The transformation appears to be a displacive one, similar in some respects to $\alpha \rightarrow \beta$ tridymite and $\alpha \rightarrow \beta$ cristobalite, and some information has been obtained by X-ray structural investigations about the nature of the atomic movements involved.

VLASOVITE, essentially $Na_2ZrSi_4O_{11}$, was first discovered by Tikhonenkova and Kazakova (1961) in a contact zone between pegmatites and fenites near Mt. Vavnbed, in the Lovozero massif, Kola Peninsula, USSR. Pyatenko and Voronkov (1961) determined the unit-cell-dimensions and space group ($C2/c$) and the crystal structure, showing that vlasovite contained a new type of silicate linkage: infinite bands of composition Si_4O_{11} formed of fourfold rings of silicon–oxygen tetrahedra linked in a stepwise arrangement (fig. 1). The crystal data of the Russian workers is summarized in table I.

More recently Michel-Lévy (1962) has recognized vlasovite among phases synthesized in the Na_2O–ZrO_2–SiO_2 system.

A second occurrence of vlasovite. During an investigation by one of us (J. R. C.) of the acid ejected blocks of Ascension Island, a mineral was discovered in some of the peralkaline granite blocks that closely resembled dalyite ($K_2ZrSi_6O_{15}$), a mineral discussed by van Tassel (1952)

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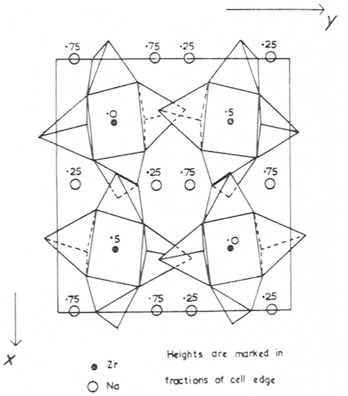
TABLE I. Chemical composition and physical properties of vlasovite

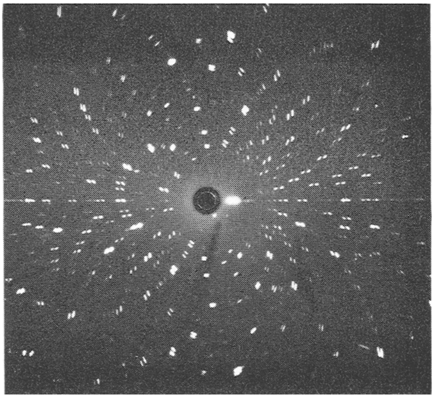
	1.		1*a*	2*a*	1*b*	2*b*
SiO_2	56·57	Si	4·010	3·912	$2V_\alpha = 40–45°$	$2V_\alpha = 50–56°$
ZrO_2	28·14	Zr	0·973	0·961	$\alpha = 1·605$, $\beta = 1·623$, $\gamma = 1·625$	$\alpha = 1·607$, $\gamma = 1·623$, $\gamma = 1·628$
MgO	0·23	Nb	—	0·011	(all $\pm 0·003$)	
CaO	0·41	Al	—	0·017	Optic axial plane (010)	Optic axial plane (010)
Na_2O	14·38	Fe	—	0·005	Cleavage: (010) good, with two other	Cleavage: (010) good
K_2O	0·15	Mg	0·024	0·006	poor cleavages of form {*h*0*l*}	
Ignition loss	0·11	Ca	0·031	0·037	Space group $P\bar{1}$	Space group $C2/c$
					$a = 10·96 \pm 0·04$Å	$a = 10·98 \pm 0·04$ Å
	——	Na	1·977	1·902	$b = 10·01 \pm 0·04$ Å	$b = 10·00 \pm 0·04$ Å
	99·99	K	0·014	0·061	$c = 8·53 \pm 0·04$ Å	$c = 8·52 \pm 0·03$ Å
		OH	—	0·150	$\alpha = 89° 42' \pm 5'$	
		F	—	0·044	$\beta = 100° 24' \pm 5'$	$\beta = 100° 24' \pm 10'$
					$\gamma = 90° 29' \pm 5'$	

1. Chemical analysis of Ascension Island vlasovite by J. H. Scoon.
1*a*. Above calculated as cations to 11 oxygens.
2*a*. Analysis of Kola vlasovite, Tikhonenkova and Kazakova (1961), calculated as cations to 11 (O, OH, F).
1*b*. Physical and optical data for Ascension Island vlasovite at 20° C.
2*b*. Physical and optical data for Kola vlasovite (Tikhonenkova and Kazakova, 1961; Pyatenko and Voronkov, 1961).

and Fleet (1965) and which is found in other peralkaline granite blocks from Ascension Island.

Optical and single-crystal X-ray investigation showed that this mineral was vlasovite. It is found in an assemblage: sanidine–quartz–arfvedsonite–aegirine–aenigmatite–fayalite–vlasovite–pyrochlore as interstitial grains moulded on quartz and feldspar and projecting into miarolitic cavities. The associated minerals are exactly the same as those found with dalyite.





FIGS. 1 and 2: FIG. 1 (left). *c*-axis projection of the structure of vlasovite showing the stepwise linkage of the fourfold rings of SiO_4 tetrahedra. FIG. 2 (right). Cylindrical Laue photograph of vlasovite. *c*-axis vertical; *b*-axis 4° from beam; temperature 20° C. The pair of 100 and $\bar{1}00$ reflexions may be seen on the equatorial zone to the right of the origin.

The vlasovite was separated, and analysed by J. H. Scoon. The results of the analysis are presented in table I, together with the analysis quoted by Tikhonenkova and Kazakova (1961). The atomic composition, calculated to 11 oxygens, fits very closely the formula $Na_2ZrSi_4O_{11}$. The optical data agree very closely with those of the Russian authors.

X-ray investigation. While Pyatenko and Voronkov (1961) reported vlasovite to be monoclinic ($C2/c$), the specimens from Ascension Island gave single-crystal photographs showing patterns corresponding to two triclinic phases in twin orientation (fig. 2). The obliquity is very slight (α and γ each differ from 90° by less than 1°) and the cell dimensions are very similar to those found by Tikhonenkova and Kazakova (1961). The twin law is that of reflection across {010}.

Some crystals were found containing the twin phases in very different proportions, so that the diffraction spots from one phase were much stronger than from the other. By this means the spots from one of the phases could readily be identified, so that precession photographs allowed the unambiguous determination of cell dimensions.

Heat treatment. Crystals of vlasovite were heated on the high-temperature single crystal camera described by Rickson, Hall, and McConnell (1963). At temperatures higher than 29° C, the crystals are monoclinic with cell dimensions in agreement with those of Tikhonenkova and Kazakova (1961) within the limit of error. Further heating to 800° C does not produce any other change of phase.

In order to study the phase change, Laue photographs (Cu radiation) were taken with the X-ray beam about 10° from the *b*-axis, and the *a*- or *c*-axis vertical. By this means the very strong pair of 001 or 100 reflections from the twin components occur at about 20° to one side of the undeviated beam, in the equatorial zone. The separation of these spots can be taken as a measure of the obliquity near the *c*- and *a*-axes respectively.

Experiments showed that this separation decreases as the crystals are heated, and the spots coalesce when the structure is truly monoclinic. Equilibrium at all temperatures appears to be reached very rapidly: the intensities of the spots were such that they appeared distinctly on photographs exposed for two minutes, and such photographs taken immediately after changing the temperature of the crystals show spots separated by a distance appropriate to the new temperature.

X-ray photographs were taken with crystals in the temperature range $-20°$ C to $+40°$ C, 2° C intervals being taken between 20° and 30° C. For each exposure the crystal was held at the required temperature for 10 minutes and then exposed to X-rays for 5 minutes. The temperature during each exposure could be maintained to $\pm\frac{1}{2}°$ C, and was monitored by a copper–constantan thermocouple placed near the crystal. The photographs taken below room temperature were obtained by cooling the crystal with air that had passed over solid carbon dioxide. Separations of spots were measured with a travelling microscope. Fig. 3 shows the results of experiments to measure the change in obliquity, expressed as the angular separation of the 100 and 001 spots, with temperature.

The obliquity shows no detectable hysteresis. It is not different if the temperature of measurement is approached from below or above, and is not affected by the number of times a crystal has been taken through the phase transition. It is not changed if the crystal is held for 2 hours at a particular temperature, nor does the rate of change of

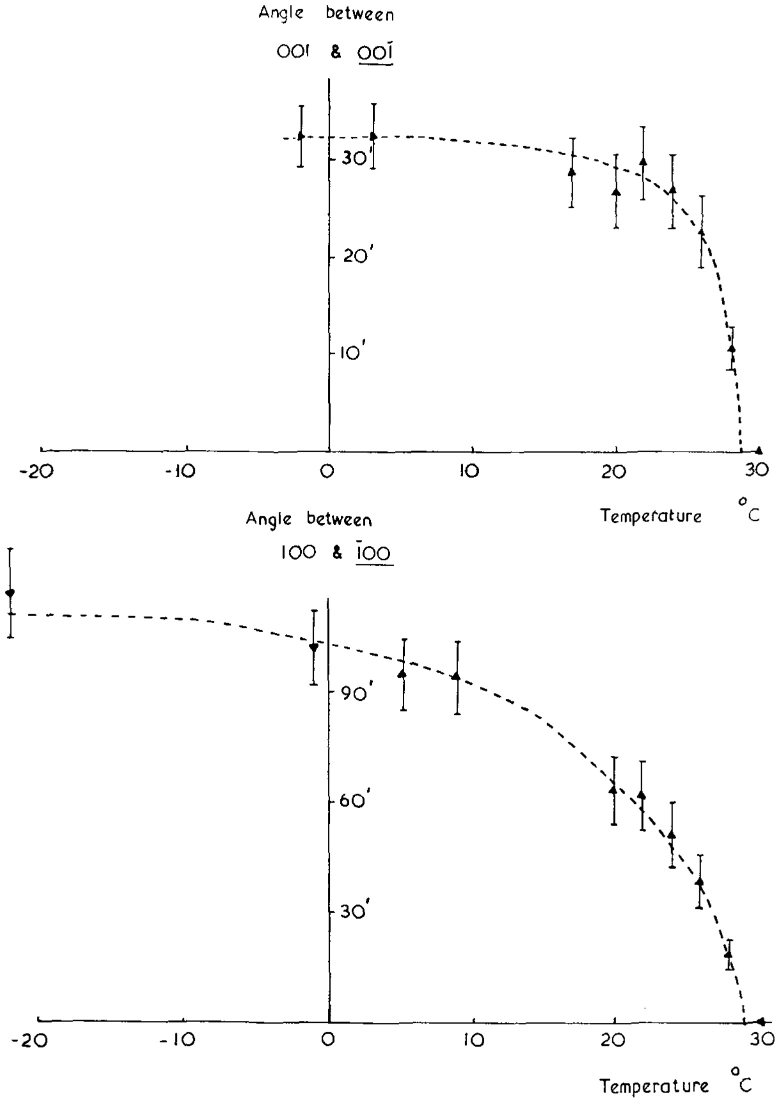


FIG. 3. Angles between 001 and $00\bar{1}$, and between 100 and $\bar{1}00$ as a function of temperature. Vertical lines indicate estimated error in angular measurement.

obliquity with temperature nor the final temperature at which inversion is complete change from crystal to crystal in this sample; the obliquity is uniquely characteristic of temperature and is not affected by the thermal history of the crystal.

At temperatures below room temperatures, satellite spots developed on each side of the intense 100 main reflections. These too, appeared faster than it was possible to take the photographs, and must indicate the formation of some superstructure within the twin lamellae, but it has not been possible to investigate them further.

Structure analysis. In order to see whether there were significant structural changes on transformation, the crystal structure of Ascension Island vlasovite was determined at 20° C for comparison with the structure of Pyatenko and Voronkov (1961) for monoclinic vlasovite.

*hk*0 and 0*kl* Weissenberg photographs were taken of a crystal at 20° C. Intensities were measured visually, and the sums of the intensities of twin pairs of spots were taken. The refinement was made on a monoclinic basis, so that the structure is the average of the two triclinic twinned components. Anisotropic temperature factors were not applied, but isotropic temperature factors were high ($B = 3{\cdot}0\mathrm{e}/\mathrm{\AA}^2$ for Na, 1·0 for Zr, 0·8 for Si, 1·2 for O); probably they incorporated a spread factor consequent on the superposition of atomic peaks. The *R*-factor in the *a*-axis projection, in which the obliquity is greatest ($\gamma = 90^\circ\ 29'$) fell to only 14·9 %, but in the *c*-axis projection ($\alpha = 89^\circ\ 42'$) it fell to 11·6 %. Final coordinates are listed in table II together with inter-atomic distances and angles.

These values are in good agreement with those obtained by Pyatenko and Voronkov (1961) (cf. table II), indicating the close similarity of the monoclinic Russian vlasovite and the average of the twinned components of our Ascension Island material. The largest differences (significant ones) are in the coordinates of sodium and oxygen atoms.

Anistropies on the difference maps will depend to some extent on the degree of departure of the two twinned triclinic phases from the monoclinic, as the refinement of the structure was made on an average monoclinic basis; and major anisotropies should point to the structural changes occurring in the transformation. Fig. 4 shows the *a*- and *c*-axis difference maps at the limit of refinement. The sodium atoms and O_1 are distinctly anisotropic, and there is a significant, but less distinct, anisotropy of O_2, but there is no significant evidence of other anisotropies. Thus the atoms likely to have moved most in the transition are the sodium and O_1 and O_2 atoms, and the most plausible mechanism for the

TABLE II. Ascension Island vlasovite: refinement of superposed triclinic constituents

(i) Atomic coordinates (coordinates of the monoclinic vlasovite of Pyatenko and Voronkov (1961) are shown in brackets for comparison).

Fraction of cell edge.

Atom	x		y		z	
Na_1	0·0000	(0·000)	0·0733	(0·081)	0·7500	(0·750)
Na_2	0·0000	(0·000)	0·4002	(0·412)	0·7500	(0·750)
Zr	0·2500	(0·250)	0·2500	(0·250)	0·0000	(0·000)
Si_1	0·2653	(0·265)	0·0724	(0·072)	0·6381	(0·638)
Si_2	0·0484	(0·049)	0·2158	(0·216)	0·4282	(0·431)
O_1	0·0000	(0·000)	0·1651	(0·166)	0·2500	(0·250)
O_2	0·1463	(0·147)	0·1035	(0·103)	0·5068	(0·504)
O_3	0·1166	(0·111)	0·3586	(0·358)	0·4140	(0·418)
O_4	0·0574	(0·054)	0·2412	(0·239)	0·9682	(0·965)
O_5	0·2425	(0·243)	0·1336	(0·137)	0·7979	(0·800)
O_6	0·2941	(0·296)	0·0852	(0·088)	0·1546	(0·158)

(ii) Average isotropic temperature factors at the limit of refinement are
Na: 3·0 Å², Zr: 1·0 Å², Si: 0·8 Å², 0: 1·2 Å².

(iii) Bond lengths (errors given are standard deviations)

Si_1–O_2	1·59 Å	Si_2–O_1	1·60 Å	Na_1–O_1	2·38 Å
–O_3	1·61 Å	–O_2	1·61 Å	–O_2	2·86 Å
–O_5	1·55 Å	–O_3	1·63 Å	–O_2	2·86 Å
–O_6	1·60 Å	–O_4	1·60 Å	–O_4	2·50 Å
Mean	1·59 ± 0·02 Å	Mean	1·61 ± 0·01 Å	–O_4	2·50 Å
Zr–O_4	2·09 Å	Na_2–O_3	2·96 Å	–O_5	2·69 Å
–O_4	2·09 Å	–O_3	2·96 Å	–O_5	2·69 Å
–O_5	2·07 Å	–O_4	2·44 Å	Mean	2·64 ± 0·17 Å
–O_5	2·07 Å	–O_4	2·44 Å		
–O_6	2·11 Å	–O_6	2·27 Å		
–O_6	2·11 Å	–O_6	2·27 Å		
Mean	2·09 ± 0·02 Å	Mean	2·56 ± 0·30 Å		

(iv) Bond Angles

O_2–Si_1–O_3	108·9°	O_1–Si_2–O_2	104·8°	Si_2–O_1–Si_2	143·0°
O_2–Si_1–O_5	107·3°	O_1–Si_2–O_3	106·6°	Si_1–O_2–Si_2	146·0°
O_2–Si_1–O_6	112·1°	O_1–Si_2–O_4	115·1°	Si_1–O_3–Si_2	143·7°
O_3–Si_1–O_5	109·9°	O_2–Si_2–O_3	111·1°		
O_3–Si_1–O_6	106·9°	O_2–Si_2–O_4	112·1°		
O_5–Si_1–O_6	111·7°	O_3–Si_2–O_4	106·9°		

transformation would be one involving slight distortion of the bands of SiO_4 tetrahedra, allowing each sodium atom to occupy a slightly different position in the coordination polyhedron. Atomic movements do not appear (to judge from anisotropies) to exceed 0·2 Å.

Discussion of phase change. The change of obliquity with temperature shown by the graphs in fig. 3 indicates that the phase change begins below room temperature and is complete by 29° C. The fact that it occurs at such a low temperature, and that equilibrium is established so rapidly at each temperature shows that the energy barrier opposing the change in structure must be very small. A test over the temperature range −20° C to +30° C on a differential scanning microcalorimeter failed to show the change, indicating that the heat of reaction is less than about 5 cal/g.

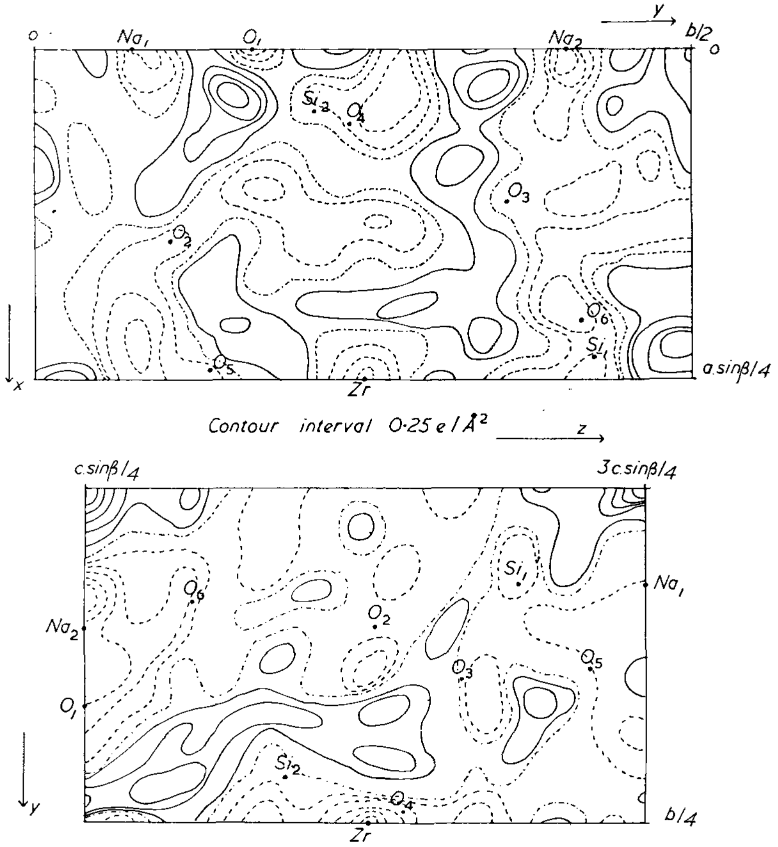


FIG. 4. Difference maps of *a*- and *c*-axis projections of vlasovite after refinement with the sum of intensities of twin spots (see text).

The transition is thus likely to be of displacive type (Buerger, 1948), the high-temperature monoclinic form of space group $C2/c$ relapsing on cooling to a mixture of triclinic forms $P\bar{1}$ related by twinning. This conclusion is confirmed by the structural investigation, which indicates a slight distortion of the silicon–oxygen bonds and a distinct movement of sodium atoms without a gross change in the over-all structure. Evidence for the nature of the change was also sought in infra-red spectra in the range 1200 to 400 cm^{-1} obtained above and below the transition point. Absorption maxima due to Si–O and Zr–O were not significantly displaced across the transition. Unfortunately peaks caused by Na–O interactions were at too long a wavelength to be measured on the instrument available.

Similar displacive transformations at low temperatures occur in $\alpha \rightarrow \beta_1$ tridymite (117° C) and $\alpha \rightarrow \beta$ cristobalite (200 to 275° C) (see e.g. Flörke, 1955 and Eitel, 1957), although the high-temperature phases are quenchable and thus the energy barrier to the transformations must be greater. A low-temperature transition from monoclinic to trigonal catapleiite, another sodium zirconium silicate, has also been reported (Flink, 1899; Bøggild, 1906). The transition temperature is extremely variable (10° C to 230° C), and this has been attributed to variation in chemical composition (Vlasov *et al.*, 1959). Perhaps minor differences in chemical composition account for the Russian vlasovite being monoclinic at room temperature.

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