

## THE CRYSTAL STRUCTURE OF VUONNEMITE, $\text{Na}_{11}\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$ , A PHOSPHATE-BEARING SOROSILICATE OF THE LOMONOSOVITE GROUP

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### ABSTRACT

The crystal structure of vuonnemite,  $\text{Na}_{11}\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$  from Ilímaussaq, Greenland,  $a$  5.4984(6),  $b$  7.161(1),  $c$  14.450(2) Å,  $\alpha$  92.60(1),  $\beta$  95.30(1),  $\gamma$  90.60(1)°,  $V$  565.9(2) Å<sup>3</sup>, and from the Kola Peninsula, Russia,  $a$  5.4970(4),  $b$  7.1630(6),  $c$  14.437(2) Å,  $\alpha$  92.55(1),  $\beta$  95.30(1),  $\gamma$  90.61(1)°,  $V$  565.4(1) Å<sup>3</sup>, has been solved by direct methods in the space group  $P\bar{1}$  ( $Z = 1$ ) to a residual  $R$  value of ~2%. Vuonnemite is a phosphate-bearing sorosilicate. The structure is layered along [001], and consists of (1) a layer of dominantly edge- and face-sharing coordination polyhedra for Na and P atoms, (2) a layer with corner-linked  $\text{Si}_2\text{O}_7$  dimers and  $\text{NbO}_6$  octahedra, reinforced with  $\text{Na}\phi_8$  hexagonal bipyramids *via* edge-sharing, and (3) a close-packed layer of  $\text{NaO}_6$  and  $\text{TiO}_6$  octahedra. For all samples of vuonnemite analyzed, the  $(\text{Mn} + \text{Ca})$  content matches the Ti content in excess of 1.0 Ti *apfu*. The substitution  $(\text{Mn} + \text{Ca})^{2+} + \text{Ti}^{4+} \rightleftharpoons \text{Nb}^{5+} + \text{Na}^+$  operates, whereby Ti in excess of 1 *apfu* is disordered onto the Nb site, and  $(\text{Mn} + \text{Ca})$  populates the Na(2) and Na(3) sites. The compositional range for vuonnemite is now extended from near end-member compositions of  $(\text{Mn} + \text{Ca})_0\text{Na}_{11}\text{Ti}_1\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$  to  $(\text{Mn} + \text{Ca})_{0.33}\text{Na}_{10.67}\text{Ti}_{1.33}\text{Nb}_{1.67}(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$ . Correlation of mineral chemistry, crystal structure and unit-cell parameters allows prediction of many of the structural features of epistolite, the only member of the lomonosovite group for which a successful structure analysis has not been done.

**Keywords:** vuonnemite, phosphosilicate, crystal structure, lomonosovite group, Ilímaussaq, Greenland, Kola Peninsula, Russia.

### SOMMAIRE

Nous avons affiné la structure cristalline de la vuonnemite,  $\text{Na}_{11}\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$ , provenant d'Ilímaussaq, au Groenland,  $a$  5.4984(6),  $b$  7.161(1),  $c$  14.450(2) Å,  $\alpha$  92.60(1),  $\beta$  95.30(1),  $\gamma$  90.60(2)°,  $V$  565.9(1) Å<sup>3</sup>, et de la péninsule de Kola, en Russie,  $a$  5.4970(4),  $b$  7.1630(6),  $c$  14.437(2) Å,  $\alpha$  92.55(1),  $\beta$  95.30(1),  $\gamma$  90.61(1)°,  $V$  565.4(1) Å<sup>3</sup>, jusqu'à un résidu  $R$  d'environ 2% par méthodes directes, dans le groupe d'espace  $P\bar{1}$  ( $Z = 1$ ). La vuonnemite est un sorosilicate contenant des groupes phosphate. Il s'agit d'une structure stratifiée le long de [001], faite de (1) une couche de polyèdres à arêtes et à coins partagés renfermant les atomes Na et P, (2) une couche de dimères  $\text{Si}_2\text{O}_7$  à coins partagés et des octaèdres  $\text{NbO}_6$ , renforcés par des bipyramides hexagonales  $\text{Na}\phi_8$  par partage d'arêtes, et (3) une couche à agencement dense d'octaèdres  $\text{NaO}_6$  et  $\text{TiO}_6$ . Dans tous les échantillons de vuonnemite qui ont été analysés, le contenu en  $(\text{Mn} + \text{Ca})$  équivaut la proportion de Ti dépassant un atome par unité formulaire. Le schéma de substitution  $(\text{Mn} + \text{Ca})^{2+} + \text{Ti}^{4+} \rightleftharpoons \text{Nb}^{5+} + \text{Na}^+$  s'applique; les atomes de Ti au delà d'un atome par unité formulaire sont distribués de façon désordonnée sur le site Nb, et  $(\text{Mn} + \text{Ca})$  se trouvent au sites Na(2) et Na(3). L'intervalle de composition de la vuonnemite se voit augmenté, à partir de compositions près du pôle  $(\text{Mn} + \text{Ca})_0\text{Na}_{11}\text{Ti}_1\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$  à  $(\text{Mn} + \text{Ca})_{0.33}\text{Na}_{10.67}\text{Ti}_{1.33}\text{Nb}_{1.67}(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F},\text{OH})$ . Une corrélation des paramètres de composition, de la structure cristalline et des paramètres réticulaires mène à prédiction de plusieurs des aspects structuraux de l'épistolite, seul membre du groupe de la lomonosovite pour lequel une ébauche de la structure cristalline n'a pas encore été possible.

(Traduit par la Rédaction)

**Mots-clés:** vuonnemite, phosphosilicate, structure cristalline, groupe de la lomonosovite, Ilímaussaq, Groenland, péninsule de Kola, Russie.

### INTRODUCTION

Vuonnemite was first described from the Khibina and Lovozero massifs, Kola Peninsula, Russia, as  $\text{Na}_4\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2 \cdot 2\text{Na}_3\text{PO}_4$  (Bussen *et al.* 1973). Khomyakov (1976) proposed the formula  $\text{Na}_{11}\text{Ti}^{4+}\text{Nb}_2$

$(\text{Si}_2\text{O}_7)_2 \cdot (\text{PO}_4)_2 \cdot (\text{F},\text{O}_2)_2$ , establishing the presence of F. Rønsho *et al.* (1983) described vuonnemite from the Ilímaussaq intrusion, Greenland, and modified the formula of Khomyakov (1976) slightly:  $\text{Na}_5\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2 \cdot 2\text{Na}_3\text{PO}_4 \cdot \text{F} \cdot 1\frac{1}{2}\text{O}_2$ . Bussen *et al.* (1973) showed vuonnemite to be triclinic, space group  $P\bar{1}$  or

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$P\bar{1}$ ,  $a$  7.02,  $b$  14.15,  $c$  5.38 Å,  $\alpha$  93.7,  $\beta$  89.5,  $\gamma$  87.5°,  $Z = 1$ , and to be a member of the lomonosovite structural group. Rønso *et al.* (1983) reset the cell to conform with the conventional setting for the group:  $a$  5.501(1),  $b$  7.162(1),  $c$  14.440(1) Å,  $\alpha$  92.63(1),  $\beta$  95.33(1),  $\gamma$  90.57(1)°,  $V$  565.8 Å<sup>3</sup> for the sample from Ilímaussa. The present study of the crystal structure of vuonnemite was spurred by our interest in the structural systematics of (Nb,Ti)-silicate minerals, accentuated by apparent Ti-Nb order in this mineral, and by the ambiguities in its chemical formula.

### EXPERIMENTAL

The crystals used in this study are from the Ilímaussa intrusion (obtained from the Department of Mineralogy, Royal Ontario Museum, sample number M35502) and from the Umboserskiy mine, Lovozero massif, Kola peninsula (purchased from the Fersman Museum). These samples are designated I (Ilímaussa) and K (Kola). Crystals were mounted on Nicolet R3m (I) and Siemens P4 (K) automated four-circle diffractometers, and intense reflections were centered using graphite-monochromated MoK $\alpha$  X-radiation. Least-squares refinement of the setting angles resulted in the unit-cell parameters given in Table 1, and the orientation matrices used for data collection. The intensity data were measured over one asymmetric unit (I) and the whole sphere (K) to a maximum  $\sin \theta/\lambda$  of 0.7035. A psi-scan absorption correction was applied to each dataset, together with corrections for Lorentz, polarization and background effects. Further experimental details are provided in Table 1.

Subsequent to the collection of the intensity data, crystal K and a crystal from a neighboring region of the same sample were analyzed with an electron microprobe. The second fragment was mounted in epoxy, ground and polished. The crystal used in the collection of the intensity data is a thin plate (Table 1); it was laid

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA OF VUONNEMITE FROM THE LOVOZERO MASSIF, KOLA PENINSULA

	wt.%	$\sigma$		apfu
P <sub>2</sub> O <sub>5</sub>	13.0	0.5	Si	4.0
SiO <sub>2</sub>	21.5	0.4		
Nb <sub>2</sub> O <sub>5</sub>	20.1	0.5	P	2.0
TiO <sub>2</sub>	9.6	0.4		
Al <sub>2</sub> O <sub>3</sub>	0.13	0.05	Nb	1.67
MnO	1.59	0.07	Ti	1.33
FeO	0.10	0.05		
CaO	0.35	0.03	Mn	0.25
Na <sub>2</sub> O	30.0	0.4	Al	0.03
F	1.4	0.2	Fe	0.02
(H <sub>2</sub> O)*	0.15	—	Ca	0.07
O=F	-0.59	—	Na	10.7
Sum	<u>97.33</u>		$\Sigma$	<u>11.04</u>
			F	0.8
			OH	0.2

\* Mg not detected; \* F + OH = 1.0 apfu; 26 anions pfu

on the same probe mount with the cleavage surface parallel to the surface of the mount and carbon-coated. Analysis was done with the electron microprobe operating in wavelength-dispersion mode at an accelerating voltage of 15 kV and a sample current of 5 nA for Na, Si and P, and 10 nA for all other elements. The following standards were used: jadeite (Na), diopside (Ca,Si), apatite (P), fluororibeckite (F), titanite (Ti), MnNb<sub>2</sub>O<sub>6</sub> (Nb), forsterite (Mg), kyanite (Al), spessartine (Mn) and fayalite (Fe). Data were reduced using the  $\phi(\rho z)$  method of Pouchou & Pichoir (1985). Chemical compositions and unit formulae are given in Table 2. Bussen *et al.* (1973) did not detect OH in the infrared spectrum. The F values from previous chemical analyses are not quantitative [Bussen *et al.* (1973) did not report F; Rønso *et al.* (1983) gave only a range in F from 1.5–2.5%]. For

TABLE 1. MISCELLANEOUS INFORMATION FOR VUONNEMITE FROM ILÍMAUSSAQ (I) AND THE KOLA PENINSULA (K)

	I	K		I	K
$a$ (Å)	5.4984(6)	5.4970(4)	Space group	$P\bar{1}$	$P\bar{1}$
$b$	7.161(1)	7.1630(6)	Crystal size (mm)	0.13 x 0.15 x 0.30	0.035 x 0.23 x 0.23
$c$	14.450(2)	14.437(2)	$\mu$ (cm <sup>-1</sup> ), radiation	20.4, MoK $\alpha$	20.4, MoK $\alpha$
$\alpha$ (°)	92.60(1)	92.55(1)	Total $ F $ , $ F_0 $	3337, 3136	3097, 3097
$\beta$	95.30(1)	95.30(1)	Final $R$ (%)	1.8	2.0
$\gamma$	90.60(1)	90.61(1)	$wR$ (1)	2.3	—
$V$ (Å <sup>3</sup> )	565.9(2)	565.4(1)	$wR$ (2)	—	4.8
$Z$	1	1	Formula:	Na <sub>11</sub> Ti <sup>4+</sup> Nb <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> O <sub>3</sub> (F,OH)	

$$R = \Sigma(|F_0| - |F|) / \Sigma|F_0|$$

$$wR(1) = [\Sigma w(F_0^2 - F^2)^2 / \Sigma wF_0^4]^{1/2}, w = 1$$

$$wR(2) = [\Sigma w(F_0^2 - F^2)^2 / \Sigma w(F_0^4)^2]^{1/2}, w = 1 / [\sigma^2(F_0^2) + (a \times P)^2 + (b \times P)^2] \text{ where } a \text{ and } b \text{ are refinable parameters, and } P = \{[\max(0, F_0^2)] + 2F_0^2\} / 3.$$

For crystal K, an extinction correction  $X$  was refined according to the equation  $F_0^2 = kF_c^2[1 + 0.001 \times X \times F_c^2 \times \lambda^3/\sin(2\theta)]^{-4}$ , where  $k$  is the scale factor.

the Kola vuonnemite (this study), there is good agreement between the population of O(13), the site occupied by F, 0.82(4) F + 1.18(4) O, and the EMPA (electron-microprobe analysis) value of 0.8(1) F *apfu* (atoms per formula unit). Thus the anion composition for the O(13) site is O<sub>1.0</sub> + F<sub>0.8</sub>OH<sub>0.2</sub> *apfu*.

## STRUCTURE SOLUTION AND REFINEMENT

The programs SHELXTL and SHELXTL PC were used for solution and refinement of the structure, respectively, with scattering factors from the International Tables for X-ray Crystallography (1992) and Azavant

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR VUONNEMITE FROM ILMAUSSAQ (UPPER ROWS) AND LOVOZERO (LOWER ROWS)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Si(1)	0.18415(10)	0.21929(7)	0.69712(4)	64(2)	48(2)	72(2)	0(2)	9(2)	0(2)	61(1)
	0.18446(7)	0.21937(5)	0.69737(3)	81(2)	67(2)	88(2)	1(1)	8(1)	2(1)	79(1)
Si(2)	0.19844(10)	0.79366(7)	0.69464(4)	64(2)	49(2)	70(2)	5(2)	9(2)	2(2)	61(2)
	0.19918(7)	0.79300(5)	0.69471(3)	78(2)	68(2)	83(2)	5(1)	8(1)	2(1)	76(1)
P	0.31392(9)	0.25633(7)	0.06638(3)	86(2)	73(2)	73(2)	-5(2)	10(2)	0(2)	77(1)
	0.31393(7)	0.25693(5)	0.06812(3)	105(2)	90(2)	92(2)	-7(1)	12(1)	2(1)	96(1)
Nb	0.30112(3)	0.49172(2)	0.28387(1)	50(1)	57(1)	63(1)	3(1)	9(1)	3(1)	57(1)
	0.30111(2)	0.49199(2)	0.28413(1)	70(1)	79(1)	88(1)	5(1)	8(1)	1(1)	78(1)
Ti	0.97235(14)	0.00888(12)	0.50786(6)	-	-	-	-	-	-	58(1)
	0.97299(30)	0.00048(30)	0.50810(13)	82(7)	82(2)	64(6)	9(4)	6(4)	-4(4)	79(2)
Na(1)	0.1832(1)	0.9821(1)	0.8997(1)	251(5)	158(5)	192(5)	-4(4)	9(4)	36(4)	201(3)
	0.1837(1)	0.9822(1)	0.89983(5)	261(4)	174(3)	203(3)	-7(3)	8(3)	37(3)	214(2)
Na(2)	0.1953(1)	0.5079(1)	0.8680(1)	232(5)	138(5)	171(5)	-9(3)	-38(4)	-25(4)	185(3)
	0.1938(1)	0.5082(1)	0.86520(5)	302(4)	163(3)	208(4)	-12(2)	-36(3)	-20(2)	229(3)
Na(3)	0.4945(2)	0.2406(1)	0.5010(1)	119(4)	154(4)	200(5)	-60(3)	79(3)	-37(3)	158(3)
	0.4945(1)	0.2419(1)	0.50112(4)	159(3)	199(3)	256(4)	-65(2)	87(2)	-42(2)	203(2)
Na(4)	0.7053(2)	0.9928(1)	0.7358(1)	188(5)	205(5)	142(4)	4(4)	21(4)	-5(4)	178(2)
	0.7060(1)	0.9918(1)	0.73624(5)	203(3)	242(3)	159(3)	-3(3)	15(3)	-55(3)	202(2)
Na(5)	0.2493(2)	0.7369(1)	0.0803(1)	271(5)	154(5)	200(5)	37(4)	46(4)	15(4)	205(3)
	0.2507(2)	0.7368(1)	0.08094(5)	320(4)	162(3)	214(3)	35(3)	57(3)	20(3)	229(2)
Na(6)	0	1/2	1/2	179(6)	194(7)	203(7)	-21(5)	71(5)	-28(5)	190(4)
	0	1/2	1/2	181(5)	209(4)	223(5)	-23(4)	89(4)	-31(4)	203(2)
O(1)	0.4349(9)	0.3235(2)	0.7427(1)	106(7)	130(7)	126(7)	7(5)	6(5)	-46(5)	121(4)
	0.4355(2)	0.3240(2)	0.74295(6)	123(5)	155(5)	138(5)	-0(4)	3(4)	-59(4)	140(2)
O(2)	0.2036(3)	0.0057(2)	0.7350(1)	180(7)	58(6)	99(7)	0(5)	16(5)	16(5)	112(4)
	0.2034(2)	0.0048(1)	0.73487(7)	201(5)	56(4)	107(5)	4(3)	7(4)	15(4)	122(2)
O(3)	0.1614(3)	0.8017(2)	0.5738(1)	131(7)	99(6)	72(6)	7(5)	8(5)	19(5)	101(4)
	0.1624(2)	0.8012(1)	0.57348(7)	161(5)	112(4)	86(4)	12(4)	4(4)	10(4)	120(2)
O(4)	0.4602(3)	0.7099(2)	0.7190(1)	101(7)	122(7)	147(7)	-2(5)	-15(5)	53(5)	125(4)
	0.4615(2)	0.7095(2)	0.71855(6)	115(5)	143(5)	173(5)	-10(4)	-20(4)	52(4)	146(2)
O(5)	0.0518(3)	0.6964(2)	0.2550(1)	100(6)	104(7)	110(7)	-2(5)	24(5)	39(5)	104(4)
	0.0526(2)	0.6962(1)	0.25513(6)	110(5)	123(4)	136(5)	-4(4)	26(4)	38(4)	122(2)
O(6)	0.3231(3)	0.5156(2)	0.4057(1)	142(7)	183(6)	86(7)	-5(5)	18(5)	1(6)	137(4)
	0.3242(2)	0.5166(2)	0.40636(6)	157(5)	218(5)	106(5)	-11(4)	21(4)	0(4)	161(2)
O(7)	0.2563(3)	0.4304(2)	0.1302(1)	144(7)	79(6)	92(6)	-9(5)	22(5)	14(5)	105(4)
	0.2552(2)	0.4307(1)	0.13009(7)	169(5)	100(4)	109(5)	-9(4)	28(4)	16(4)	125(2)
O(8)	0.2369(3)	0.0734(2)	0.1081(1)	217(6)	87(7)	156(7)	10(5)	39(6)	-24(6)	152(6)
	0.2370(2)	0.0730(2)	0.10740(6)	249(6)	100(5)	173(5)	12(4)	42(4)	-29(4)	173(2)
O(9)	0.1802(3)	0.2094(2)	0.5855(1)	114(7)	100(6)	81(6)	-1(5)	8(5)	-9(5)	99(4)
	0.1610(2)	0.2093(1)	0.58525(7)	145(5)	111(4)	88(4)	3(3)	8(4)	-8(4)	115(2)
O(10)	0.4118(3)	0.7422(2)	0.9434(1)	87(7)	168(6)	212(6)	-34(6)	44(6)	3(6)	155(4)
	0.4113(2)	0.7415(2)	0.94321(6)	119(5)	188(5)	237(6)	-21(4)	54(4)	7(4)	180(2)
O(11)	0.1710(3)	0.2745(2)	0.9710(1)	247(6)	157(6)	103(7)	-12(6)	-57(6)	22(6)	174(5)
	0.1728(2)	0.2752(2)	0.97009(6)	273(6)	175(5)	133(5)	-8(4)	-67(5)	14(4)	199(2)
O(12)	0.0173(3)	0.3163(2)	0.2722(1)	116(7)	144(7)	142(7)	22(6)	29(5)	62(6)	133(4)
	0.0176(2)	0.3174(2)	0.27290(6)	141(5)	174(5)	165(5)	24(4)	28(4)	-68(4)	159(2)
O(13)	0.2887(3)	0.0024(2)	0.4230(1)	175(6)	201(7)	171(6)	2(5)	32(5)	-7(5)	181(4)
	0.2899(2)	0.0026(1)	0.42335(7)	165(5)	184(5)	130(5)	7(4)	28(4)	-15(4)	159(3)

\*U<sub>4</sub> × 10<sup>4</sup>

& Lichanot (1993). The structure was solved by direct methods. The  $|E|$ -statistics are inconclusive; the space group  $P\bar{1}$  was initially assumed, and its validity was confirmed by successful refinement of the structure. Of the four phase-sets passing the figure of merit threshold, only one generated an interpretable  $E$ -map based on the vuonnemite formula of Rønso *et al.* (1983). All cation positions were derived from this initial model, and were refined. The resulting difference-Fourier map gave all anion positions. Crystal I was refined using  $|F_o|$ , whereas crystal K was refined using  $F_o^2$  using the expression for  $wR(2)$  in Table 1. For crystal K, an extinction correc-

tion  $X$  was refined (Table 1). The shape of the displacement ellipsoid for  $Ti$  suggested that the atoms at the  $Ti$  site might be positionally disordered. On the basis of these data,  $Ti$  was modeled as two general positions about the center of inversion. Refinement converged rapidly to the  $R$  indices given in Table 1. Final positional and displacement parameters are given in Table 3, bond lengths in Table 4, and empirical bond-valences in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa K1A 0S2, Canada.

TABLE 4 INTERATOMIC DISTANCES (Å) IN VUONNEMITE FROM ILÍMAUSSAQ (I) AND THE LOVOZERO MASSIF, KOLA PENINSULA (K)

	I	K		I	K
$Si(1)-O(1)$	1.630(2)	1.633(1)	$P-O(7)$	1.569(2)	1.571(1)
$Si(1)-O(2)$	1.649(2)	1.653(1)	$P-O(8)$	1.539(2)	1.541(1)
$Si(1)-O(5)a$	1.634(2)	1.637(1)	$P-O(10)c$	1.527(2)	1.529(1)
$Si(1)-O(9)$	<u>1.604(2)</u>	<u>1.610(1)</u>	$P-O(11)d$	<u>1.533(2)</u>	<u>1.536(1)</u>
$\langle Si(1)-O \rangle$	1.629	1.633	$\langle P-O \rangle$	1.542	1.544
$Si(2)-O(2)b$	1.652(2)	1.651(1)	$Nb-O(1)c$	2.028(2)	2.024(1)
$Si(2)-O(3)$	1.600(2)	1.604(1)	$Nb-O(4)c$	1.963(2)	1.957(1)
$Si(2)-O(4)$	1.610(2)	1.609(1)	$Nb-O(5)$	2.048(2)	2.043(1)
$Si(2)-O(12)a$	<u>1.604(2)</u>	<u>1.606(1)</u>	$Nb-O(6)$	1.753(2)	1.756(1)
$\langle Si(2)-O \rangle$	1.617	1.618	$Nb-O(7)$	2.235(2)	2.238(1)
			$Nb-O(12)$	<u>1.984(2)</u>	<u>1.978(1)</u>
$Ti-O(3)c$	1.999(2)	1.992(2)	$\langle Nb-O \rangle$	2.002	2.000
$Ti-O(3)e$	1.986(2)	1.996(3)			
$Ti-O(9)f$	2.057(2)	2.038(2)	$Na(3)-O(3)c$	2.280(2)	2.274(1)
$Ti-O(9)g$	2.039(2)	2.057(2)	$Na(3)-O(6)c$	2.317(2)	2.299(1)
$Ti-O(13)g$	1.732(2)	1.734(1)	$Na(3)-O(8)$	2.590(2)	2.582(1)
$Ti-O(13)f$	<u>2.128(2)</u>	<u>2.129(1)</u>	$Na(3)-O(9)$	2.313(2)	2.306(1)
$\langle Ti-\phi \rangle$	1.990	1.991	$Na(3)-O(13)$	2.290(2)	2.291(1)
			$Na(3)-O(13)g$	<u>2.425(2)</u>	<u>2.427(1)</u>
$Na(1)-O(2)b$	2.406(2)	2.407(1)	$\langle Na(3)-\phi \rangle$	2.369(2)	2.363
$Na(1)-O(8)a$	2.332(2)	2.334(1)			
$Na(1)-O(10)$	2.219(2)	2.220(1)	$Na(4)-O(1)b$	2.813(2)	2.822(1)
$Na(1)-O(11)b$	<u>2.296(2)</u>	<u>2.294(1)</u>	$Na(4)-O(2)j$	2.759(2)	2.737(1)
$\langle Na(1)-O \rangle$	2.313	2.314	$Na(4)-O(2)b$	2.743(2)	2.764(1)
			$Na(4)-O(4)$	2.410(2)	2.407(1)
$Na(2)-O(1)$	2.629(2)	2.625(1)	$Na(4)-O(5)l$	2.577(2)	2.579(1)
$Na(2)-O(5)a$	2.517(2)	2.508(1)	$Na(4)-O(8)c$	2.317(2)	2.318(1)
$Na(2)-O(7)a$	2.531(2)	2.516(1)	$Na(4)-O(12)c$	2.706(2)	2.704(1)
$Na(2)-O(10)$	2.241(2)	2.244(1)	$Na(4)-O(13)c$	<u>2.313(2)</u>	<u>2.322(1)</u>
$Na(2)-O(11)$	2.318(2)	2.312(1)	$\langle Na(4)-\phi \rangle$	2.580	2.582
$Na(2)-O(12)a$	<u>2.801(2)</u>	<u>2.590(1)</u>			
$\langle Na(2)-O \rangle$	2.473	2.466	$Na(5)-O(1)c$	3.006(2)	2.989(1)
			$Na(5)-O(5)$	2.864(2)	2.856(1)
$Na(6)-O(3),a \times 2$	2.483(1)	2.481(1)	$Na(5)-O(7)$	2.341(2)	2.335(1)
$Na(6)-O(6),a \times 2$	2.342(2)	2.339(1)	$Na(5)-O(8)b$	2.427(2)	2.424(1)
$Na(6)-O(9),a \times 2$	<u>2.590(2)</u>	<u>2.588(1)</u>	$Na(5)-O(10)d$	2.246(2)	2.250(1)
$\langle Na(6)-O \rangle$	2.472	2.469	$Na(5)-O(11)a$	<u>2.361(2)</u>	<u>2.376(1)</u>
			$\langle Na(5)-O \rangle$	2.541	2.538

a:  $\bar{x}, \bar{y}+1, \bar{z}+1$ ; b:  $x, y+1, z$ ; c:  $\bar{x}+1, \bar{y}+1, \bar{z}+1$ ; d:  $x, y, z-1$ ; e:  $x+1, y-1, z$ ; f:  $x+1, y, z$ ;  
g:  $\bar{x}+1, \bar{y}, \bar{z}+1$ ; h:  $x, y+1, z+1$ ; i:  $\bar{x}+1, \bar{y}+2, \bar{z}+1$ ; j:  $x+1, y+1, z$

TABLE 5. BOND-VALENCE\* TABLE FOR VUONNEMITE FROM THE LOVOZERO MASSIF, KOLA PENINSULA

	Si(1)	Si(2)	P	Nb	Ti	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Σ
O(1)	0.98			0.71			0.11		0.07	0.05		1.92
O(2)	0.92	0.93				0.18			0.09 0.08			2.20
O(3)		1.06			0.62 <sup>vu</sup> <sub>-</sub> 0.61 <sup>vu</sup> <sub>-</sub>			0.25			0.16 <sup>vu</sup> <sub>!</sub>	2.09
O(4)		1.04		0.85			0.04		0.18			2.11
O(5)	0.97			0.67			0.15		0.12	0.07		1.98
O(6)				1.46				0.23 0.12			0.21 <sup>vu</sup> <sub>!</sub>	2.02
O(7)			1.15	0.40		0.14 0.04				0.22		1.95
O(8)			1.25			0.22			0.22	0.18		1.87
O(9)	1.04				0.55 <sup>vu</sup> <sub>-</sub> 0.52 <sup>vu</sup> <sub>-</sub>			0.23			0.12 <sup>vu</sup> <sub>!</sub>	1.93
O(10)			1.29			0.28	0.27			0.26		2.10
O(11)			1.26			0.24	0.23			0.20		1.93
O(12)		1.05		0.80			0.12		0.09			2.06
O(13)					0.37 <sup>vu</sup> <sub>-</sub> 1.24 <sup>vu</sup> <sub>-</sub>			0.21 0.16	0.20			1.38
Σ	3.91	4.08	4.95	4.89	3.91	0.92	1.10	1.20	1.05	0.98	0.98	

\* bond valences (*vu*) from curves of Brese & O'Keeffe (1991) for Si, Nb, Ti, and those of Brown (1981) for P, Na

## DESCRIPTION OF THE STRUCTURE

### Coordination of the cations

*The tetrahedrally coordinated sites:* There are two unique *Si* tetrahedra that link through the O(2) atom to form an [Si<sub>2</sub>O<sub>7</sub>] group with an Si(1)–O(2)–Si(2) angle of ~135°. The O(2) atom also bonds to three Na atoms, and hence the Si–O(2) distances are the longest in each tetrahedron in order to satisfy the local bond-valence requirements at the O(2) atom (Table 5). There is one unique *P* tetrahedron, and the P–O distances fall within the normal range exhibited by phosphate minerals (Baur 1974). There is no indication of any Si–P disorder over the *Si* and *P* sites.

*The high-valence octahedrally coordinated sites:* There are two high-valence octahedrally coordinated cation sites, *Nb* and *Ti*. There is a wide range of Nb–O distances (Table 4), from 1.75 to 2.25 Å. Table 5 shows that this distortion of the polyhedron is induced by the bond-valence requirements of the coordinating anions. The *Ti* cation shows significant positional disorder. This was modeled in the refinement by a split site, the Ti–Ti distance being 0.40 Å in both crystals. There is a wide range of Ti–O distances (Table 4), from 1.73 to 2.13 Å. There are four meridional Ti–O distances of ~2.0 Å and two axial distances of 1.73 and 2.13 Å, and the displacement (splitting) of the *Ti* site is along the direction of the axial bonds.

Refined site-scattering values and the unit formula (derived from the electron-microprobe results, Table 3) are available for crystal K, enabling reliable site-populations to be assigned. The SREF result indicates that the *Ti* site is completely occupied by Ti, and there is more than sufficient Ti in the unit formula for this assignment. The SREF result for the *Nb* site indicates that this site is occupied primarily by Nb, but also by a minor amount of a weaker X-ray scatterer. The unit formula (Table 3) suggests that this species is Ti. Refining the (Nb,Ti) occupancy of the *Nb* site gives extremely close agreement between the SREF results and the unit formula (Table 6).

*The Na sites:* There are six distinct Na positions, all fully or dominantly occupied by Na; these are illustrated in Figure 1. Na(1) is coordinated by a tetrahedron of O-atoms with a <Na(1)–O> distance of ~2.30 Å. The next-nearest O-atom is at ~3.03 Å, contributing an incident bond-valence of 0.05 *vu* only. Na(2), Na(3), Na(5) and Na(6) are each coordinated by six anions in a distorted octahedral arrangement. Na(4) is coordinated by eight anions in a hexagonal bipyramidal arrangement.

Site-scattering refinement for the Na(1), Na(4), Na(5) and Na(6) sites shows them to be fully occupied by Na. The occupancies of Na(2) and Na(3) were refined in terms of Na and Mn scattering factors, and the electron totals and site populations are presented in Table 6. The Na(3) site shows the most significant departure from "ideal Na occupancy" at 24.9(1) *epfu*; the Na(2)

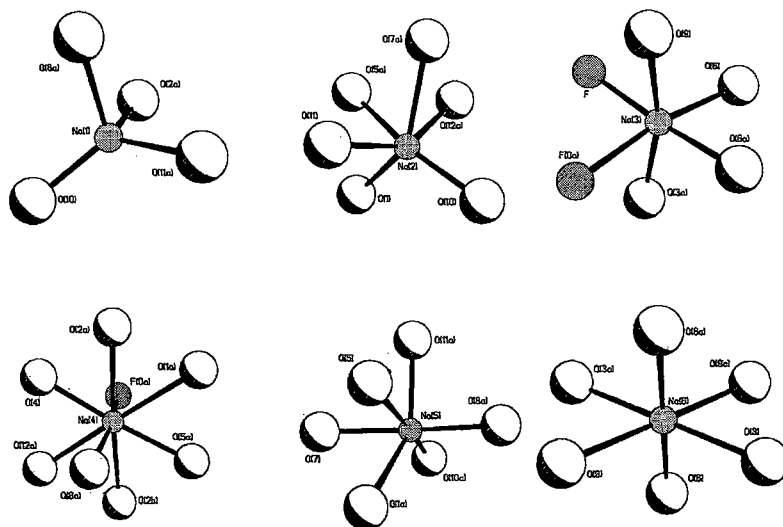


FIG. 1. The coordination of the six Na sites in vuonnemite; Na: dot-shaded circles; O: large highlighted circles; F: cross-hatched circles.

site has 23.3(1) *epfu* (electrons per formula unit). Bond-valence calculations (Table 5) using the Na curve of Brown (1981) give incident bond-valence sums for Na(1,4,5,6) very close to the ideal value of 1 *vu* (valence unit). The bond-valence sum for Na(2) is 1.10 *vu*, and for Na(3), 1.20 *vu*. These slight increases in valence totals are consistent with additional constituents 0.04 Mn + 0.07 Ca at Na(2) and 0.21 Mn at Na(3) in the Lovozero crystal. Substitution of Na and Mn<sup>2+</sup> at a site is unusual but not unknown; it occurs in samuelsonite (Moore & Araki 1977), barytolamprophyllite (Rastsvetaeva & Dorfman 1995), griphite (Rinaldi 1978) and alluaudite (Moore 1971), as well as many synthetic compounds.

*The O(13) site:* The chemical compositions (Table 2) indicate that there is only one F *apfu* to occupy the O(13) site, which has a formula multiplicity of 2. For the K crystal, the site occupancy of the O(13) position was refined and converged to 0.82(4) F + 1.18(4) O *apfu*. The bond valences incident at the O(13) site are listed

in Table 7 for occupancy of the O(13) site by O<sup>2-</sup>, F and OH. For the arrangement involving the short Ti–O(13) distance, occupancy of O(13) by O<sup>2-</sup> gives an incident bond-valence sum of 1.88 *vu* (Table 7), reasonably close to the ideal value of 2.0 *vu*, whereas occupancy of O(13) by F gives an incident bond-valence sum of 1.56 *vu*, in poor agreement with the ideal value of 1.0 *vu*. This indicates that the short Ti–O(13) configuration must involve O<sup>2-</sup> at the O(13) site. For the arrangement involving the long Ti–O(13) distance, similar occupancies give incident bond-valence sums of 1.07 and 0.86 *vu*, both reasonably close to the ideal value of 1.0 *vu*. This indicates that the long Ti–O(13) configuration must involve F or OH at the O(13) site. Moreover, for each short Ti–O(13) configuration, there must be a long Ti–O(13) configuration, indicating that the O(13) site must be occupied by 0.5 O<sup>2-</sup> + 0.5 (F + OH), giving 1.0 O<sup>2-</sup> and 1.0 (F + OH) *pfu*.

*A digression on [4]-coordinated Na:* The Na(1) site in vuonnemite is [4]-coordinated. This coordination for Na is unusual in minerals, but does occur in certain struc-

TABLE 6. SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS IN VUONNEMITE (K) FROM THE LOVOZERO MASSIF, KOLA PENINSULA

Site	Scattering species	SREF value ( <i>epfu</i> )	EMP value ( <i>epfu</i> )	Site-population ( <i>apfu</i> )
Nb	Nb, Ti	75.0(1)	75.7	1.67 Nb + 0.33 Ti <sup>4+</sup>
Ti	Ti	22.0	22.0	1.00 Ti <sup>4+</sup>
Na(1)	Na	22.0	22.0	2.00 Na
Na(2)	Na, Mn	23.3(1)	23.2	1.69 Na + 0.04 Mn <sup>2+</sup> + 0.07 Ca
Na(3)	Na, Mn	24.9(1)	24.9	1.79 Na + 0.21 Mn <sup>2+</sup>
Na(4)	Na	22.0	22.0	2.00 Na
Na(5)	Na	22.0	22.0	2.00 Na
Na(6)	Na	11.0	11.0	1.00 Na
O(13)	O <sup>2-</sup> , F <sup>-</sup>	16.8(1)	16.8	0.8 F <sup>-</sup> + 0.2 (OH) <sup>-</sup> + 1.0 O <sup>2-</sup>

TABLE 7. BOND VALENCES\* (*vu*) FOR VARIOUS OCCUPANCIES OF THE O(13) SITE BY DIFFERENT ANIONS IN VUONNEMITE CRYSTAL K

Bond	(Å)	O(13) =			
		O <sup>2-</sup>	(OH) <sup>-</sup>	F <sup>-</sup>	F <sup>-</sup>
O(13)–Na(3)	2.291	0.24	0.24	0.18	0.18
O(13)–Na(3)	2.427	0.18	0.18	0.14	0.14
O(13)–Na(4)	2.322	0.22	0.22	0.17	0.17
O(13)–Ti	1.734	1.24	–	1.07	–
O(13)–Ti	2.129	–	0.43	–	0.37
		1.88	1.07	1.58	0.86

\* Using Bragg & O'Keefe (1991) for Ti–φ and Brown (1981) for Na–φ (φ = O, F)

TABLE 8. MEAN BOND LENGTHS (Å) FOR TETRAHEDRALLY COORDINATED Na IN SELECTED MINERALS; THE FIFTH SHORTEST Na-O DISTANCE IS LARGER THAN 3.00 Å

Formula	Formula	Site	$\langle^{[4]}Na-O\rangle$	Ref.		
Atlitite	$Na_3K_6Ti^F(Al_2Si_6O_{28})Cl_3$	Na(1)	2.410	(1)		
		Na(2)	2.348			
Galeite	$Na_{15}(SO_4)_5F_2Cl$	Na(1)	2.431	(2)		
		Na(2)	2.440			
		Na(3)	2.382			
		Na(4)	2.393			
		Na(5)	2.419			
		Na(6)	2.430			
		Na(7)	2.447			
		Na(8)	2.421			
		Na(9)	2.416			
		Na(10)	2.443			
Kogarkolite	$Na_3(SO_4)F$	Na(1)	2.418	(3)		
		Na(3)	2.468			
		Na(4)	2.415			
		Na(5)	2.406			
		Na(7)	2.455			
		Na(8)	2.375			
		Na(9)	2.370			
		Na(10)	2.451			
		Na(11)	2.414			
		Na(13)	2.399			
		Sborgite	$Na[B_3O_6(OH)_4](H_2O)_3$	Na(2)	2.287	(4)
		Schalrerite	$Na_{21}(SO_4)_7F_6Cl$	Na(1)	2.459	(5)
				Na(2)	2.448	
Na(3)	2.437					
Na(4)	2.425					
Na(5)	2.442					
Na(6)	2.440					
Na(7)	2.372					
Na(8)	2.376					
Na(9)	2.475					
Na(10)	2.477					
Na(11)	2.442					
Na(12)	2.406					
Na(13)	2.395					
Na(14)	2.428					
Sulphohalite	$Na_6(SO_4)_2FCl$	Na(1)	2.428	(6)		
Teepelite	$Na_3[B(OH)_4]Cl$	Na(1)	2.454	(7)		
Tunilite	$NaCa_2Al_4(CO_3)_4(OH)_6Cl$	Na(1)	2.429	(8)		
Vlasovite	$Na_2ZrSi_4O_{11}$	Na(2)	2.427	(9)		

Refs: (1) Ferraris *et al.* (1995); (2) Fanfani *et al.* (1975a); (3) Fanfani *et al.* (1980); (4) Merlino & Sartori (1972); (5) Fanfani *et al.* (1975b); (6) Sakamoto (1968); (7) Effenberger (1982); (8) Effenberger *et al.* (1981); (9) Voronkov *et al.* (1974).

tures, and a brief review of this feature is warranted. A selected list of minerals with  $[^4]Na$ , together with the stereochemical details, is given in Table 8. The grand  $\langle[^4]Na-O\rangle$  distance in the structures of Table 8 is 2.432 Å, with an observed range in  $\langle Na-O\rangle$  of 2.29–2.48 Å. The  $\langle Na(1)-O\rangle$  distance for vuonnemite, 2.313 Å, occurs in the lower part of this range. The variation in individual  $[^4]Na-\phi$  ( $\phi$ : unspecified anion) is 2.28–2.58 Å, and the fifth nearest anion is always  $>3$  Å from the central Na site. Thus there is no question of the occurrence of the [4]-coordination around Na in any of these structures.

### Chemical substitution in vuonnemite

Rønso *et al.* (1983) gave a range of Ti contents for vuonnemite from Ilímaussaq [0.95 to 1.12 Ti *apfu*, based on  $(25 O^{2-} + 1 F^-)$  *pfu*]. With increased Ti values, Rønso *et al.* (1983) noted that Nb contents decrease progressively (1.95 to 1.88 Nb *apfu*), and a coupled substitution involving  $Ti \rightleftharpoons Nb$  and  $P \rightleftharpoons Si$  was proposed. The Ilímaussaq vuonnemite analyzed by Rønso *et al.* (1983) contains 0.01 to 0.02 Mn *apfu* and 0.06 to 0.10 Ca *apfu*; the maximum (Mn + Ca) content is 0.12 *apfu*. Similarly, the Kola vuonnemite analyzed by Bussen *et al.* (1983) and Khomyakov (1976) contains 0.08 Mn and 0.05 Ca *apfu*, giving an (Mn + Ca) sum of 0.13 *apfu*. The Kola vuonnemite analyzed in this study contains 0.25 Mn and 0.07 Ca, giving an (Mn + Ca) sum of 0.32 *apfu*. The Ti content of crystal K is 1.33 *apfu*. This sample contains the largest (Mn + Ca) and Ti values reported thus far. For the crystals of vuonnemite analyzed, the (Mn + Ca) content matches the Ti content in excess of 1.0 Ti *apfu*. The substitution  $(Mn + Ca)^{2+} + Ti^{4+} \rightleftharpoons Nb^{5+} + Na^+$  operates, whereby Ti in excess of 1 *apfu* is disordered at the Nb site and (Mn + Ca) populates the Na(2) and Na(3) sites. The compositional range for vuonnemite is now extended from near end-member compositions of  $(Mn + Ca)_0Na_{11}Ti_1Nb_2(Si_2O_7)_2$

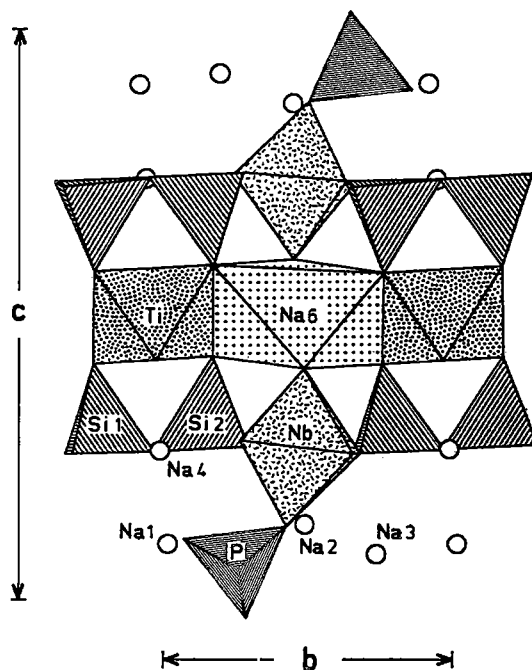


FIG. 2. The structure of vuonnemite projected down [001]. For simplicity, Na(1) to Na(4) are given as spheres rather than represented by their coordination polyhedra. Na(5) is located behind the  $TiO_6$  and  $Na(6)O_6$  octahedra.

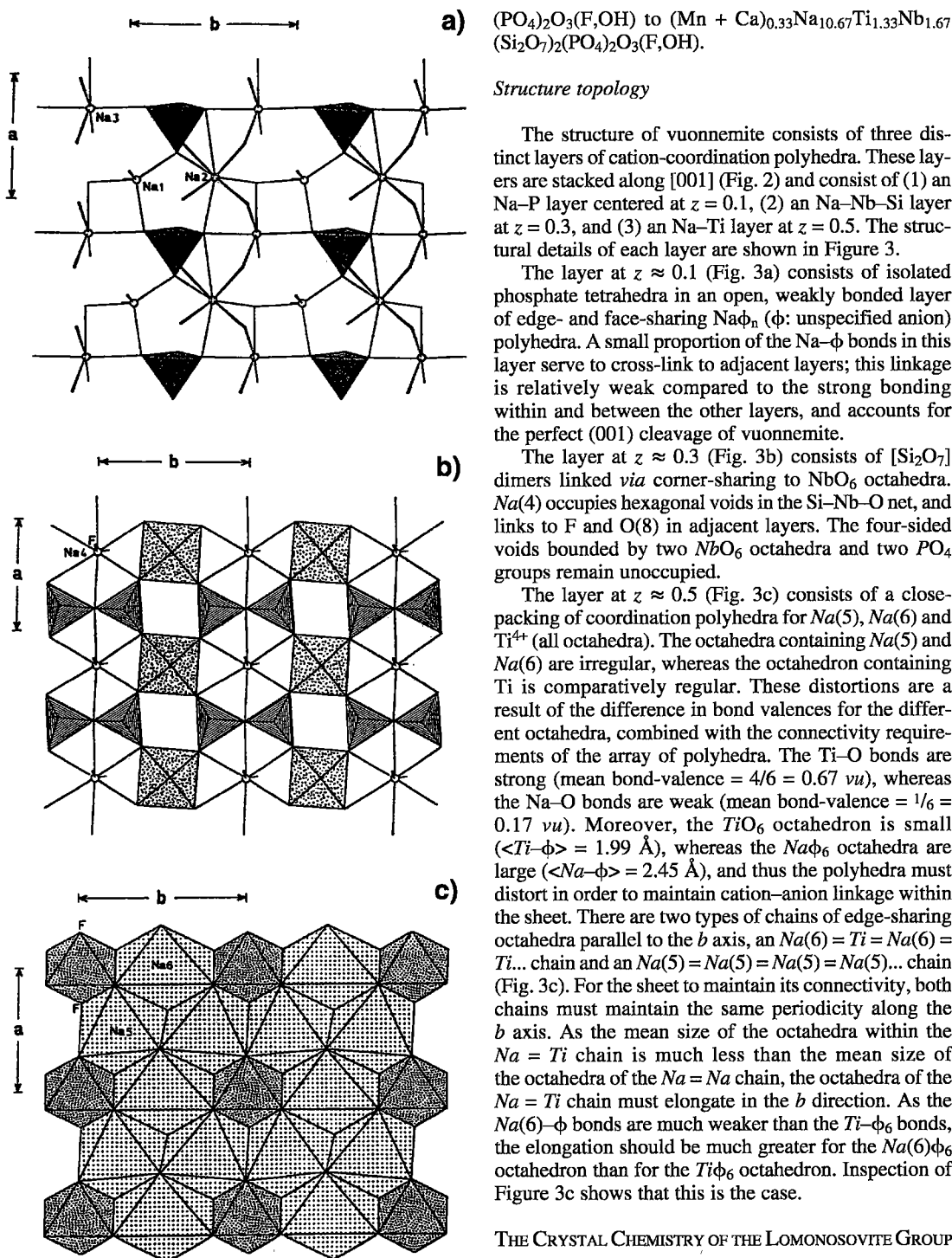


FIG. 3. The layers of the vuonnemite structure (perpendicular projections): (a): layer at  $z = 0.1$ ; (b): layer at  $z = 0.3$ ; (c): layer at  $z = 0.5$ . Polyhedron shading is as in Figure 2.

#### THE CRYSTAL CHEMISTRY OF THE LOMONOSOVITE GROUP

Vuonnemite is a member of the lomonosovite group of silicate and P-bearing silicate minerals, and to date, is the only member of this group with appreciable



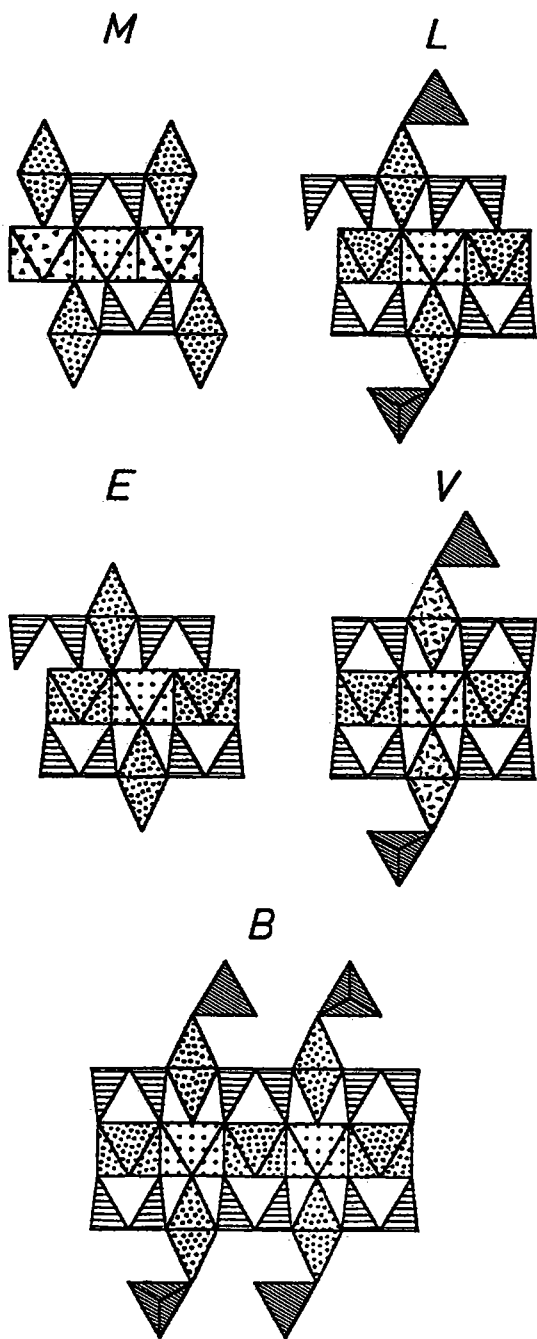


FIG. 4. Aspects of the structural crystallography of the minerals of the lomonosovite group: murmanite (M), epistolite (E), lomonosovite (L), vuonnemite (V) and  $\beta$ -lomonosovite (B). Polyhedron shading is derived from Figure 1: phosphate tetrahedra in narrow ruling, silicate tetrahedra in broader ruling,  $Na\phi_x$  polyhedra in regular stippling,  $TiO_6$  octahedra in dense random stippling,  $NbO_6$  octahedra in short hatching, and  $MnO_6$  octahedra in triangles.

Ti-Nb order. The layers of the vuonnemite structure at  $z = 0.3$  and  $z = 0.5$  have topological analogues with the other members of the group (lomonosovite,  $\beta$ -lomonosovite, murmanite and epistolite), from which they differ mainly in terms of cation order and layer stacking (Fig. 4). These structural similarities translate into predictable similarities in unit-cell parameters: (1) all members of the group have an  $a$  cell-edge similar to that of murmanite, (2) the  $b$  cell-edge corresponds to a two-octahedron repeat of the fundamental building block (FBB) pictured in Figure 4; the exception is  $\beta$ -lomonosovite, which has a doubled FBB and thus a doubled  $b$  cell-edge, (3) the  $c$  cell-edge is approximately 12 Å for phosphate-free members of the group; if phosphate is present,  $c$  is 2.5 Å longer, and (4) with regard to interaxial angles,  $\alpha \approx \beta \approx \gamma \approx 90^\circ$  for a nearly orthogonal vuonnemite-like motif; interaxial angles that approach or exceed  $100^\circ$  indicate varying degrees of inclination of layer-stacking sequences.

To date, the structures of all members of the lomonosovite group are known, except that of epistolite (Karup-Møller 1986). We have made several attempts to date to obtain a crystal of epistolite suitable for structure analysis, with no success. However, correlation between chemistry, structure and unit-cell parameters ( $a$  5.4,  $b$  7.0,  $c$  12.0 Å,  $\alpha$  103,  $\beta$  96,  $\gamma$  88°) of the minerals of this group allow prediction of many aspects of the epistolite structure: (1) epistolite has a  $b$  cell-edge similar to that of murmanite, and thus should have a two-octahedron repeat along  $b$ ; (2) epistolite has a  $c$  cell-edge and composition that indicate an absence of phosphate; (3) epistolite has interaxial angles nearly identical to those of lomonosovite, and thus should have a topologically identical layer-stacking sequence to lomonosovite. The resulting FBB for epistolite, analogous to those in Figure 4 for other members of the lomonosovite group, is given in Figure 4(E). The only topological aspect of the crystal structure that cannot be predicted at present is the structure of the layer that connects adjacent FBBs along  $Z$ . This weakly bonded Na-rich layer is topologically different for each member of the group for which a structure is known. Although epistolite is similar to lomonosovite in terms of its layer stacking, the absence of phosphate in the Na-layer of the epistolite structure should result in a topology of the Na-layer different from that of lomonosovite.

## CONCLUSIONS

1. The ideal formula of vuonnemite is  $Na_{11} Ti^{4+} Nb_2 (Si_2O_7)_2 (PO_4)_2 O_3 (F, OH)$ .
2. Titanium and niobium order at different sites, atypical behavior for (Nb,Ti)-silicates.
3. Vuonnemite has a layer structure consisting of three layers of polyhedra along  $Z$ : (1) a layer of phosphate tetrahedra and various  $Na\phi_n$  polyhedra, (2) a layer of corner-sharing  $[Si_2O_7]$  dimers and  $NbO_6$  octahedra,

reinforced with  $Na\phi_8$  polyhedra, and (3) a layer of edge-sharing  $Na\phi_6$  and  $TiO_6$  octahedra. Elements of the structure, particularly layers (2) and (3), occur in other members of the lomonosovite group, as well as other titanosilicates.

4. By analogy with other members of the lomonosovite group, many structural elements of the crystal structure of epistolite can be predicted from its unit-cell parameters: (1) epistolite has a two-octahedron repeat along  $b$ , (2) epistolite does not have phosphate in its structure, and (3) epistolite has a layer-stacking sequence similar to that in lomonosovite.

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