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PARAVINOGRADOVITE, $(Na,\square)_2\ [(Ti^{4+},Fe^{3+})_4\ \{Si_2\ O_6\}_2\ \{Si_3\ Al\ O_{10}\}\ (OH)_4]\ H_2O$, A NEW MINERAL SPECIES FROM THE KHIBINA ALKALINE MASSIF, KOLA PENINSULA, RUSSIA: DESCRIPTION AND CRYSTAL STRUCTURE

Alexander P. KHOMYAKOV and Inna E. KULIKOVA

Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, 121357 Moscow, Russia

Elena SOKOLOVA[§] and Frank C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Pavel M. KARTASHOV

Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry, Staromonetny per. 35, 109017 Moscow, Russia

Abstract

Paravinogradovite is a new mineral species from Mount Kukisvumchorr, Khibina alkaline massif, Kola Peninsula, Russia. Paravinogradovite forms prismatic crystals elongate along [100] and up to 0.5–1.0 cm long; crystals in some cases occur in fan-shaped aggregates sporadically scattered throughout a matrix of feldspar, nepheline and natrolite in a strongly mineralized nepheline–feldspar pegmatite. Associated minerals are nepheline, K-feldspar, albite, analcime, natrolite, aegirine, biotite, chlorite, zircon, ilmenite, pyrochlore, ancylite-(Ce), nordstrandite, carbonate-fluorapatite, fluorite, galena and cerussite. Crystals of paravinogradovite are colorless to white, with a white streak and a luster that varies from vitreous to pearly. The mineral is translucent to transparent, and shows weak yellow-green fluorescence under 240–400 nm ultraviolet radiation. Paravinogradovite has a perfect cleavage on {001} and an indistinct cleavage on {010}. It is brittle, has a splintery fracture and a Mohs hardness of 5. Its observed and calculated densities are 2.77(2) and 2.76 g/cm^3, respectively. It is biaxial negative with α 1.707(2), β 1.741(2), γ 1.755(2), $2V$(obs.) = 64(1)°, $2V$(calc.) = 64°, nonpleochroic with dispersion $r > v$, with $Z \approx b$, $X \wedge a = 30°$. Paravinogradovite is triclinic, space group $P1$, a 5.2533(1), b 8.7411(3), c 12.9480(5) Å, α 70.466(1), β 78.472(1), γ 89.932(1)°, V 547.65(5) Å^3, Z = 1. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(I)((hkl)] are: 3.182(100)(013,014), 5.88(65)(011,012), 11.9(58)(001), 4.35(38)(021,102), 5.98(35)(002), 3.085(29)(123) and 2.735(21)(122). Chemical analysis by electron microprobe gave SiO_2 43.54, Al_2O_3 6.12, Fe_2O_3 4.11, Nb_2O_5 0.50, TiO_2 29.59, BeO 0.76, MgO 0.13, Na_2O 7.77, K_2O 0.87, H_2O 6.23, sum 99.62 wt.%, where the amount of Be and the amount of H_2O were determined by crystal-structure analysis, and the valence state of Fe was determined by Mössbauer spectroscopy. The resulting empirical formula on the basis of 26 anions (including OH = 4 *apfu* and excluding H_2O) is $(Na_{2.293}\,K_{0.169})\ (Ti^{4+}{}_{3.386}\,Fe^{3+}{}_{0.471}\,Mg_{0.029}\,Nb_{0.034})\ (Si_{6.626}\,Al_{1.098}\,Be_{0.276})\ O_{22}\ (OH)_4\ (H_2O)_{1.16}$. There are prominent endothermic effects at 280 and 460°C; the principal losses in weight are within the temperature ranges 150–400 (3.8%) and 400–600°C (2.8%), and the total loss in weight at 980°C is 7.1%. The principal absorptions in the infrared are as follows: 3520, 3330, 3240, 1633, 1105, 989, 940, 725, 691, 638, 599, 568, 523, 459 and 418 cm^{-1}, indicative of both OH and H_2O in the structure. The name recognizes the close structural and chemical relations between paravinogradovite and vinogradovite, ideally $Na_5\ Ti^{4+}{}_4\ (Si_7Al)\ O_{26}\ (H_2O)_3$. The crystal structure of paravinogradovite was solved by direct methods and refined to an R_1 index of 4.5% based on 4373 observed [$F_o > 4\sigma F$] unique reflections measured with Mo$K\alpha$ X-radiation and a Bruker $P4$ diffractometer with a CCD detector. Four (SiO_4) tetrahedra form pyroxene-like $[Si_2O_6]$ chains, and three (SiO_4) tetrahedra and one (AlO_4) tetrahedron form vinogradovite-like $[Si_3AlO_{10}]$ chains parallel to [100]. (MO_6) octahedra ($M \approx Ti^{4+}$) share common edges to form two distinct zig-zag brookite-like chains along [100]. One chain is decorated by (XO_6) octahedra ($X \approx$ Na) and linked into a sheet parallel to (100) by $[Si_3AlO_{10}]$ chains. The other distinct brookite-like chain is not decorated by (XO_6) octahedra, but is linked into a sheet parallel to (100) by $[Si_3AlO_{10}]$ chains. Chains of tetrahedra and chains of octahedra link to form a framework with channels along [100]. These channels contain disordered (H_2O) groups, the $A(5)$ site partly occupied (14%) by K, and the $A(1)$–$A(4)$ sites partly occupied (15–19%) by Na, giving a channel content of $[Na_{0.72}\,K_{0.14}\,(H_2O)_{1.16}]$. The triclinic cell of paravinogradovite is related to the C-centered monoclinic cell of vinogradovite, ideally $Na_5\ Ti^{4+}{}_4\ (Si_7Al)\ O_{26}\ (H_2O)_3$ [monoclinic, a 24.490(10), b 8.657(4), c 5.203(2) Å, β 100.2(0)°, V 1085.8 Å^3, space group $C2/c$, Z = 2] by the matrix transformation (0 0 1, 0 1 0, –½ 1 0).

Keywords: paravinogradovite, new mineral species, crystal structure, Ti silicate, vinogradovite, Khibina massif, Kola Peninsula, Russia.

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§ *E-mail address*: elena_sokolova@umanitoba.ca

Sommaire

La paravinogradovite est une nouvelle espèce minérale découverte au mont Kukisvumchorr, complexe alcalin de Khibina, péninsule de Kola, en Russie. Elle se présente en cristaux prismatiques allongés sur [100] et jusqu'à 0.5–1.0 cm en longueur; dans certains cas, les cristaux sont fibroradiés et disséminés aléatoirement dans une matrice de feldspath, néphéline et natrolite d'une pegmatite à néphéline–feldspath fortement minéralisée. Lui sont associés néphéline, feldspath potassique, albite, analcime, natrolite, aegyrine, biotite, chlorite, zircon, ilménite, pyrochlore, ancylite-(Ce), nordstrandite, carbonate-fluorapatite, fluorite, galène et cérussite. Les cristaux de paravinogradovite sont incolores à blancs, avec une rayure blanche et un éclat de vitreux à nacré. Ils sont translucides à transparents, et montrent une faible fluorescence dans le jaune à vert à 240–400 nm en lumière ultraviolette. La paravinogradovite possède un clivage parfait sur {001} et un clivage indistinct {010}. Elle est cassante, avec une fracture en échapes, et sa dureté de Mohs est 5. Les densités, observée et calculée, sont 2.77(2) et 2.76 g/cm^3, respectivement. Elle est biaxe négative, avec α 1.707(2), β 1.741(2), γ 1.755(2), $2V$(obs.) = 64(1)°, $2V$(calc.) = 64°, non pléochroïque, avec dispersion $r > v$, et $Z \approx b$, $X \wedge a = 30°$. La paravinogradovite est triclinique, groupe spatial $P1$, a 5.2533(1), b 8.7411(3), c 12.9480(5) Å, α 70.466(1), β 78.472(1), γ 89.932(1)°, V 547.65(5) Å^3, $Z = 1$. Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å(I)((hkl)] sont: 3.182(100)(013,014), 5.88(65)(011,012), 11.9(58)(001), 4.35(38)(021,102), 5.98(35)(002), 3.085(29)(123) et 2.735(21)(122). Une analyse chimique par microsonde électronique a donné SiO_2 43.54, Al_2O_3 6.12, Fe_2O_3 4.11, Nb_2O_5 0.50, TiO_2 29.59, BeO 0.76, MgO 0.13, Na_2O 7.77, K_2O 0.87, H_2O 6.23, somme 99.62% (poids); la teneur en Be et la quantité de H_2O ont été déterminées par ébauche de la structure, et la valence du Fe a été déterminée pas spectroscopie de Mössbauer. La formule empirique qui résulte de ces mesures, calculée sur une base de 26 anions (y inclus OH = 4 groupes par unité formulaire, et excluant le H_2O) est $(Na_{2.293}\ K_{0.169})\ (Ti^{4+}{}_{3.386}\ Fe^{3+}{}_{0.471}\ Mg_{0.029}\ Nb_{0.034})\ (Si_{6.626}\ Al_{1.098}\ Be_{0.276})\ O_{22}\ (OH)_4\ (H_2O)_{1.16}$. Le minéral montre des effets endothermiques prominents à 280 et 460°C; les pertes en poids principales ont lieu sur les intervalles 150–400 (3.8%) et 400–600°C (2.8%), et la perte totale en poids en chauffant jusqu'à 980°C est 7.1%. Les absorptions principales dans l'infrarouge sont comme suit: 3520, 3330, 3240, 1633, 1105, 989, 940, 725, 691, 638, 599, 568, 523, 459 et 418 cm^{-1}, indication de la présence de OH et de H_2O dans la structure. Le nom signale le lien chimique et structural étroit avec la vinogradovite, dont la formule idéale est $Na_5\ Ti^{4+}{}_4\ (Si_7Al)\ O_{26}\ (H_2O)_3$. La structure cristalline de la paravinogradovite a été résolue par méthodes directes et affinée jusqu'à un résidu R_1 de 4.5% sur une base de 4373 réflexions uniques observées [$F_o > 4\sigma F$], et mesurées avec rayonnement Mo$K\alpha$ et un diffractomètre Bruker $P4$ muni d'un détecteur de type CCD. Quatre tétraèdres (SiO_4) forment des chaînes [Si_2O_6], comme dans les pyroxènes, et trois tétraèdres (SiO_4) et un tétraèdre (AlO_4) forment des chaînes [Si_3AlO_{10}] ressemblant à celles de la vinogradovite, parallèles à [100]. Les octaèdres (MO_6, $M \approx Ti^{4+}$) partagent des arêtes pour former deux chaînes en zig-zag distinctes le long de [100], ressemblant à celles de la brookite. Une de ces chaînes est décorée avec des octaèdres (XO_6, $X \approx$ Na) et de telles chaînes sont liées en feuillets parallèles à (100) par les chaînes [Si_3AlO_{10}]. L'autre chaîne, ressemblant à celle de la brookite, n'est pas décorée par des octaèdres (XO_6); ces chaînes sont aussi liées en feuillets parallèles à (100) par les chaînes [Si_3AlO_{10}]. Les chaînes de tétraèdres et les chaînes d'octaèdres forment ensemble une trame munie de canaux le long de [100]. Ces canaux contiennent des groupes (H_2O) désordonnés; le site A(5) serait partiellement occupé (14%) par le K, et les sites A(1)–A(4) le seraient (15–19%) par le Na, pour un contenu des canaux de $[Na_{0.72}\ K_{0.14}\ (H_2O)_{1.16}]$. La maille triclinique de la paravinogradovite est apparentée à la maille monoclinique à C centré de la vinogradovite, dont la formule idéale est $Na_5\ Ti^{4+}{}_4\ (Si_7Al)\ O_{26}\ (H_2O)_3$ [monoclinique, a 24.490(10), b 8.657(4), c 5.203(2) Å, β 100.2(0)°, V 1085.8 Å^3, groupe spatial $C2/c$, $Z = 2$] par la matrice de transformation (0 0 1, 0 1 0, –½ 1 0).

(Traduit par la Rédaction)

Mots-clés: paravinogradovite, nouvelle espèce minérale, structure cristalline, silicate de Ti, vinogradovite, complexe alcalin de Khibina, péninsule de Kola, Russie.

Introduction

Evolved nepheline syenites with hyperagpaitic pegmatites are the products of extremely alkaline melts (Khomyakov 1995). The Khibina and Lovozero massifs in the Kola Peninsula, Russia, are a gigantic (about 2000 km^2) complex of agpaitic nepheline syenites with associated large deposits of rare metals and phosphates. This complex is the type locality of about 150 minerals, and over 500 mineral species are known to occur there.

Here we describe a new Ti silicate, referred to as a vinogradovite-like mineral (M48) by Khomyakov (1995). This mineral was discovered about 20 years ago, but at that time, its study could not be completed because of a lack of crystals suitable for crystal-structure investigation. Improved detector technology remedied this situation, and a single-crystal study of the new mineral shows that its chemical composition and structure are closely related to those of vinogradovite; as a result, the new species is named paravinogradovite, from Greek *para* (close by) and *vinogradovite*. Paravinogradovite was approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (IMA 2002–033). The holotype specimen is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia (catalogue number 2883/1).

Occurrence

The type specimens of paravinogradovite were collected by A.P.K. in 1986 and by P.M.K. in 1988, and the mineral was originally recognized as a potentially new species (M48) by Khomyakov (1990, 1995). The mineral occurs in the central part of the Khibina alkaline massif, Kola Peninsula, Russia, on the northeastern spur of Mt. Kukisvumchorr.

The specimens were collected from a pegmatite emplaced at the contact between a xenolith of corundum-bearing hornfels and the enclosing foyaite. The lenticular pegmatite, approximately 1–1.5 m wide, is asymmetrically zoned. There are four zones from the contact with hornfels toward the contact with foyaites: (1) coarse-grained aegirine – diopside – orthoclase rock with altered nepheline and abundant disseminated pyrochlore, (2) a blocky K-feldspar zone, (3) a rounded nepheline core with disseminated ilmenite and pyrochlore, and (4) a banded medium- to coarse-grained biotite – aegirine – diopside – nepheline – feldspar rock. In the pegmatite, there are two types of superimposed alteration, occurring primarily within the nepheline zone. The earlier albite-type alteration resulted in aggregates of tabular albite with miarolitic cavities and disseminated bipyramidal zircon. The later zeolite-type alteration consists of aggregates of analcime–natrolite. Both types of alteration seem to involve late-stage hydrothermal infilling.

Paravinogradovite occurs in miarolitic cavities associated with the albite-type alteration, growing directly on albite. Carbonate-fluorapatite, ancylite-(Ce), natrolite and aegirine are closely associated with paravinogradovite. Usually, aegirine and paravinogradovite form radial aggregates. All miarolitic minerals are encrusted with fine flakes of a glauconite-like mineral, which occasionally completely fills the miarolitic cavity. Other associated species include nordstrandite, anatase, fluorite, galena and cerussite as a pseudomorph after galena. Paravinogradovite crystals contain very small inclusions of vinogradovite.

PHYSICAL AND OPTICAL PROPERTIES

Paravinogradovite forms fan-shaped aggregates of columnar and acicular crystals up to 0.5–1.0 cm long and elongate along [100]. The crystals are colorless to white, with a white streak and a luster that varies from vitreous to pearly. They are transparent or translucent and show weak yellow-green fluorescence under 240–400 nm ultraviolet radiation. They have perfect cleavage on {001} and indistinct cleavage on {010}. The mineral is brittle, has a splintery fracture and a Mohs hardness of 5. Measured (using the volumetric method) and calculated densities are 2.77(2) and 2.76 g/cm^3, respectively. The mineral is not reactive in 1:1 HCl and HNO_3 at room or higher temperature.

Optical measurements were made with a Fedorov universal stage, using sodium light (λ = 589 nm). Paravinogradovite is biaxial negative, α 1.707(2), β 1.741(2), γ 1.755(2), $2V(obs) = 64(1)°$, $2V(calc) = 64°$, nonpleochroic with dispersion $r > v$. We were only able to obtain partial information on the optical orientation owing to the nature of the crystals: $b \approx Z$, $a \wedge X = 30°$. This orientation is quite different from that of vinogradovite: $b \approx X$, $a \wedge Z = 7°$. Owing to this difference, paravinogradovite has negative elongation and vinogradovite has positive elongation of cleavage fragments, making the two minerals readily distinguishable in thin section.

CHEMICAL COMPOSITION

Crystals of pararinogradovite were analyzed with a Camebax Microbeam and a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, and beam diameters of 5 and 20 μm. The following standards were used: (for Camebax Microbeam) albite (Na$K\alpha$, Si$K\alpha$), orthoclase ($KK\alpha$, Al$K\alpha$), diopside (Mg$K\alpha$), ilmenite (Fe$K\alpha$, Ti$K\alpha$), and synthetic $LiNbO_3$ (Nb$L\alpha$); (for Cameca SX–50) parakeldyshite (Na), $K_2 Zr Si_2 O_7$ (K), diopside (Mg, Si), almandine (Fe), $Y_3 Al_5 O_{12}$ (Al), $Sr Ti O_3$ (Ti), $Li Nb O_3$ (Nb). Also sought but not detected were Ca, Mn and F. The data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1984, 1985). The amount of H_2O was determined by the Penfield method, and the presence and quantity of OH and H_2O groups were established by crystal-structure solution and refinement; their presence was also confirmed by infrared spectroscopy. Both chemical compositions (Table 1) indicate a minor deficiency in the sum of the tetrahedrally coordinated cations. Rønsbo *et al.* (1990) showed that vinogradovite from Ilímaussaq contains minor Be. This observation is

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF PARAVINOGRADOVITE

	(1)	(2)		(1)	(2)
TiO_2	29.38	29.59	Be	–	0.276
Fe_2O_3	4.44	4.11	Al	1.11	1.098
MgO	0.15	0.13	Si	6.81	6.626
Nb_2O_5	0.58	0.50	Σ	7.92	8.000
Na_2O	6.98	7.77			
K_2O	0.74	0.87	Ti^{4+}	3.36	3.386
BeO *	–	0.76 *	Fe^{3+}	0.51	0.471
Al_2O_3	6.13	6.12	Mg	0.03	0.029
SiO_2	43.82	43.54	Nb	0.04	0.034
H_2O	6.67 †	6.23 *	Σ	3.94	3.920
Total	98.89	99.62			
			Na	2.06	2.293
			K	0.14	0.169
			(OH)	4	4
			(H_2O)	1.4	1.160

(1) Mean of seven points on three seperate grains;
(2) Mean of eighteen points on the crystal used for structure analysis.
* derived by stoichiometry;
† determined by the Penfield method.

in accord with the apparent deficiency in tetrahedrally coordinated cations in the formulae of Table 1. Moreover, Be minerals (*e.g.*, barylite, bromellite, leucophanite, leifite, chrysoberyl, epididymite) are common in the pegmatites of this region. Thus Be was assumed to be present in paravinogradovite; the Be content given in Table 1 was calculated by the relation Be = 8 – Si – Al *apfu*. Table 1 gives the chemical composition and formula unit based on 26 anions [including 4 (OH) and excluding (H_2O)] *pfu* (per formula unit).

The principal absorptions in the infrared spectrum are as follows: 3520, 3330, 3240, 1633, 1105, 989, 940, 725, 691, 638, 599, 568, 523, 459 and 418 cm^{-1}. The Mössbauer spectrum of paravinogradovite (pers. commun., V.S. Rusakov, Moscow State University) is a symmetrical doublet with a CS (center shift) of 0.35(1) mm/s relative to α-Fe and a QS (quadrupole splitting) value of 0.47(2) mm/s. These values are indicative of Fe^{3+} in octahedral coordination. The presence of a very weak doublet with a CS of 1.28 and QS of 3.1 mm/s indicates minor [6]-coordinated Fe^{2+}. The amount of Fe^{2+} does not exceed 2–3% of the total Fe content and corresponds approximately to the amount of relict grains of primary vinogradovite included in paravinogradovite. The sharp absorption band at 3520 cm^{-1} is attributed to the stretching vibrations of (OH) groups, whereas the broad envelope centered at 3240 cm^{-1} and the narrow band at 1633 cm^{-1} correspond to H_2O stretching and bending vibrational modes, respectively. Differential thermal analysis showed prominent endothermic effects at 280 and 460°C. The principal losses in weight are within the temperature ranges 150–400 (3.8 wt%) and 400–600ºC (2.8 wt%), and the total loss in weight at 980°C is 7.1 wt%. This value is in accord with the amount of H_2O (6.67 wt.%) determined by the Penfield method (Table 1).

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR PARAVINOGRADOVITE

I	d_{meas} Å	d_{calc} Å	*h k l*	I	d_{meas} Å	d_{calc} Å	*h k l*
58	11.9	12.0	0 0 1	6	2.388	2.390	2 0 3
35	5.98	5.98	0 0 2	"	"	2.388	2 1 3
65	5.88	5.89	0 $\bar{1}$ 1	3	2.216	2.216	2 2 1
"	"	5.89	0 1 2	"	"	2.216	0 3 5
14	4.49	4.50	1 1 1	4	2.178	2.178	2 0 4
"	"	4.49	$\bar{1}$ 1 0	6	2.140	2.140	1 3 5
38	4.35	4.37	0 2 1	6	2.078	2.075	1 2 6
"	"	4.36	1 0 2	5	2.007	2.007	$\bar{1}$ 4 1
3	4.22	4.23	1 1 0	3	1.955	1.955	$\bar{1}$ 4 3
"	"	4.22	$\bar{1}$ 1 1	5	1.934	1.933	1 3 6
3	4.19	4.20	0 $\bar{1}$ 2	3	1.914	1.915	0 $\bar{4}$ 1
"	"	4.20	1 1 2	"	"	1.915	0 4 5
"	"	4.19	1 $\bar{1}$ 1	5	1.855	1.855	1 4 5
4	4.10	4.10	0 2 0	4	1.819	1.818	1 2 7
"	"	4.100	0 2 2	"	"	1.818	1 $\bar{2}$ 5
4	3.611	3.612	$\bar{1}$ 1 2	3	1.802	1.800	0 1 7
3	3.522	3.526	0 2 3	"	"	1.800	2 3 5
7	3.323	3.323	1 2 2	5	1.747	1.748	$\bar{1}$ 3 6
100	3.182	3.182	0 $\bar{1}$ 3	"	"	1.746	3 0 1
"	"	3.182	0 1 4	11	1.739	1.739	$\bar{1}$ 4 5
29	3.085	3.086	1 2 3	"	"	1.738	1 3 7
5	2.945	2.945	0 $\bar{2}$ 2	7	1.710	1.713	3 0 0
"	"	2.944	0 2 4	"	"	1.708	0 0 7
8	2.761	2.760	$\bar{1}$ $\bar{2}$ 1	14	1.705	1.706	0 5 1
21	2.735	2.735	1 $\bar{2}$ 2	"	"	1.706	0 5 4
"	"	2.735	0 3 0	4	1.664	1.665	2 4 2
3	2.570	2.569	2 0 0	3	1.620	1.620	$\bar{3}$ 2 0
6	2.544	2.544	$\bar{1}$ 3 1	10	1.612	1.613	2 4 5
9	2.485	2.485	$\bar{1}$ 3 0	"	"	1.613	0 $\bar{4}$ 3
4	2.467	2.467	0 $\bar{2}$ 3	"	"	1.612	0 4 7
"	"	2.467	0 2 5				
9	2.405	2.406	$\bar{1}$ $\bar{2}$ 2				
"	"	2.403	$\bar{1}$ 2 4				

Indexing based on cell: a = 5.246(1), b = 8.734(3), c = 12.968(5) Å, α = 70.32(1), β = 79.01(1), γ = 89.90(2)°

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a DRON–2 powder diffractometer using Cu*K*α X-radiation. Table 2 shows the X-ray powder-diffraction data for paravinogradovite, together with the refined unit-cell dimensions; the latter are in close agreement with corresponding values determined by single-crystal diffraction (Table 3).

CRYSTAL STRUCTURE

Data collection and structure refinement

A crystal was mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a Smart 1K CCD detector. The intensities of 9428 reflections with 7 < h < 6, $\overline{12}$ < k < 12, $\overline{18}$ < l < 18 were collected to 59.99°2θ using 30 s per 0.1° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 3) were obtained from 3772 reflections with $I > 10\sigma I$. The triclinic cell of paravinogradovite is related to the *C*-centered monoclinic cell of vinogradovite by the matrix transformation (0 0 1, 0 1 0, –½ 1 0).

TABLE 3. MISCELLANEOUS INFORMATION FOR PARAVINOGRADOVITE

a (Å)	5.2533(2)	crystal size (mm)	0.02 x 0.08 x 0.12
b	8.7411(3)	radiation	Mo*K*α
c	12.9480(5)	maximum 2θ (°)	59.99
α (°)	70.466(1)		
β	78.472(1)	Reflections collected	9428
γ	89.932(1)	Unique reflections	5649
V (Å^3)	547.65(5)	$F_o > 4\sigma F$	4373
Space Group	*P*1	Refinement method	Least-squares on F^2; fixed weights ∝ $1/\sigma F$
Z	1	No. of refined parameters	
D_{calc} (g cm^{-3})	2.754	Goodness of fit on F^2	0.994
		Final R index (%) [$F_o > 4\sigma F$]	4.45
Absorption coefficient (mm^{-1})	2.16	R index (%) (all data)	6.35
F (000)	447.4	wR_2 (%)	10.91

The crystal structure of paravinogradovite was solved by direct methods and refined to an *R* index of 4.5% for 4373 independent observed reflections (418 refined parameters including extinction) with the SHELXTL 5.1 system of programs (Sheldrick 1997). Site occupancies were refined for four *M* sites (occupied primarily by Ti), three *X* sites, five *A* sites (occupied primarily by Na), and three (H_2O) sites [O(27), O(28) and O(29)], and the isotropic-displacement parameters for *A*(1)–*A*(5) and O(27–29) were fixed at 0.05 Å^2. In the last stages of the refinement, four H atoms of four (OH) groups were found in the difference-electron-density map and included in the refinement with two types of constraints: (1) the distances O (donor)–H were fixed at the distances taken from a difference-Fourier map, and (2) the isotropic-displacement factor for a H atom was constrained to be 1.5 times bigger than the displacement parameter of the O atom of the associated (OH) group. Final atom coordinates and displacement parameters are given in Table 4, selected interatomic distances are listed in Table 5, Table 6 gives details of established and proposed scheme of hydrogen bonding, refined site-scattering values and assigned populations for selected sites are given in Table 7, and Table 8 gives the bond valences for paravinogradovite. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

The T sites

There are eight *T* sites, each of which is coordinated by a tetrahedral array of O atoms. Seven *T* sites are occupied primarily by Si, with minor amounts of Be and Al ($Si_{6.60}\,Be_{0.30}\,Al_{0.10}$) and a <*T*–O> distance of 1.620 Å. The equivalent-displacement factor at *T*(4) is the lowest of all the *T* sites, suggesting that there is somewhat less scattering at this site, as would be the case if Be were ordered at *T*(4) and were not included in the site-scattering model during crystal-structure refinement (as was the case here). Thus we assign minor Be to *T*(4). The *T*(8) site has a <*T*–O> distance of 1.720 Å, indicating that it is dominantly to completely occupied by Al. Note that the existence of the *T*(8) site (with a multiplicity of 1) is incompatible with the presence of a center of symmetry in paravinogradovite. The ideal <*T*–O> distance for *T*(8) = 1.0 Al may be derived from the hard-sphere model: 1.356 + 0.39 = 1.746 Å, significantly greater than the observed value of 1.720 Å. We have two possible approaches here: (1) we can assume *T*(8) = 1.0 Al and accept the difference in the observed and calculated bond-lengths, or (2) we can assign an Al–Si occupancy that is consonant with the observed distance of 1.720 Å: 0.80 Al + 0.20 Si.

We can find no compelling reason for preferring one model over the other, and hence present both (Table 9). In vinogradovite (Kalsbeek & Rønsbo 1992), Al is distributed randomly over the eight tetrahedra of the *T*(2) site (as required by the space-group symmetry), whereas in paravinogradovite, Al is predominantly ordered at the *T*(8) tetrahedron. Hence the *T*-site populations in paravinogradovite can be considered as an ordered derivative of the analogous arrangements in vinogradovite.

The M sites

There are four *M* sites, each of which is coordinated by a distorted octahedral array of four O atoms and two (OH) groups, with a grand <*M*–ϕ> distance of 1.968 Å. We refined the occupancies of the *M* sites: there was no difference in site scattering among the four sites; the site-scattering values were all close to 22 electrons, in accord with the dominance of Ti at these sites indicated by the formula unit (Table 7).

The X sites

The *X*(1), *X*(2) and *X*(3) sites are each coordinated by an octahedral arrangement of five O atoms and one (OH) group, and are partly occupied by Na (Table 5), with <*X*–ϕ> = 2.446, 2.459 and 2.430 Å, respectively. The total refined scattering at the *X*(1) to *X*(3) sites is 14.9(2) *epfu*, which corresponds to 1.35 *apfu* Na.

Structure topology

There are two types of chains of tetrahedra in the structure of paravinogradovite. (1) Three (SiO_4) tetrahedra, *T*(5–7), and the (AlO_4) tetrahedron, *T*(8), link to form a vinogradovite-like [Si_3AlO_{10}] chain (Figs. 1a, b), with four-membered [T_4O_{12}] rings connected through two common vertices to form a [T_4O_{10}] chain. (2) Two pairs of (SiO_4) tetrahedra, *T*(1) + *T*(3) and *T*(2) + *T*(4), form two distinct pyroxene-like [T_2O_6] chains (Fig. 2a).

There are one [T_4O_{10}] and two [T_2O_6] chains per unit cell in paravinogradovite. These two type of chains also occur in vinogradovite, ideally $Na_5\,Ti^{4+}{}_4\,(Si_7Al)\,O_{26}\,(H_2O)_3$, monoclinic, *a* 24.490(10), *b* 8.657(4), *c* 5.203(2) Å, β 100.2(0)°, *V* 1085.8 Å^3, *C*2/*c* (Kalsbeek & Rønsbo 1992, Rastsvetaeva & Andrianov 1984). In the structure of paravinogradovite, (MO_6) octahedra form two crystallographically distinct kinked brookite-like chains that extend along [100] (Figs. 1a, b). The repeat distances along these two chains are ~ 5.3 Å and define the *a* cell-parameter. The *M*(1) and *M*(3) octahedra each link to three *X*(1,2) octahedra (through common edges) and to one tetrahedron of a vinogradovite chain (through a common vertex). The *M*(1)–*M*(3) brookite-like chain is decorated by *X*(1) and *X*(2) octahedra to form a ribbon extending in the *c* direction. These ribbons are linked in the *b* direction by vinogradovite chains to form a sheet (sheet I) parallel to (001) at *z* ~ 0.19 (Fig. 1a). This sheet is identical to the sheets in vinogradovite (Fig. 1c). There is another type of sheet at *z* ≈ 0.81 in the structure

TABLE 4. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR PARAVINOGRADOVITE

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M(1)	–0.0026(2)	0.04863(15)	0.19107(11)	0.0126(6)	0.0087(7)	0.0082(7)	–0.0017(6)	–0.0024(5)	0.0020(5)	0.0101(3)
M(2)	–0.0129(2)	–0.04434(15)	–0.19148(10)	0.0090(6)	0.0083(7)	0.0089(7)	–0.0027(6)	–0.0004(5)	0.0003(5)	0.0090(3)
M(3)	–0.4946(2)	0.26018(16)	0.19098(11)	0.0129(6)	0.0094(7)	0.0106(8)	–0.0053(6)	0.0003(5)	–0.0011(5)	0.0109(3)
M(4)	0.4862(2)	–0.26523(15)	–0.18922(10)	0.0080(6)	0.0104(7)	0.0077(7)	–0.0042(6)	–0.0002(5)	–0.0005(5)	0.0086(3)
T(1)	0.2915(3)	0.3566(2)	–0.03811(17)	0.0075(8)	0.0078(10)	0.0081(11)	–0.0037(8)	–0.0007(7)	0.0007(7)	0.0077(4)
T(2)	–0.3067(3)	–0.3511(2)	0.03801(17)	0.0070(8)	0.0075(10)	0.0090(11)	–0.0008(8)	–0.0027(7)	0.0006(7)	0.0082(4)
T(3)	–0.2082(3)	0.1883(3)	–0.04019(17)	0.0066(8)	0.0109(10)	0.0065(10)	–0.0035(8)	–0.0010(7)	0.0020(7)	0.0079(4)
T(4)	0.1950(3)	–0.1767(2)	0.03601(17)	0.0049(8)	0.0064(10)	0.0092(10)	–0.0029(8)	–0.0010(7)	–0.0008(6)	0.0068(4)
T(5)	0.2062(3)	0.3336(2)	–0.36896(16)	0.0123(9)	0.0107(10)	0.0074(9)	–0.0005(7)	–0.0009(7)	–0.0002(7)	0.0109(4)
T(6)	–0.6435(3)	0.4611(3)	0.37055(17)	0.0099(8)	0.0134(10)	0.0088(9)	–0.0034(7)	–0.0012(7)	0.0004(7)	0.0109(4)
T(7)	0.7022(3)	–0.4672(2)	–0.36715(16)	0.0151(9)	0.0113(10)	0.0082(10)	–0.0046(8)	0.0006(7)	–0.0015(7)	0.0116(4)
T(8)	–0.1473(4)	–0.3384(3)	0.37178(18)	0.0082(9)	0.0068(10)	0.0085(10)	–0.0023(8)	–0.0002(7)	–0.0001(7)	0.0081(4)
X(1)	–1.0044(7)	0.4533(4)	0.2092(3)	0.022(2)	0.017(2)	0.027(2)	–0.0075(15)	–0.0120(15)	0.0033(14)	0.0213(11)
X(2)	–0.5125(12)	–0.1599(9)	0.2099(6)	0.014(3)	0.026(4)	0.017(4)	–0.008(3)	–0.009(3)	0.007(3)	0.018(2)
X(3)	–0.522(4)	0.154(3)	–0.202(2)	0.054(15)	0.025(14)	0.09(2)	–0.031(14)	–0.051(15)	0.001(10)	0.048(10)
A(1)	–0.144(4)	–0.007(3)	–0.5069(19)	0.05						
A(2)	–0.338(4)	–0.009(3)	–0.4949(18)	0.05						
A(3)	0.250(6)	–0.007(4)	–0.504(2)	0.05						
A(4)	0.403(4)	–0.069(3)	–0.5053(17)	0.05						
A(5)	–0.167(4)	0.119(2)	–0.5018(15)	0.05						
O(1)	0.2298(8)	0.2759(6)	0.1001(4)	0.009(2)	0.006(2)	0.010(3)	–0.001(2)	–0.0023(18)	0.0003(17)	0.0089(10)
O(2)	–0.2727(8)	0.1280(6)	0.0982(4)	0.010(2)	0.009(3)	0.008(3)	–0.002(2)	–0.0015(18)	–0.0013(17)	0.0092(10)
O(3)	0.1820(8)	–0.0266(6)	0.0796(4)	0.013(2)	0.014(3)	0.015(3)	–0.010(2)	–0.004(2)	0.0026(19)	0.0125(11)
O(4)	–0.3190(8)	0.4508(6)	0.0874(4)	0.012(2)	0.011(3)	0.011(3)	0.002(2)	–0.0032(18)	–0.0035(18)	0.0127(11)
O(5) = (OH)	–0.2230(8)	0.1845(5)	0.2703(4)	0.010(2)	0.009(3)	0.007(3)	–0.002(2)	0.0009(18)	–0.0020(18)	0.0090(10)
O(6) = (OH)	0.2806(8)	0.0462(6)	0.2696(4)	0.013(2)	0.010(3)	0.006(3)	–0.001(2)	–0.0028(19)	–0.0019(18)	0.0102(10)
O(7)	0.0622(8)	0.2984(6)	–0.0880(4)	0.007(2)	0.017(3)	0.012(3)	–0.007(2)	–0.0018(19)	–0.0074(19)	0.0117(11)
O(8)	0.5633(8)	0.2926(6)	–0.0873(4)	0.008(2)	0.011(3)	0.011(3)	–0.004(2)	–0.0021(19)	0.0024(18)	0.0103(10)
O(9)	–0.1598(9)	–0.1403(6)	0.2851(4)	0.020(2)	0.011(3)	0.007(3)	0.002(2)	–0.003(2)	–0.003(2)	0.0138(11)
O(10)	–0.2439(11)	–0.3399(7)	0.5074(5)	0.047(3)	0.014(3)	0.014(3)	–0.003(2)	–0.004(2)	0.003(2)	0.0259(13)
O(11)	–0.6661(8)	0.3483(6)	0.2922(5)	0.016(2)	0.018(3)	0.017(3)	–0.010(2)	–0.004(2)	0.0035(19)	0.0153(11)
O(12)	–0.8384(9)	0.6044(6)	0.3455(4)	0.017(2)	0.019(2)	0.018(2)	–0.0092(19)	0.0009(19)	0.0018(18)	0.0182(10)
O(13)	–0.3498(9)	0.5320(6)	0.3436(4)	0.016(2)	0.019(3)	0.024(3)	–0.007(2)	–0.0023(19)	–0.0019(18)	0.0199(10)
O(14) = (OH)	0.2123(8)	–0.1833(6)	–0.2710(4)	0.011(2)	0.021(3)	0.014(3)	–0.008(2)	–0.007(2)	0.010(2)	0.0144(12)
O(15) = (OH)	–0.2848(8)	–0.0542(6)	–0.2727(4)	0.011(2)	0.014(3)	0.016(3)	–0.005(2)	–0.001(2)	–0.0005(19)	0.0141(11)
O(16)	0.2560(8)	–0.1311(6)	–0.0987(4)	0.007(2)	0.014(3)	0.008(3)	–0.005(2)	0.0002(18)	–0.0013(18)	0.0100(10)
O(17)	–0.2460(8)	–0.2707(6)	–0.0975(4)	0.011(2)	0.015(3)	0.004(3)	–0.000(2)	–0.0028(18)	–0.0011(19)	0.0102(11)
O(18)	–0.1855(8)	0.0323(6)	–0.0837(4)	0.009(2)	0.010(3)	0.017(3)	–0.007(2)	–0.0015(19)	0.0020(18)	0.0116(11)
O(19)	–0.0820(9)	–0.2910(6)	0.0875(4)	0.006(2)	0.015(3)	0.007(3)	–0.001(2)	–0.0002(18)	–0.0017(18)	0.0103(10)
O(20)	0.3102(8)	0.5513(6)	–0.0778(4)	0.011(2)	0.007(2)	0.014(3)	–0.003(2)	–0.0024(18)	0.0039(17)	0.0107(10)
O(21)	–0.5839(9)	–0.2929(7)	0.0880(4)	0.010(2)	0.018(3)	0.006(3)	0.002(2)	–0.0011(18)	0.0044(19)	0.0128(11)
O(22)	0.1528(8)	0.1419(7)	–0.2923(5)	0.015(2)	0.014(3)	0.017(3)	–0.002(2)	0.004(2)	–0.008(2)	0.0175(12)
O(23)	0.2698(10)	0.3409(7)	–0.4990(4)	0.027(2)	0.020(3)	0.006(3)	–0.003(2)	0.003(2)	–0.001(2)	0.0188(12)
O(24)	0.6509(9)	–0.3643(7)	–0.2839(5)	0.025(3)	0.023(3)	0.015(3)	–0.012(2)	–0.003(2)	0.008(2)	0.0197(12)
O(25)	0.9577(11)	–0.5687(7)	–0.3444(5)	0.034(3)	0.042(4)	0.027(3)	–0.009(3)	0.001(3)	0.018(3)	0.0359(13)
O(26)	0.4552(11)	0.4075(7)	–0.3431(4)	0.041(3)	0.027(3)	0.020(3)	–0.001(2)	–0.008(2)	–0.019(2)	0.0312(13)
O(27) *	0.260(3)	–0.1620(18)	–0.5003(12)	0.05						
O(28) *	–0.316(5)	0.120(3)	–0.4936(16)	0.05						
O(29) *	0.092(5)	–0.065(3)	–0.4922(19)	0.05						
H(1)	–0.239(12)	0.151(7)	0.3484(8)	0.0108						
H(2)	0.276(12)	–0.042(5)	0.345(3)	0.012						
H(3)	0.118(11)	–0.243(7)	–0.309(5)	0.017						
H(4)	–0.360(11)	0.029(5)	–0.298(5)	0.017						

* = (H_2O)

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR PARAVINOGRADOCITE

M(1)–O(1)	2.166(5)	*M*(2)–O(14)	2.068(5)	*M*(3)–O(1)	2.018(4)
M(1)–O(2)	2.015(4)	*M*(2)–O(15)	1.953(5)	*M*(3)–O(2)	2.122(5)
M(1)–O(3)	1.879(5)	*M*(2)–O(16)	2.019(4)	*M*(3)–O(4)	1.855(5)
M(1)–O(5)	2.035(5)	*M*(2)–O(17)	2.167(5)	*M*(3)–O(5)	1.913(5)
M(1)–O(6)	1.959(4)	*M*(2)–O(18)	1.827(5)	*M*(3)–O(6)	2.045(5)
M(1)–O(9)	1.774(5)	*M*(2)–O(22)	1.800(5)	*M*(3)–O(11)	1.823(5)
<*M*(1)–O>	1.971	<*M*(2)–O>	1.972	<*M*(3)–O>	1.963
M(4)–O(14)	1.950(4)	*T*(1)–O(1)	1.652(5)	*T*(2)–O(4)	1.630(5)
M(4)–O(15)	2.042(5)	*T*(1)–O(7)	1.630(4)	*T*(2)–O(17)	1.620(5)
M(4)–O(16)	2.135(5)	*T*(1)–O(8)	1.622(5)	*T*(2)–O(19)	1.615(5)
M(4)–O(17)	2.006(4)	*T*(1)–O(20)	1.602(5)	*T*(2)–O(21)	1.624(5)
M(4)–O(20)	1.853(5)	<*T*(1)–O>	1.627	<*T*(2)–O>	1.622
M(4)–O(24)	1.812(5)				
<*M*(4)–O>	1.966	*T*(3)–O(2)	1.652(5)	*T*(4)–O(3)	1.589(5)
		T(3)–O(7)	1.606(5)	*T*(4)–O(16)	1.618(5)
X(1)–O(1)	2.584(5)	*T*(3)–O(8)	1.600(5)	*T*(4)–O(19)	1.652(5)
X(1)–O(4)	2.507(5)	*T*(3)–O(18)	1.636(5)	*T*(4)–O(21)	1.639(5)
X(1)–O(5)	2.422(6)	<*T*(3)–O>	1.617	<*T*(4)–O>	1.625
X(1)–O(11)	2.293(5)				
X(1)–O(13)	2.516(6)	*T*(5)–O(22)	1.627(6)	*T*(6)–O(11)	1.653(5)
X(1)–O(19)	2.355(6)	*T*(5)–O(23)	1.629(5)	*T*(6)–O(12)	1.606(5)
<*Nai*(1)–O>	2.446	*T*(5)–O(25)	1.596(5)	*T*(6)–O(13)	1.590(4)
		T(5)–O(26)	1.600(5)	*T*(6)–O(23)	1.634(5)
X(2)–O(2)	2.619(9)	<*T*(5)–O>	1.613	<*T*(6)–O>	1.621
X(2)–O(3)	2.559(8)				
X(2)–O(6)	2.370(8)	*T*(7)–O(10)	1.601(6)	*T*(8)–O(9)	1.730(5)
X(2)–O(9)	2.290(7)	*T*(7)–O(24)	1.605(6)	*T*(8)–O(10)	1.723(6)
X(2)–O(12)	2.578(9)	*T*(7)–O(25)	1.630(6)	*T*(8)–O(12)	1.700(5)
X(2)–O(21)	2.335(8)	*T*(7)–O(26)	1.611(5)	*T*(8)–O(13)	1.727(5)
<*X*(2)–O>	2.459	<*T*(7)–O>	1.612	<*T*(8)–O>	1.720
X(3)–O(8)	2.31(2)			*T*(1)–O(7)–*T*(3)	137.8(4)
X(3)–O(15)	2.52(3)			*T*(1)–O(8)–*T*(3)a	138.2(4)
X(3)–O(16)	2.55(3)			*T*(6)–O(12)–*T*(8)b	147.3(3)
X(3)–O(18)	2.56(2)			*T*(6)–O(13)–*T*(8)c	143.3(3)
X(3)–O(22)	2.28(2)			*T*(2)–O(19)–*T*(4)	136.8(3)
X(3)–O(26)	2.38(3)			*T*(2)–O(21)–*T*(4)d	136.2(4)
<*X*(3)–O>	2.43			*T*(5)–O(23)–*T*(6)e	144.6(4)
				T(5)f–O(25)–*T*(7)	158.2(4)
				T(7)c–O(26)–*T*(5)	156.5(4)
				<*T*–O–*T*>	144.3

a: *x*+1, *y*, *z*; b: *x*–1, *y*+1, *z*; c: *x*, *y*+1, *z*; d: *x*–1, *y*, *z*; e: *x*+1, *y*, *z*–1; f: *x*+1, *y*–1, *z*

of paravinogradovite (Fig. 1b). The *M*(2) and *M*(4) octahedra of the brookite-like chain are linked into a sheet (sheet II) by vinogradovite-like chains, but the brookite-like chain is not decorated by (XO_6) octahedra [ignoring the *X*(3) site with 16% occupancy].

Linkage of pyroxene-like [Si_2O_6] chains with sheet II is shown in Figure 2a: each (MO_6) octahedron shares three common vertices with three (SiO_4) tetrahedra, and the H atoms of the (OH) groups of the (MO_6) octahedra occur on the opposite side of the octahedra. Figure 2b shows the linkage of the [Si_2O_6] chains to a sheet in vinogradovite: this linkage is identical to the linkage of [Si_2O_6] chains to sheet I in paravinogradovite [the only difference is that (MO_6) octahedra in paravinogradovite have two (OH) ligands].

TABLE 6. HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF PARAVINOGRADOVITE

D–H...A	D–A (Å)	D–H (Å)	H...A (Å)	∠D–H...A (°)
O(5)–H(1)–O(28)	2.86(2)	0.940(1)	1.93(2)	178(3)
O(6)–H(2)–O(27)	2.92(2)	1.010(1)	1.95(2)	161(3)
O(14)–H(3)–O(27) *	2.87(2)	1.021(1)	2.25(3)	116(2)
O(14)–H(3)–O(29) *	2.90(2)	1.021(1)	2.37(4)	111(2)
O(15)–H(4)–O(28)	2.79(2)	0.83(1)	2.13(3)	138(2)
Proposed hydrogen bonding				
O(27)–H(5)–O(10)	3.04(2)			
O(27)–H(6)–O(10)′	3.04(2)			
O(28)–H(7)–O(15)	2.79(2)			
O(28)–H(8)–O(23)	2.90(2)			
O(29)–H(9)–O(14)	2.90(2)			
O(29)–H(10)–O(28)	2.68(3)			

* bifurcated bond

TABLE 7. REFINED SITE-SCATTERING (RSS) VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) IN PARAVINOGRADOVITE

Site	RSS	Assigned site-populations
M(1)	22	0.88 Ti* + 0.12 Fe^{3+}
M(2)	22	0.88 Ti + 0.12 Fe^{3+}
M(3)	22	0.88 Ti + 0.12 Fe^{3+}
M(4)	22	0.88 Ti + 0.12 Fe^{3+}
X(1)	8.4(1)	0.76 Na
X(2)	4.7(1)	0.43 Na
X(3)	1.8(1)	0.16 Na
A(1)	2.0(1)	0.18 Na
A(2)	2.1(1)	0.20 Na
A(3)	1.7(1)	0.15 Na
A(4)	2.1(1)	0.19 Na
A(5)	2.5(1)	0.13 K
O(27)	3.8(1)	0.48 (H_2O)
O(28)	3.0(1)	0.38 (H_2O)
O(29)	2.5(1)	0.31 (H_2O)

* includes ~0.01 Mg and 0.01 Nb

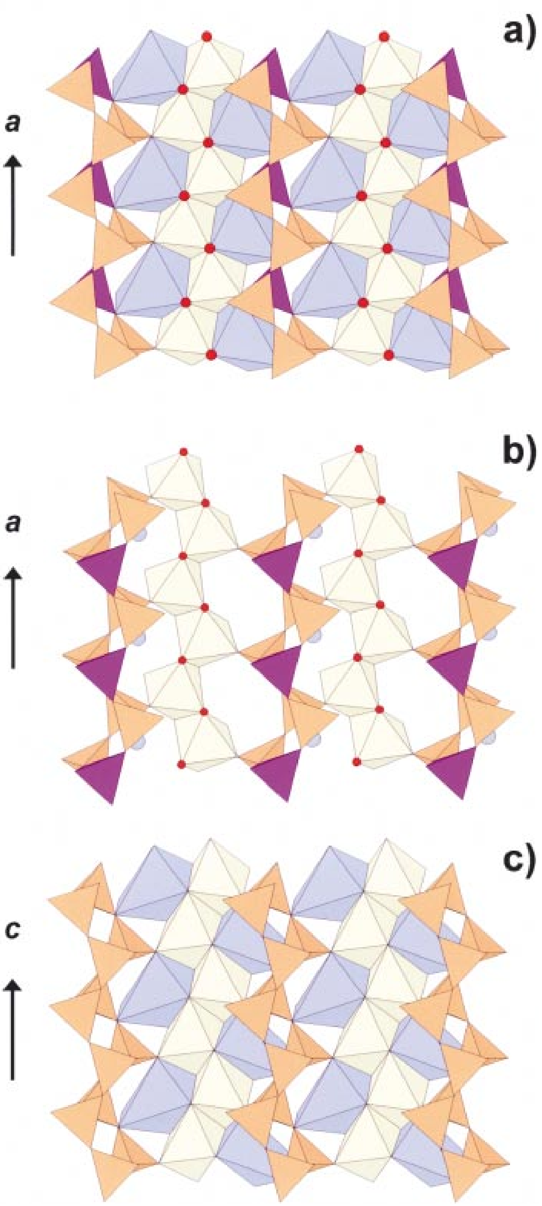

FIG. 1. Linkage of vinogradovite-like (T_4O_{10}) chains and *M* octahedra in the crystal structures of paravinogradovite and vinogradovite: (a) paravinogradovite: *M* octahedra decorated with *X*(1) and *X*(2) octahedra; (b) paravinogradovite: *M* octahedra and *X*(3) sites with 16% occupancy; (c) vinogradovite. *M* octahedra are yellow, *X* octahedra are blue, *Si* tetrahedra are orange, *Al* tetrahedra are purple, *X*(3) atoms and (OH) groups are shown as blue and red circles.

Linkage of both types of chains of tetrahedra with sheets I and II forms a mixed octahedron–tetrahedron framework in paravinogradovite (Fig. 3a), with one-dimensional channels with a diameter ~6 Å extending along [100]. There is a close relation between the topology of the frameworks in paravinogradovite and vinogradovite (Fig. 3b). Vacancy–Na order in paravinogradovite results in two types of sheets, one being Na-dominant (sheet I, Fig. 1a) and the other being vacancy-dominant (sheet II, Fig. 1b). In vinogradovite, there is only one (Na-dominant) sheet (Figs. 1c and 2b).

Interstitial cations

In the structure of paravinogradovite, the prominent channels along [100] contain eight sites. The *A* sites,

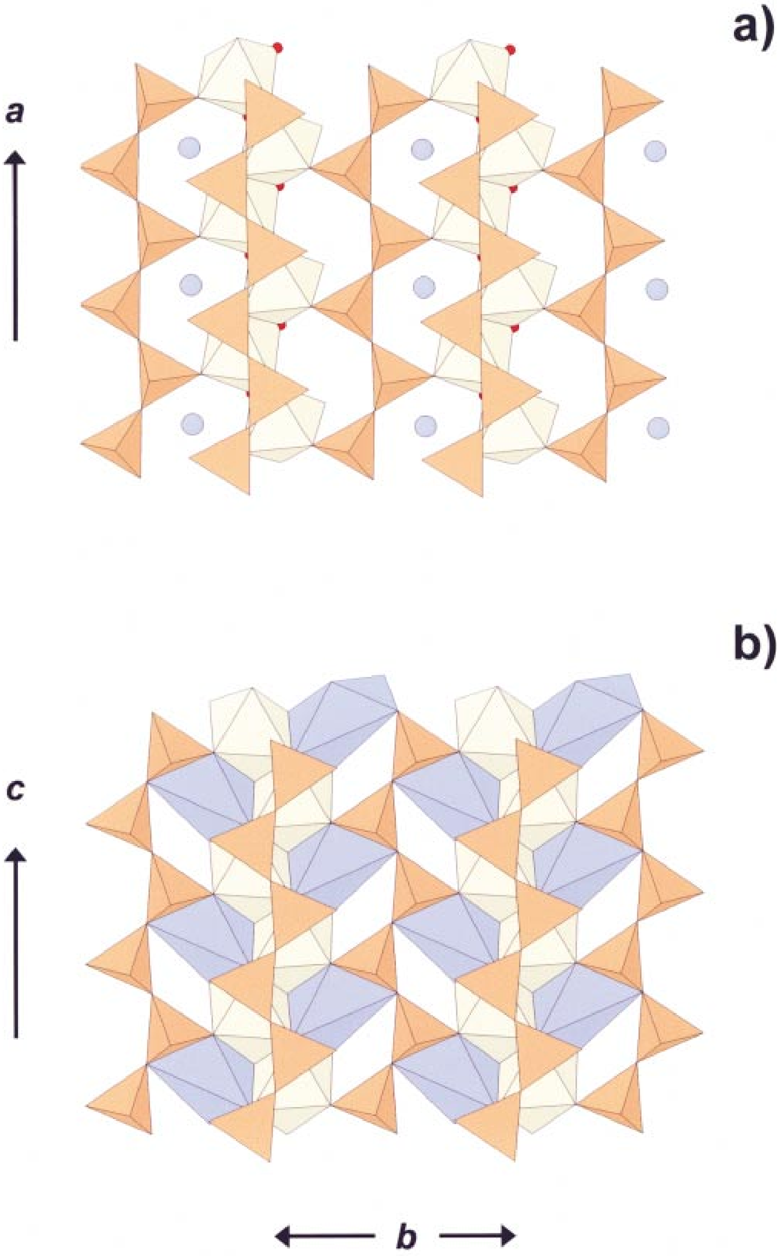

FIG. 2. Linkage of pyroxene-like (T_2O_6) chains and M octahedra in the crystal structure of (a) paravinogradovite, and (b) vinogradovite. Legend as in Figure 1.

TABLE 8. BOND-VALENCE* TABLE FOR PARAVINOGRADOVITE

	M(1)	*M*(2)	*M*(3)	*M*(4)	*T*(1)	*T*(2)	*T*(3)	*T*(4)	*T*(5)	*T*(6)	*T*(7)	*T*(8)	*X*(1)	*X*(2)	*X*(3)	Σ	H(1)	H(2)	H(3)	H(4)	Σ
O(1)	0.38		0.54		0.94								0.12			1.98					
O(2)	0.55		0.43				0.95							0.06		1.99					
O(3)	0.81							1.11						0.07		1.99					
O(4)			0.87			1.00							0.13			2.00					
O(5)	0.53		0.73										0.15			1.41	0.86				2.27
O(6)	0.64		0.52											0.09		1.25		0.85			2.10
O(7)					1.01		1.07									2.08					
O(8)					1.03		1.08								0.04	2.15					
O(9)	1.02											0.8		0.11		1.93					
O(10)											1.09	0.81				1.90					
O(11)			0.95							0.94			0.19			2.08					
O(12)										1.07		0.83		0.06		1.96					
O(13)										1.12		0.78	0.13			2.03					
O(14)		0.48		0.66												1.14			0.92		2.06
O(15)		0.65		0.52											0.03	1.20				0.94	2.14
O(16)		0.54		0.38				1.03							0.03	1.98					
O(17)		0.38		0.57		1.03										1.98					
O(18)		0.93					0.99								0.02	1.94					
O(19)						1.03		0.94					0.17			2.14					
O(20)				0.86	1.08											1.94					
O(21)						1.01		0.98						0.10		2.09					
O(22)		1.01							1.01						0.04	2.06				0.03	2.09
O(23)									1.01	0.98						1.99					
O(24)				0.97							1.07					2.04					
O(25)									1.09		1.01					2.10					
O(26)									1.08		1.05				0.03	2.16					
Σ	3.93	3.99	4.06	3.96	4.06	4.07	4.09	4.06	4.19	4.11	4.22	3.22	0.88	0.49	0.19						
Σ(ideal)	4	4	4	4	4	4	4	4	4	4	4	3	0.77	0.43	0.16						
O(27)																		0.15	0.04		
O(28)																	0.14			0.03	
O(29)																			0.04		

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

TABLE 9. ASSIGNED *T*-SITE POPULATIONS (*apfu*) IN THE CRYSTAL STRUCTURE OF PARAVINOGRADOVITE

	Model (1)	Model (2)
T(1)	0.90 Si + 0.10 Al	0.86 Si + 0.14 Al
T(2)	1.00 Si	1.00 Si
T(3)	1.00 Si	0.96 Si + 0.04 Al
T(4)	0.70 Si + 0.30 Be	0.70 Si + 0.30 Be
T(5)	1.00 Si	0.96 Si + 0.04 Al
T(6)	1.00 Si	0.96 Si + 0.04 Al
T(7)	1.00 Si	0.96 Si + 0.04 Al
T(8)	1.00 Al	0.80 Al + 0.20 Si

A(1)–*A*(4), are partly occupied by Na atoms, the *A*(5) site is partly occupied by K, and the O(27), O(28) and O(29) sites are partly occupied by (H_2O) groups. Assigned site-populations are given in Table 9. In total, the channel content is 0.72 Na + 0.14 K + 1.16 (H_2O) *apfu*. These sites are separated by distances of 0.77–2.09 Å, and hence local occupancy of one site must be accompanied by local vacancies at close adjacent sites. Assignment of a scattering species to a specific site was made on the basis of the required geometry of hydrogen bonding for the four H atoms of the (OH) groups. Possible distances and angles were analyzed in terms of O–O distances of 2.5–3.2 Å and D–H...A of 130–180°. Three sites, associated with (OH) groups in this manner, were assigned as (H_2O) groups, O(27–29). The five other sites were assigned as Na and K, as indicated by the formula unit (Table 1).

Hydrogen bonding

Details of hydrogen bonding in paravinogradovite are given in Table 6. Figures 5a and 5b show the arrangement of hydrogen bonds in the [100] channel through the structure. Hydrogen bonds between H(1–4) and O atoms of three (H_2O) groups are in the range 1.95–2.37 Å. The H(3) atom of the (OH) group at the O(14) site is involved in a bifurcated hydrogen-bond with D–H...A angles of of 111 and 116°, respectively. The O atom O(14) is bonded to two *M* atoms, whereas the O(4), O(5) and O(15) atoms are ligands of two *M* atoms and one Na atom as well. There must be extensive hydrogen bonding involving H atoms of the (H_2O) groups; the constituent H atoms were not located, but proposed hydrogen bonds are given in Table 6.

ORIGIN OF PARAVINOGRADOVITE

In immersion liquids, many paravinogradovite grains appear heterogeneous under crossed nicols, and look relatively homogeneous in plane-polarized light. The reason for this optical heterogeneity is the presence of relics of vinogradovite. Both minerals have similar indices of refraction; both are biaxial negative with parallel extinction, but differ in sign of elongation (negative for paravinogradovite and positive for vinogradovite). In paravinogradovite, relics of vinogradovite form chains of particles that extinguish simultaneously. Paravinogradovite thus is a secondary mineral formed from vinogradovite. This argument is in accord with the similarity in the topology of both crystal structures (this study, Rastsvetaeva *et al*. 1967).

Khomyakov (1980) established similar relations for highly alkaline primary minerals and the associated moderately alkaline secondary species, and developed the concept of "transformation" mineral species (Khomyakov 1990, 1995, 1996). Such a transformation mineral develops through alteration of a corresponding protophase, from which the newly formed mineral inherits the principal features of its composition and structure. The most detailed work has been done on minerals belonging to the following families: lomonosovite (lomonosovite → murmanite, vuonnemite → epistolite), lovozerite (zirsinalite → lovozerite, kazakovite → tisinalite), and keldyshite (parakeldyshite → keldyshite → species M34). This one-to-one relation between primary and secondary minerals in these series suggests the possibility of reconstructing the primary mineralogy of such rocks from products of their alteration.

Replacement of highly alkaline minerals by less alkaline analogues usually proceeds easily. However, this is not the case for the epithermal and supergene alteration of vinogradovite, $Na_5Ti_4(Si_7Al)O_{26}(H_2O)$, which is highly stable in pegmatites. The main reason for lessened stability of vinogradovite (which is present as relics in paravinogradovite) is its high Fe^{2+} content, corresponding to possible ideal compositions $Na_5(Ti^{4+}_3Fe^{2+})(Si_7Al)O_{24}(OH)_2(H_2O)$ or $Na_3(Ti^{4+}_3Fe^{2+})(Si_7Al)O_{24}(OH)_4(H_2O)$. These ideal formulae suggest that Fe is divalent in "proto-vinogradovite", in contrast to the presence of Fe^{3+} in paravinogradovite, $Na_2(Ti^{4+}_3Fe^{3+})(Si_7Al)O_{24}(OH)_4(H_2O)$. This argument is in accord with the divalent state of Fe in the majority of titanium silicates in the Khibina–Lovozero complex, and with the reducing conditions of formation of the main mineral associations in differentiates of agpaitic nepheline syenites.

THE END-MEMBER COMPOSITION OF PARAVINOGRADOVITE

We may simplify the part of the structure containing tetrahedra, together with the anions, to give $[(Si_7Al)(OH)_4O_{22}]^{17-}$. The difficulty in assigning an end-member formula arises in deciding what the most appropriate end-members are with regard to the *M*, *X* and *A* sites. A possible end-member composition in this regard is $\{Na\,Ti^{4+}_4\}^{17+}$, as this is completely ordered at the *M* sites, and only one *X* site (and no *A* site) is occupied by Na, in accord with the fact that only at the *X*(1) site is Na dominant over a vacancy (Table 7). The result is the formula $Na\,Ti^{4+}_4(Si_7Al)(OH)_4O_{22}(H_2O)$. However, comparison with the empirical formula of Table 7 indicates that it is closer to a composition $Na_2(Ti^{4+}_3Fe^{3+})(Si_7Al)(OH)_4O_{22}(H_2O)$. Can this latter composition be considered as an end-member? Two problems now arise: (1) Fe^{3+} seems disordered over the four distinct *M* sites, and at no site is it ever dominant; (2) Na is not dominant at two *X* (or *A*) sites, as required by this formula. However, an ordered arrangement of $Na_2(Ti^{4+}_3Fe^{3+})$ is formally possible in the triclinic structure of paravinogradovite, even if it is not actually observed here. Thus we might consider the composition $Na_2(Ti^{4+}_3Fe^{3+})(Si_7Al)(OH)_4O_{22}(H_2O)$ as forming an order–disorder series between ordered and disordered arrangements of this composition. The ordered end of the series constitutes a *bona fide* end-member composition and structural arrangement. The disordered arrangement (which is close to what we actually observe) *does not constitute an end-member according to normal convention* (*i.e.*, sites dominated by the principal chemical constituents). This presents us with somewhat of a quandary in defining the end-member: $Na\,Ti^{4+}_4(Si_7Al)(OH)_4O_{22}(H_2O)$ or $Na_2(Ti^{4+}_3Fe^{3+})(Si_7Al)(OH)_4O_{22}(H_2O)$? It is apparent that this issue of order–disorder and its influence on the definition of an end-member composition deserves further consideration.

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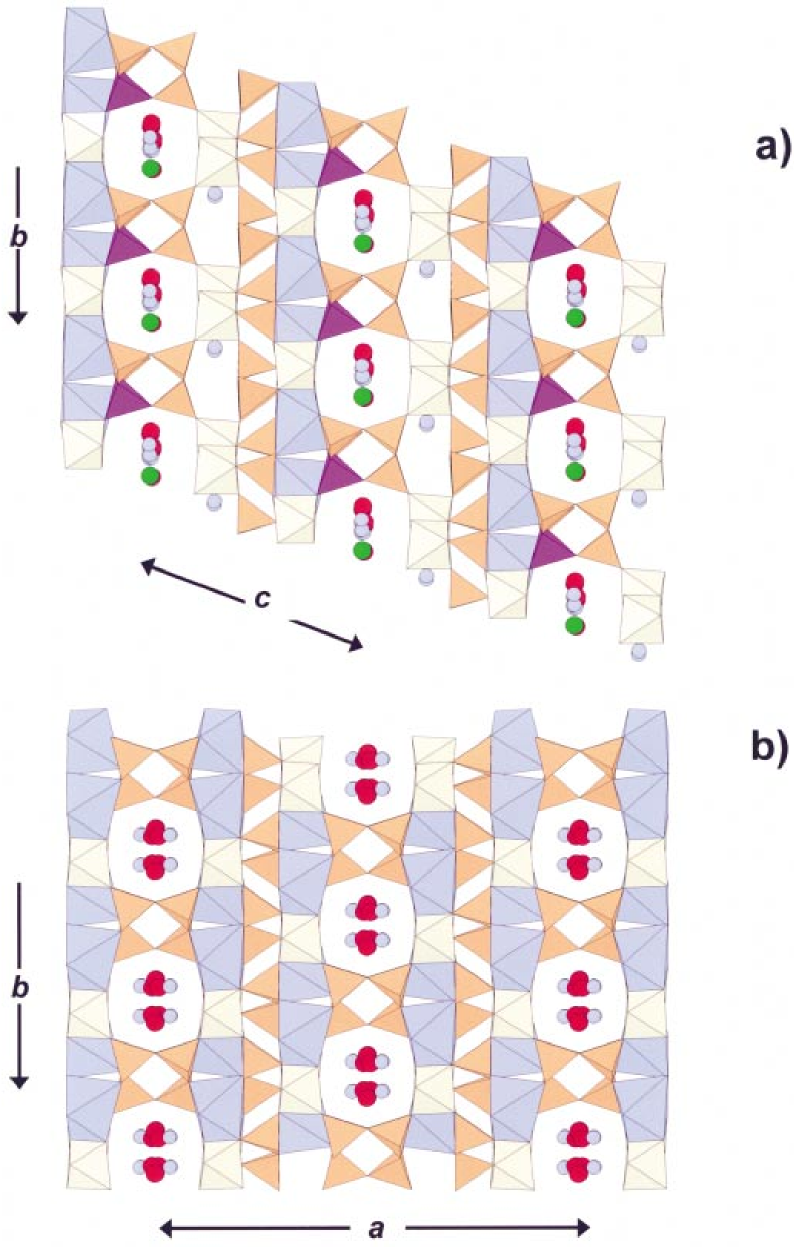

FIG. 3. General view of the crystal structure of (a) paravinogradovite and (b) vinogradovite, $Na_5 Ti^{4+}_4 (Si_7Al) O_{26} (H_2O)_3$. *M* octahedra are yellow, *X* octahedra are blue, *Si* tetrahedra are orange, *Al* tetrahedra are purple; H_2O groups, Na and K atoms in the channels of the crystal structure are shown as red, blue and green circles; *X*(3) atoms are shown as blue circles.

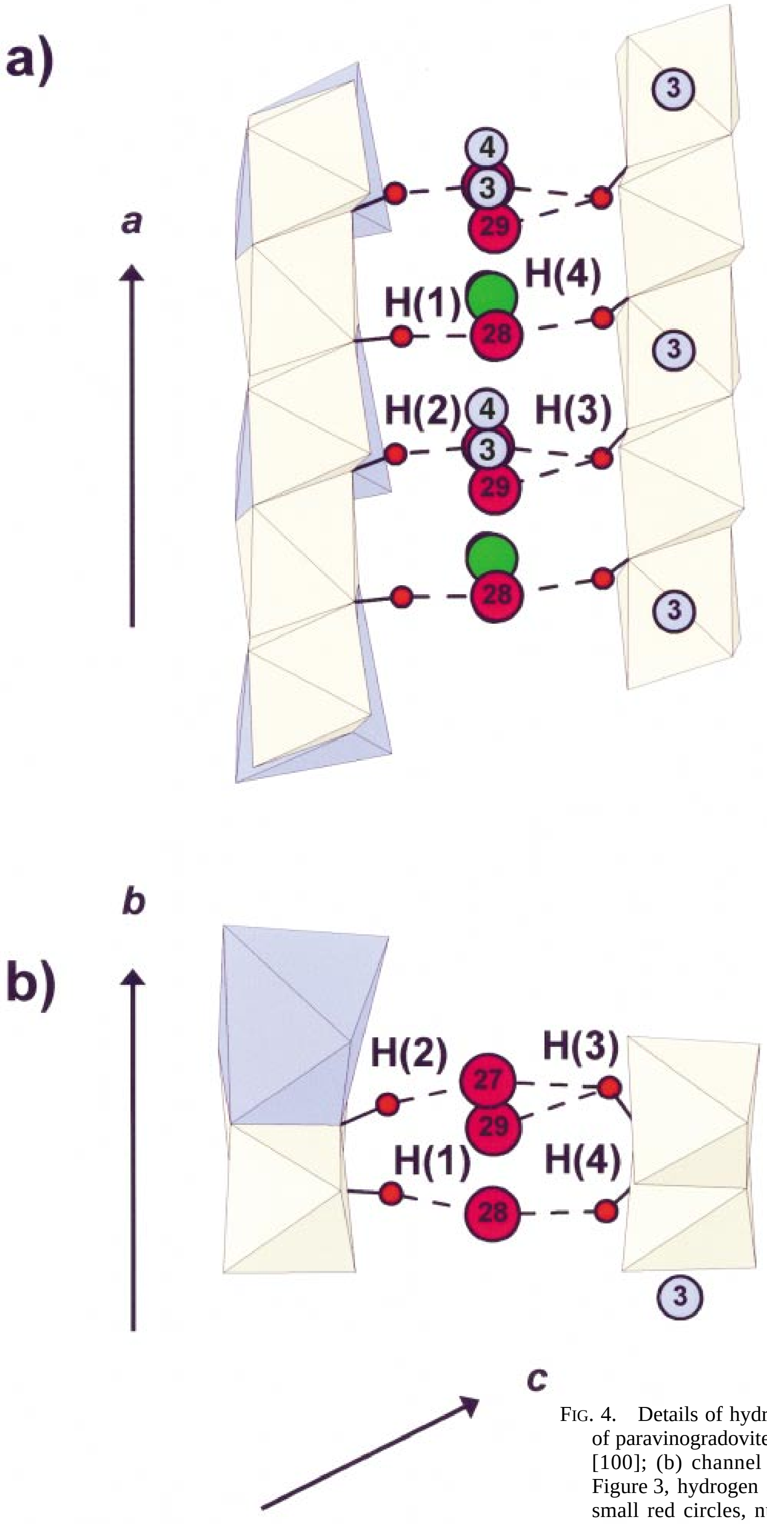

FIG. 4. Details of hydrogen bonding in the crystal structure of paravinogradovite: (a) cross-section of a channel along [100]; (b) channel viewed down [100]. Legend as in Figure 3, hydrogen atoms of (OH) groups are shown as small red circles, numbers in magenta and blue circles indicate (H_2O), *A* and *X*(3) sites.

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