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VLASOVITE, Na_2 Zr (Si_4O_{11}), FROM THE KIPAWA ALKALINE COMPLEX, QUEBEC, CANADA: CRYSTAL-STRUCTURE REFINEMENT AND INFRARED SPECTROSCOPY

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Abstract

The crystal structure of vlasovite, Na_2 Zr (Si_4O_{11}), from the Kipawa alkaline complex, Quebec, Canada, monoclinic, *a* 11.0390(5), *b* 10.0980(3), *c* 8.5677(4) Å, β 100.313(1)°, *V* 939.6(1) $Å^3$, space group *C*2/*c*, *Z* = 4, *D* (calc.) = 3.008 g.cm^{-3}, was refined to an R_1 index of 1.9% based on 1352 observed [$|F_o| > 4\sigma F$] unique reflections measured with Mo*K*α X-radiation on a Bruker *P*4 diffractometer equipped with a 4K CCD detector. An electron-microprobe analysis gave the composition $Na_{1.98}$ $Zr_{1.00}$ (Si_4O_{11}) based on 11 O *apfu*. In the crystal structure, there are two tetrahedrally coordinated *Si* sites with a grand <*Si*–O> distance of 1.612 Å, and one octahedrally coordinated *Zr* site with <*Zr*–O> = 2.085 Å. There are two *Na* sites: the *Na*(1) site is [7]-coordinated with <*Na*(1)–O> = 2.620 Å. The *Na*(2) site is split into two subsites, *Na*(2A) and *Na*(2B), with a separation of 0.829 Å, and the symmetry-related *Na*(2B) sites are separated by 1.525 Å. *Na*(2A) is octahedrally coordinated, and *Na*(2B) is [5]-coordinated, and their occupancies are 0.826(8) and 0.092(4) *Na*, respectively. Thus the *Na*(1) and aggregate *Na*(2) sites are each fully occupied. In the crystal structure of vlasovite, four-membered rings of (SiO_4) tetrahedra link together to form an $[Si_4O_{11}]^{6-}$ chain. Chains of tetrahedra and *Zr* octahedra link together to form a heteropolyhedral framework with channels extending along [001]. Three channels contain the Na atoms, which are bonded to O atoms of the octahedron–tetrahedron framework. Vlasovite is not significantly damaged by exposure to X-rays. Infrared spectroscopy shows that vlasovite can be free of H_2O or can contain variable amounts of H_2O; single crystals can be anhydrous in some regions and hydrous in other regions. Moreover, the H_2O content and its spectral response are unaffected by exposure of crystals to X-rays.

Keywords: vlasovite, Na–Zr silicate, crystal-structure refinement, infrared spectroscopy, H_2O.

Sommaire

Nous avons affiné la structure cristalline de la vlasovite, Na_2 Zr (Si_4O_{11}), provenant du complexe alcalin de Kipawa, au Québec, Canada, monoclinique, *a* 11.0390(5), *b* 10.0980(3), *c* 8.5677(4) Å, β 100.313(1)°, *V* 939.6(1) $Å^3$, groupe spatial *C*2/*c*, *Z* = 4, *D* (calc.) = 3.008 g.cm^{-3}, jusqu'à un résidu R_1 de 1.9% en utilisant 1352 réflexions uniques observées [$|F_o| > 4\sigma F$] et mesurées avec rayonnement Mo*K*α et un diffractomètre Bruker *P*4 muni d'un détecteur de type CCD 4K. Une analyse effectuée avec une microsonde électronique a donné la composition $Na_{1.98}$ $Zr_{1.00}$ (Si_4O_{11}) sur une base de 11 atomes d'oxygène par unité formulaire. Dans la structure, il y a deux sites *Si* à coordinence tétraédrique, avec une longueur de liaison <*Si*–O> moyenne de 1.612 Å, et un site *Zr* à coordinence octaédrique, avec <*Zr*–O> = 2.085 Å. Il y a deux sites *Na*: le site *Na*(1) a une coordinence [7], avec <*Na*(1)–O> = 2.620 Å. Le site *Na*(2) est partagé en deux sous-sites, *Na*(2A) et *Na*(2B), séparés par 0.829 Å, et les sites symétriquement liés *Na*(2B) montrent une séparation de 1.525 Å. *Na*(2A) a une coordinence octaédrique, et *Na*(2B) a une coordinence [5], et leurs taux d'occupation sont 0.826(8) et 0.092(4) *Na*, respectivement. Les sites *Na*(1) et l'aggrégat des sites *Na*(2) sont donc remplis. Dans la structure de la vlasovite, des anneaux à quatre tétraèdres (SiO_4) sont agencés pour former une chaîne $[Si_4O_{11}]^{6-}$. Des chaînes de tétraèdres et d'octaèdres *Zr* sont interconnectés pour former une trame hétéropolyédrique avec des canaux le long de [001]. Trois canaux contiennent les atomes Na, qui sont liés aux atomes d'oxygène de la trame d'octaèdres et de tétraèdres. La vlasovite ne semble pas endommagée de façon importante par le faisceau de rayons X. Les spectres infrarouges

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montrent que la vlasovite peut être dépourvue de H_2O ou bien peut contenir des quantités variables de H_2O; les monocristaux peuvent être anhydres dans certaines régions et hydratés dans d'autres. De plus, la teneur en H_2O et sa réponse spectrale semblent invariables si les cristaux sont exposés aux rayons X.

(Traduit par la Rédaction)

Mots-clés: vlasovite, silicate Na–Zr, affinement de la structure cristalline, spectroscopie infrarouge, H_2O.

INTRODUCTION

Vlasovite, $Na_2 Zr (Si_4O_{11})$, is an inosilicate mineral that occurs in alkaline rocks. It was originally described by Tikhonenkova & Kazakova (1961, 1978) from the Lovozero massif, Kola Peninsula, Russia, where it occurs as a metasomatic replacement of eudialyte in the contact zone of albitized eudialyte–microcline fenites and pegmatitic nepheline syenites (Gerasimovsky *et al.* 1974). Fleet & Cann (1967) found vlasovite as an accessory mineral in ejected blocks of peralkaline granite on Ascension Island (British Overseas Territory). Gittins *et al.* (1973) reported vlasovite as a primary phase in a K-feldspar – eudialyte – vlasovite – mosandrite – amphibole rock of the Kipawa complex in Villedieu Township, Quebec, Canada. Furthermore, Gittins *et al.* (1973) showed that vlasovite melts incongruently at 1250–1300°C to zircon + liquid, in accord with the textural evidence at Kipawa that indicates a primary origin for vlasovite at this locality. The crystal structure of vlasovite was solved by Voronkov & Pyatenko (1962), who showed that the principal silicate motif is an $[Si_4O_{11}]$ chain that links through octahedrally coordinated Zr and [6]- and [7]-coordinated Na. Fleet & Cann (1967) reported that vlasovite from Ascension Island is monoclinic but inverts to triclinic symmetry at 29°C, whereas Gittins *et al.* (1973) showed that vlasovite from the Kipawa complex is monoclinic from liquid-nitrogen temperature to 600°C. The structure was refined by Voronkov *et al.* (1974), who noted the high displacement-factor (B = 5.0 Å^2) for Na at the *Na*(2) site, and ascribed the monoclinic–triclinic transition to "possible ordered displacement [of Na] within the cavities of the framework". Gobechiya *et al.* (2003) refined the structure of vlasovite from the Kipawa complex and obtained some unusual results: the aggregate occupancy of the *Na* sites refined to 1.72 Na *apfu*, whereas the composition derived from electron-microprobe analysis indicated 2.02 Na *apfu*. Gobechiya *et al.* (2003) also showed that the infrared spectra of vlasovite before and after exposure to X-radiation (1) differ slightly in the wavenumber region of the Si–O stretching vibrations, and (2) show the presence of conspicuous absorption-bands due to the presence of H_2O in the irradiated crystal. They concluded that vlasovite suffered radiation damage when exposed to X-rays. We have refined the structure of vlasovite, also from Kipawa, Quebec, and obtained results that differ significantly from those of Gobechiya *et al.* (2003); we report them here.

EXPERIMENTAL

Crystals of vlasovite were obtained from the Kipawa region, Quebec, Canada. Typical crystals from this locality are shown in Figure 1. Vlasovite occurs as euhedral crystals up to 2 cm across, embedded in a matrix of pink to reddish eudialyte and separated from the eudialyte by a thin rind of gittinsite. There are actually two distinct locations for vlasovite at this locality, the uraninite pit and the eudialyte pit (pers. commun., Darrell B. MacFarlane, Grenville Minerals). Material deposited at the Canadian Museum of Nature is from the uraninite pit; material from both pits was examined during the course of this study, but most of the work was done on the material from the eudialyte pit.

Data collection and structure refinement

A single crystal was mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a Smart 4K CCD detector. The intensities of 7988 reflections with $\overline{15} < h < 15$, $\overline{14} < k < 14$, $\overline{12} < l < 12$ were collected to 60.00°2θ using 15 s per 0.2° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 1) were obtained from 5204 reflections with $I > 10\sigma(I)$.

On the basis of 1352 unique observed reflections, the crystal structure of vlasovite (initial atom-coordinates from Voronkov *et al.* 1974) was refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to R_1 = 1.9% and a GoF of 1.147. Scattering curves for neutral atoms were taken from Ibers & Hamilton (1992). The *R* indices are of the form given in Table 1, and are expressed as percentages. The *Na*(1) and *Na*(2) atoms were found to have U_{eq} values of 0.0301(5) and 0.0550(7) Å^2, similar to the analogous values of Voronkov *et al.* (1974) (0.043 and 0.066, respectively). At this stage, the difference-Fourier map (R_1 = 2.5%) revealed a peak 1.55 ± 0.9 Å from the *Na*(2) site. We included this peak in the refinement as the general site *Na*(2B) and renamed *Na*(2) as *Na*(2A). Site occupancies for these *Na* sites were refined with the scattering curves for Na, together with all other variables, and the refinement converged at R_1 = 1.9%. Atom positions and displacement parameters for vlasovite are given in Table 2, selected interatomic distances in Table 3, and bond valences in Table 4. Observed and calculated structure-factors are available from The Depository of

Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Electron-microprobe analysis

The chemical composition of the single crystal used for X-ray data collection was determined with a Cameca SX–100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 15 μm and count times on peak and background of 2 and 10 s, respectively. The following standards and crystals were used for *K* or *L* X-ray lines: diopside (Si, Ca), fayalite (Fe), zircon (Zr), albite (Na), olivine (Mg), eifelite (K) and andalusite (Al). On the basis of 11 O *apfu* (atoms per formula unit), the following chemical formula for vlasovite was obtained: $Na_{1.98}$ $Zr_{1.00}$ (Si_4O_{11}) (Table 5).

Infrared spectroscopy

Unpolarized single-crystal FTIR spectra were collected at room temperature using a Bruker Hyperion microscope, equipped with an MCT–A detector and a KBr beamsplitter, at a nominal resolution of 4 cm^{-1}; final spectra are the average of 128 scans. Samples were prepared as doubly polished slices ~200 μm thick. Polarized spectra were collected with a Nicolet Magna 760 spectrophotometer equipped with a MCT–A detector, a KBr beamsplitter and a gold-wire-grid ZnSe-substrate IR-polarizer. *In situ* high-temperature spectra were collected in the range 25–550°C on a single crystal with unpolarized light using a Linkam T600 heating stage equipped with ZnSe windows and a BaF_2 sample holder.

TABLE 1. MISCELLANEOUS REFINEMENT-DATA FOR VLASOVITE

a (Å)	11.0390(5)	Radiation / filter	Mo*K*α / graphite
b	10.0980(4)	2θ range for data collection (°)	60
c	8.5677(4)	*R*(int) (%)	1.5
β (°)	100.313(1)	Reflections collected	7988
V (Å^3)	939.6(1)	$F_o > 4\sigma F$	4583
Space group	*C*2/*c*	Independent reflections	1372
Z	4	$F_o > 4\sigma F$	1352
Absorption coefficient (mm^{-1})	1.83	Refinement method*	
F(000)	824	Goodness of fit on F^2	1.147
D_{calc} (g/cm^3)	3.008	Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]	R_1 = 1.9
Crystal size (mm)	0.08 × 0.16 × 0.18	*R* indices (all data) (%)	*R*1 = 1.9 *wR*2 = 5.5 Go*F* = 1.174

* Full-matrix least-squares on F^2, fixed weights proportional to $1/\sigma F_o^2$.

DESCRIPTION OF THE STRUCTURE

Coordination of the cations

In the crystal structure of vlasovite, there are two tetrahedrally coordinated Si sites with <*Si*–O> distances of 1.611 and 1.613 Å, respectively. The *Si*–O distances range from 1.637– 1.609 (to bridging O-atoms) to 1.594 Å (minimal, to apical O-atoms) (Table 3). There is one octahedrally coordinated *Zr* site with <*Zr*–O> = 2.085 Å. There are two *Na* sites occupied by Na: the [7]-coordinated *Na*(1) site (fully occupied by Na), with <*Na*(1)–O> = 2.620, the octahedrally coordinated *Na*(2A) site (occupied by 0.82 Na), with <*Na*(2A)–O> = 2.625, and the [5]-coordinated *Na*(2B) site (occupied by 0.09 Na), with <*Na*(2B)–O> = 2.525 Å. The *Na*(2A) site has a multiplicity of 4, and the *Na*(2B) general site has a multiplicity of 8; thus the *Na*(2A) and *Na*(2B) octahedra occur in the ratio 1 : 2. The *Na*(2A) atom has two close *Na*(2B) atoms (0.829 Å), and two *Na*(2B) atoms are separated by 1.525 Å. Figure 2 shows the difference electron-density distribution around a triplet *Na*(2B)–*Na*(2A)–*Na*(2B) (see Table 3). The shape of the triplet maxima indicates the presence of three sites and no splitting of the *Na*(2A) site.

TABLE 2. FINAL POSITIONS AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN VLASOVITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Zr	1/4	1/4	0	0.01314(13)	0.01159(13)	0.01088(13)	–0.00015(6)	0.00323(8)	0.00069(6)	0.01173(9)
Na(1) *	0	0.07593(13)	3/4	0.0406(8)	0.0229(6)	0.0308(7)	0	0.0151(5)	0	0.0304(4)
Na(2A) *	0	0.3985(2)	3/4	0.0265(9)	0.0312(10)	0.068(2)	0	–0.0140(10)	0	0.0448(8)
Na(2B) *	0.9851(12)	0.4308(15)	0.834(2)	0.0265(9)	0.0312(10)	0.068(2)	0	–0.0140(10)	0	0.0448(8)
Si(1)	0.26448(4)	0.07231(4)	0.63875(5)	0.0143(2)	0.0123(2)	0.0126(2)	–0.00110(15)	0.00227(15)	0.00067(14)	0.01306(11)
Si(2)	0.04996(4)	0.21676(5)	0.42721(5)	0.0120(2)	0.0161(2)	0.0135(2)	–0.00019(16)	0.00238(16)	0.00001(16)	0.01386(11)
O(1)	0	0.16001(19)	1/4	0.0265(9)	0.0209(9)	0.0133(8)	0	–0.0001(7)	0	0.0207(4)
O(2)	0.14362(14)	0.10274(16)	0.50471(18)	0.0260(7)	0.0284(7)	0.0281(7)	–0.0041(6)	–0.0083(6)	0.0125(6)	0.0291(3)
O(3)	0.11547(14)	0.35857(15)	0.4155(2)	0.0286(7)	0.0220(7)	0.0411(8)	–0.0070(6)	0.0182(6)	–0.0104(6)	0.0291(3)
O(4)	0.05651(13)	0.23057(14)	0.97038(17)	0.0156(6)	0.0249(6)	0.0206(6)	0.0016(5)	0.0065(5)	0.0001(5)	0.0200(3)
O(5)	0.23987(14)	0.13443(14)	0.80125(16)	0.0384(8)	0.0192(6)	0.0173(6)	–0.0052(5)	0.0091(5)	0.0006(5)	0.0244(3)
O(6)	0.28874(12)	0.08336(12)	0.14471(15)	0.0225(6)	0.0128(5)	0.0180(6)	0.0019(4)	0.0022(5)	–0.0014(4)	0.0179(2)

* The site occupancies for Na(1), Na(2A) and Na(2B) atoms are 4, [3.28Na + 0.72□] and [0.72Na + 7.28□], respectively.

Structure topology

In the crystal structure of vlasovite, Si tetrahedra link together to form an $[Si_4O_{11}]^{6-}$ chain (Fig. 3a). This chain was first described in vlasovite by Voronkov & Pyatenko (1962), and it has not been found in any other crystal structure as yet. In the chain, four-membered rings of (SiO_4) tetrahedra link *via* the anion O(3), a vertex common to two *Si*(2) tetrahedra. Figures 3b and 3c show linkage of the $[Si_4O_{11}]$ chains and (ZrO_6) octahedra in perpendicular directions. Each (ZrO_6) octahedron is connected to four Si–O chains (Fig. 4); it shares two *trans* vertices with two chains (Fig. 2b) and four vertices with two chains (Fig. 3c). In the crystal structure of vlasovite, Si–O chains and *Zr* octahedra link to form a heteropolyhedral framework (Fig. 4). Sodium atoms are located within the framework in channels that extend along [001] (Figs. 5a, b).

FIG. 1. Vlasovite from the Kipawa complex, Quebec. In both photographs, lozenge-shaped crystals of vlasovite (silver to dark grey) are embedded in a matrix of eudialite (brownish pink) with a thin rind of gittinsite (white to very pale yellow) separating the two minerals. The crystals of vlasovite are both ~2 cm in the longer dimension. Photographs by Jeff Scovil.

The presence of H_2O in vlasovite

Vlasovite, ideally $Na_2\ Zr\ (Si_4O_{11})$, is a nominally anhydrous mineral. Gobechiya *et al.* (2003) reported the presence of H_2O in vlasovite from Kipawa, Quebec, and suggested that H_2O was absorbed by the crystals of vlasovite after structural damage caused by exposure to Mo$K\alpha$ X-rays. In the present work, we first examined vlasovite from Kipawa by infrared spectroscopy prior

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR VLASOVITE

Zr–O(4)	×2	2.115(1)	*Na*(2A)–O(3)	×2	3.001(2)
Zr–O(5)	×2	2.051(1)	*Na*(2A)–O(4)	×2	2.532(2)
Zr–O(6)	×2	2.089(1)	*Na*(2A)–O(6)	×2	2.352(1)
<*Zr*–O>		2.085	<*Na*(2A)–O>		2.625
Na(1)–O(1)		2.383(2)	*Na*(2B)–O(3)a		2.593(14)
Na(1)–O(2)	×2	2.863(2)	*Na*(2B)–O(3)b		2.692(19)
Na(1)–O(4)	×2	2.444(2)	*Na*(2B)–O(4)		2.399(14)
Na(1)–O(5)	×2	2.672(2)	*Na*(2B)–O(6)c		2.474(14)
			Na(2B)–O(6)d		2.466(13)
<*Na*(1)–O>		2.620			
			<*Na*(2B)–O>		2.525
Si(1)–O(2)		1.626(1)			
Si(1)–O(3)		1.637(1)	*Na*(2A)–*Na*(2B)	×2	0.829(21)
Si(1)–O(5)		1.594(1)	*Na*(2B)–*Na*(2B)e		1.525(41)
Si(1)–O(6)		1.594(1)			
<*Si*(1)–O>		1.613			
Si(2)–O(1)		1.624(8)	*Si*(2)–O(1)–*Si*(2)f		138.7(1)
Si(2)–O(2)		1.609(2)	*Si*(1)–O(2)–*Si*(2)		144.3(1)
Si(2)–O(3)		1.616(2)	*Si*(1)g–O(3)–*Si*(2)		142.2(1)
Si(2)–O(4)		1.594(1)			
			<*Si*–O–*Si*>		141.7
<*Si*(2)–O>		1.611			

a: *x* + 1, –*y* + 1, *z* + 1/2; b: –*x* + 1, *y*, –*z* + 3/2; c: –*x* + 3/2, –*y* + 1/2, –*z* + 1; d: *x* + 1/2, –*y* + 1/2, *z* + 1/2; e: –*x* + 2, *y*, –*z* + 3/2; f: –*x*, *y*, –*z* + 1/2; g: –*x* + 1/2, –*y* + 1/2, –*z* + 1.

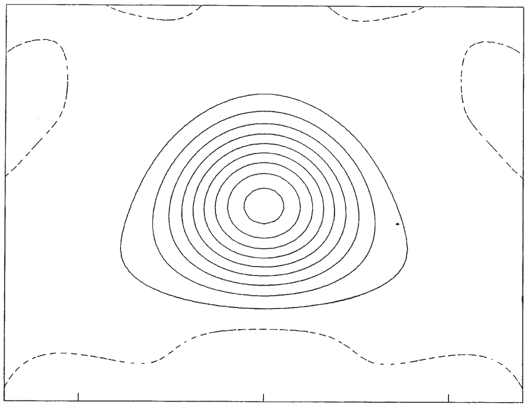

FIG. 2. Difference electron-density map with the *Na*(2A) site omitted from the calculation. Contours are at intervals of 2 $e/\text{Å}^3$, negative contours are dashed, zero contour omitted. Section x = 0.5, the *Na*(2A) atom with $x = 0.5$, $y = -0.1015$, $z = 0.75$ is the center of the plot. Length of the horizontal edge is 2.8 Å.

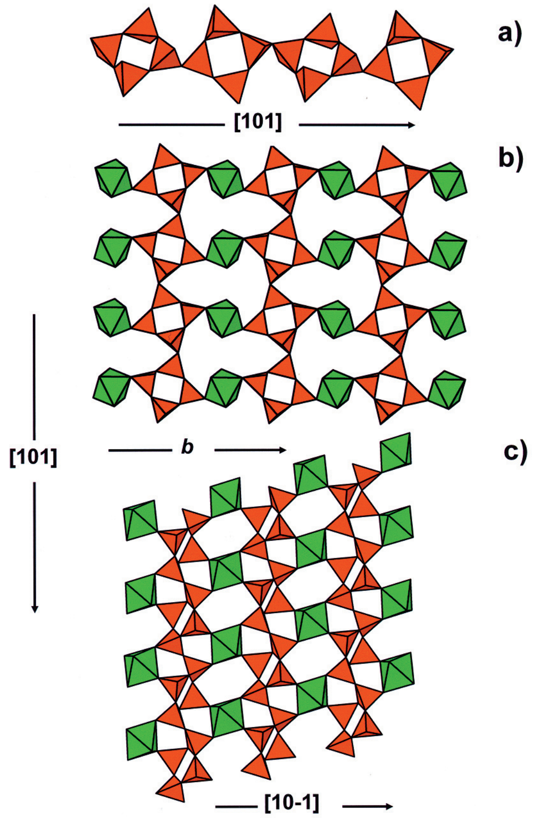

FIG. 3. The crystal structure of vlasovite: (a) an infinite Si–O chain $[Si_4O_{11}]^{6-}$; (b) linkage of $[Si_4O_{11}]^{6-}$ chains and (ZrO_6) octahedra viewed down [$\bar{1}01$] and (c) (010). The (SiO_4) tetrahedra are shown in orange, and the (ZrO_6) octahedra are green.

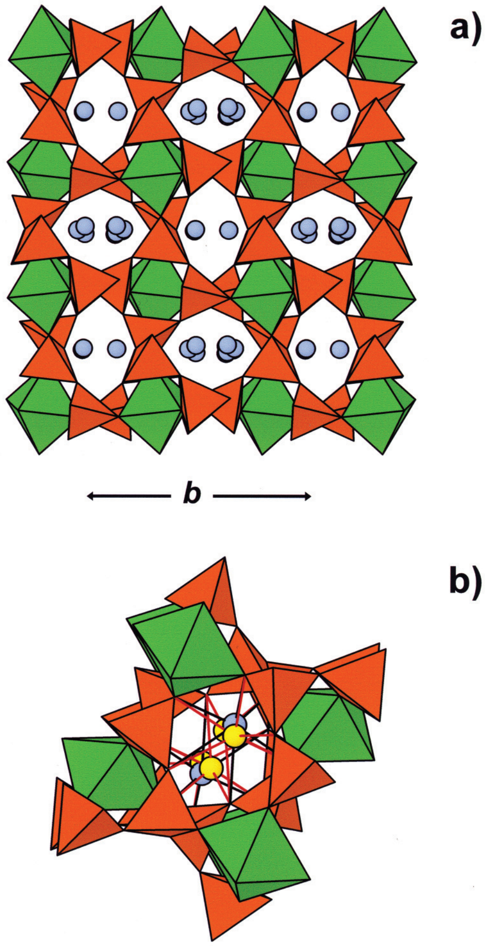

FIG. 5. (a) The crystal structure of vlasovite projected onto (001), (b) a fragment of the crystal structure of vlasovite showing coordination of *Na*(2A) and *Na*(2B) atoms. The *Si* tetrahedra are shown in orange, the *Zr* octahedra are green, the *Na* atoms are shown as blue circles in (a), and the *Na*(2A) and *Na*(2B) atoms are shown as blue and yellow circles (b), and bonds between *Na*(2A) and *Na*(2B) and oxygen atoms are shown as black and red lines.

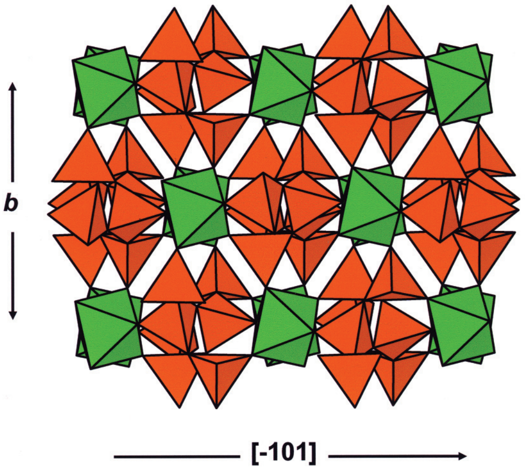

FIG. 4. The crystal structure of vlasovite: a mixed framework of $[Si_4O_{11}]^{6-}$ chains and (ZrO_6) octahedra. The legend is as in Figure 1.

TABLE 4. BOND-VALENCE* TABLE FOR VLASOVITE

	Zr	*Na*(1)	*Na*(2A)	*Na*(2B)	*Si*(1)	*Si*(2)	Σ
O(1)		0.213				$0.995^{\times2}\rightarrow$	2.203
O(2)		$0.097^{\times2}\downarrow$			0.989	1.035	2.121
O(3)			$0.065^{\times2}\downarrow$	$0.013^{\times2}\rightarrow$ $0.011^{\times2}\rightarrow$	0.961	1.016	2.054
O(4)	$0.614^{\times2}\downarrow$	$0.191^{\times2}\downarrow$	$0.138^{\times2}\downarrow$	0.019		1.078	2.040
O(5)	$0.739^{\times2}\downarrow$	$0.130^{\times2}\downarrow$			1.078		1.947
O(6)	$0.662^{\times2}\downarrow$		$0.186^{\times2}\downarrow$	$0.016^{\times2}\rightarrow$ $0.017^{\times2}\rightarrow$	1.078		1.959
Σ	4.030	1.049	0.778	0.076	4.106	4.174	

* Bond-valence parameters (*vu*) from Brown (1981).

TABLE 5. CHEMICAL COMPOSITION* (wt.%) AND UNIT FORMULA (*apfu*) FOR VLASOVITE

	(1)*	(2)**		(1)	(2)
SiO_2	56.52	56.82	Si	4.00	4.00
ZrO_2	28.98	29.19	Zr	1.00	1.00
Na_2O	14.50	14.53	Na	1.99	1.98
Total	100.00	100.54			

* Calculated from structural refinement. ** Chemical composition established by electron-microprobe analysis.

to any exposure of the samples to X-rays. Unpolarized microbeam infrared spectra of single crystals of vlasovite showed a patchy distribution of H_2O in single crystals: some areas of the polished crystals are anhydrous, whereas other areas contain sufficient H_2O to give a significant absorption in the 3600 (Fig. 6) and 1540 cm^{-1} regions. This patchy distribution of H_2O was confirmed on cleavage fragments of vlasovite, ensuring that H_2O had not been introduced to the crystal during sample preparation. Moreover, spectra show some (polarization) dependence on crystal orientation (Fig. 6), indicating that the H_2O contributing to the spectral response is not present as water in fluid inclusions. Figure 7 shows a series of spectra collected on a H_2O-rich area of a (non-irradiated) crystal. Although some detail in the spectra is lost with increasing temperature, the main signal remains to at least 550°C, indicating that the H_2O is strongly bound in the crystal.

The effects of irradiation of vlasovite by X-rays

Gobechiya *et al.* (2003) stated that vlasovite undergoes extensive radiation-damage when exposed even to weak X-rays (Mo X-ray tube operated at 30 kV and 5 mA for 19 h). We exposed both anhydrous and hydrous vlasovite to X-ray irradiation doses from 30 kV and 5 mA (0.15 kW) for 19 h to 50 kV and 40 mA (2.0 kW) for 24 h. There were no significant differences in the infrared spectra before and after irradiation (Fig. 8).

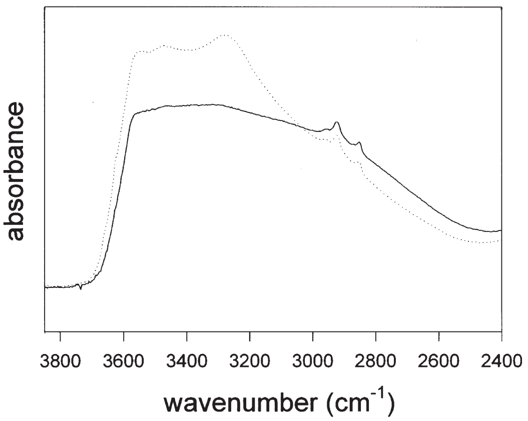

FIG. 6. Polarized infrared spectra of an (H_2O)-rich region of a randomly oriented doubly polished single crystal of vlasovite after irradiation by X-rays; the minor bands at 2800–3000 cm^{-1} are due to grease on the crystal). The spectra were collected at 90° rotation of the polarizer.

The origin of H_2O in vlasovite

There are several points to be considered in examining this issue:

(1) The presence of H_2O in vlasovite is not related to irradiation by X-rays;

(2) No mineral with radioactive components was found close to the crystals of vlasovite examined here. Uraninite is present in the uraninite pit at Kipawa, but is not closely associated with vlasovite. Moreover, there is no radioactive mineral in the eudialyte pit at Kipawa (Darrell MacFarlane, pers. commun.).

(3) Polarized infrared spectra measured on single crystals of vlasovite (Fig. 6) show a very prominent "wing" to the low-wavenumber side of the band maximum at ~3590 cm^{-1}. This behavior is seen in the infrared spectra of titanite (Hawthorne *et al.* 1991) and zircon (Aines & Rossman 1986), where it has been ascribed to the presence of a large number of local environments of OH due to structural damage.

It seems that the presence and character of H_2O in vlasovite cannot be assigned to radiation damage.

SUMMARY

(1) The crystal-structure refinement of vlasovite reported here confirms the basic model of Voronkov & Pyatenko (1962).

(2) There is positional disorder of Na at the *Na*(2) site in a channel in the mixed framework of (ZrO_6) octahedra and [Si_4O_{11}] chains; there are two sites, *Na*(2A) and *Na*(2B), separated by 0.83(2) Å.

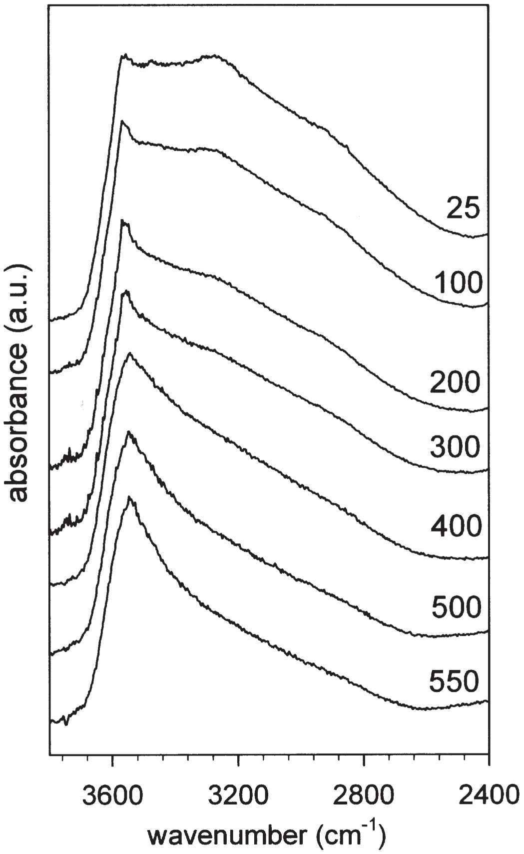

FIG. 7. Unpolarized infrared spectra of a doubly polished single-crystal of vlasovite in an (H_2O)-rich region of the crystal collected over a range of different temperatures (denoted on the right in °C).

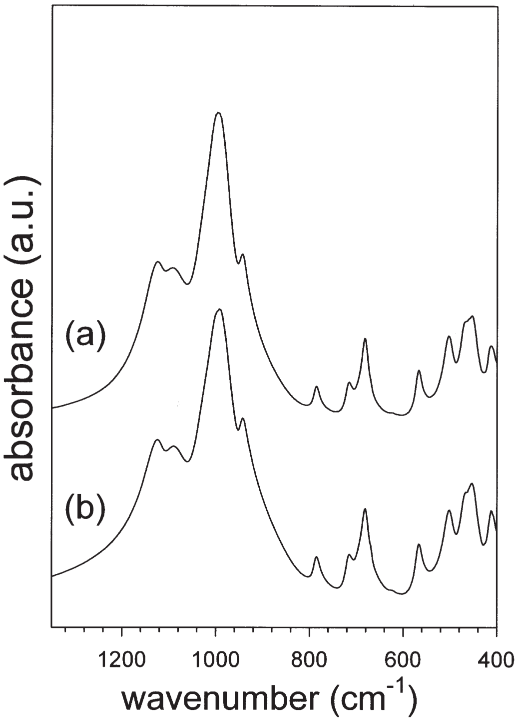

FIG. 8. Powder FTIR spectra of vlasovite (a) before irradiation, and (b) after irradiation.

(3) The chemical formula of vlasovite is $Na_2 Zr (Si_4O_{11})$. This formula agrees with structural data of Voronkov & Pyatenko (1962) and Voronkov *et al.* (1974), and disagrees with the structural data of Gobechiya *et al.* (2003).

(4) H can occur in vlasovite, and different parts of the same crystal can be anhydrous and hydrous, respectively.

(5) The method of incorporation of H_2O into vlasovite is not clear. Hydrogen may or may not be present in vlasovite, and it may be present as (H_2O) and possibly (OH). It is tempting to draw a parallel with the incorporation of H into quartz, leading to hydrolytic weakening. Indeed, the H-bearing species in vlasovite may be associated with microstructures that disturb the continuity of the crystal rather than being incorporated into the interstices of the undisturbed structure.

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