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Refinement of the vinogradovite structure, positioning of Be and excess Na

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Abstract. Vinogradovite from the Ilímaussaq alkaline Intrusion has been investigated by X-ray diffraction at ca. 295 K and ca. 110 K. $a = 24.50(1)$, $b = 8.662(2)$, $c = 5.211(2)$ Å, $\beta = 100.13(3)°$ (295 K). $a = 24.49(1)$, $b = 8.657(4)$, $c = 5.203(2)$ Å, $\beta = 100.15(4)°$ (110 K), space group $C2/c$, $R = 0.034$ (295 K) and 0.036 (110 K). Two major differences were observed in the crystal structure compared to earlier studies of the mineral. The site occupancy factor for Si(2) lead to chemical analysis for Be, which was confirmed to be present in this crystallographic site. Chemical analysis showed an excess of Na, which could be localized in the zeolite like channels found in the crystal structure. Finally it can be concluded that the disorder in the channels is static.

Introduction

The unique character of the vinogradovite structure, the presence of a pyroxene like Si_2O_6 single chain and a $(Si,Al)_4O_{10}$ double chain in the same structure, was established by Rastsvetaeva, Simonov and Belov (1968) and later confirmed by Rastsvetaeva and Andrianov (1984), who suggested the chemical formula to be $(Na,Ca)_8(Ti,Nb)_8O_8(Si_2O_6)_4[(Si,Al)_4O_{10}]_2 \cdot (H_2O,K)_6$, $Z = 1$. Mineral chemical investigations of vinogradovite from the Ilímaussaq alkaline Intrusion and Lovozero alkaline

Massiv (Rønsbo, Petersen and Leonardsen, 1990) showed a low Al content for some samples, Al < 2.0 cations/formula unit, and excess Na. In order to investigate whether these chemical differences cause structural changes, one sample from the Ilímaussaq alkaline Intrusion was examined by X-ray diffraction. The selected crystal belongs to the euhedral type (Rønsbo et al., 1990) and the chemical analysis of a similar crystal (op. cit. Table 2 analysis 2) lead to the cation content $Na_{10.0}K_{0.7}Si_{14.0}Al_{1.2}$-$Be_{0.8}Ti_{7.4}Nb_{0.5}Fe_{0.1}$. Like the material described by Rønsbo et al. (1990) the crystal used for the present investigation might show a depletion of Na, K, Nb and Fe in the rim.

Experimental

X-ray data collection at ca. 295 K (RT) was performed on a CAD-4 diffractometer using a single crystal with dimensions $0.10 \times 0.33 \times 0.45$ mm with graphite monochromatized Mo$K\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å). The formula weight of vinogradovite is 2063.5 g mol^{-1}. Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined from least squares refinement of the setting angles for 22 reflections ($16.0 < \theta < 24.2°$). Three standard reflections (002, 020 and 710) were measured every 10000 s and the orientation of the crystal was checked after every 300 reflections. These measurements did not indicate any variations in the experimental conditions.

Data reduction included corrections for Lorentz, polarization and absorption effects. The latter correction was performed using the Gaussian integration method (Coppens, Leiserowitz and Rabinovich, 1965); details are given in Table 1.

Structure solution and refinement

Vinogradovite crystallizes in the monoclinic space group $C2/c$. Due to the ambiguity with the earlier studies the structure was solved by Patterson and Fourier techniques. O(1) is located on a crystallographic two fold axis. The coordinates given in this paper are related to the ones given by Rastsvetaeva et al. (1968) by interchanging the x and z coordinates (conversion from the non-standard setting A2/a to C2/c). The structure was refined by the full matrix least squares method minimizing $\Sigma w\,(|F_o| - |F_c|)^2$. The SDP system (Enraf-Nonius, 1985) was used for the crystallographic computations. Neutral scattering factors and anomalous dispersion values for all atoms were from International Tables for X-ray Crystallography (1974).

A subsequent difference Fourier calculation showed three maxima in the large channels in the structure. These were introduced as O atoms. One

Table 1. Crystal data and a summary of results from data reduction and structure refinements for vinogradovite.

	RT	LT
Determination of unit cell:		
a (Å)	24.50(1)	24.49(1)
b (Å)	8.662(2)	8.657(4)
c (Å)	5.211(2)	5.203(2)
β (°)	100.13(3)	100.15(4)
V (Å^3)	1089(1)	1086(2)
Z	1	1
D_x (g cm^{-3})	3.15	3.16
Intensity data collection:		
Limits of θ (°)	1, 43	1, 45
Range of h	$0-46$	$\bar{48}-48$
Range of k	$\bar{16}-16$	$\bar{17}-17$
Range of l	$\bar{9}-9$	$\bar{10}-10$
Type of scan	ω	ω
Linear absorption coefficient μ (cm^{-1})	21.63	21.69
Max. and min. transmission factors	0.8051, 0.4984	0.8017, 0.5232
Structure refinement:		
Number of observed reflections	7470	10594
Number of unique reflections	4011	4472
Number of reflections used in the refinement [$I/\sigma(I) > 2$]	2586	2934
Number of variables	116	116
Weights w^{-1}	$\sigma_{cs}^2(F) + 0.0016\lvert F\rvert^2$	$\sigma_{cs}^2(F) + 0.0016\lvert F\rvert^2$
Final R	0.034	0.036
Final R_w	0.055	0.053
S	1.613	1.473
Final max. shift/error	0.02	0.01
Final max. and min. in $\Delta\varrho$ (e Å^{-3})	1.1, −0.8	1.7, −1.3

of the O atoms had a distance to an O atom in the double chain of 2.39 Å. As this O−O distance is unrealistically short the atom was identified as a Na atom. The large displacement parameter 6.4 Å^2 for OW(2) (about twice as large as for the two other atoms) could indicate two atomic sites too close to be resolvable, this is why OW(2) was refined anisotropically. The three atomic positions in the channels are found within 1 Å and the highest peaks in the final difference Fourier map 0.3−0.5 Å from Na(2). Site occupancy factors (s.o.f.'s) were included in the refinements for Ti, Si(2) and the three atoms in the channels.

In order to investigate the nature of the disorder (static or dynamic) X-ray diffraction studies were performed at ca. 110 K (LT) using the same crystal. The experimental conditions and refinement procedure are similar to the ones described for the RT study; details are given in Table 1.

Table 2. Positional and displacement parameters (Å^2) for vinogradovite (RT).

Atom	Site symm.	s.o.f.*	x	y	z
Ti	1	1.008(1)	0.34958(1)	0.40339(3)	0.21224(6)
Si(1)	1	1.000	0.76689(2)	0.40836(6)	0.7250(1)
Si(2)	1	0.893(2)	0.43556(2)	0.89957(4)	0.7228(1)
Na(1)	1	1.000	0.64873(4)	0.1887(1)	0.7952(2)
O(1)	2	1.000	0.5000	0.8441(3)	0.7500
O(2)	1	1.000	0.42093(6)	0.9631(2)	1.0002(3)
O(3)	1	1.000	0.79183(5)	0.5111(2)	0.9850(3)
O(4)	1	1.000	0.61535(5)	0.5679(2)	0.4532(3)
O(5)	1	1.000	0.79248(5)	0.2396(2)	0.7808(3)
O(6)	1	1.000	0.70004(5)	0.4181(2)	0.6660(3)
O(7)	1	1.000	0.39563(6)	0.7507(2)	0.6247(3)
OW(1)	2	0.348(8)	0.000	0.141(1)	0.250
OW(2)	1	0.549(7)	0.0076(3)	0.910(1)	0.646(1)
Na(2)	1	0.197(4)	0.4655(3)	0.4005(9)	0.973(2)

	B (iso)/ B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0.596(6)	0.518(7)	0.471(7)	0.024(7)	0.075(6)	0.044(7)
Si(1)	0.57(1)	0.47(1)	0.34(1)	0.04(1)	0.07(1)	0.00(1)
Si(2)	0.66(1)	0.58(2)	0.61(2)	−0.05(1)	0.11(1)	−0.03(1)
Na(1)	2.05(3)	1.36(3)	0.94(3)	0.26(3)	−0.13(3)	0.16(3)
O(1)	0.86(5)	1.18(7)	1.84(8)	0.00	0.23(6)	0.00
O(2)	1.34(4)	1.19(5)	1.30(5)	−0.15(4)	0.43(4)	−0.43(4)
O(3)	0.71(3)	0.85(4)	0.50(3)	0.01(3)	0.11(3)	−0.20(3)
O(4)	0.70(3)	0.82(4)	0.50(3)	0.14(3)	0.04(3)	−0.07(3)
O(5)	0.88(3)	0.60(3)	0.68(3)	0.25(3)	0.11(3)	0.06(3)
O(6)	0.54(3)	0.67(3)	0.50(3)	0.02(3)	−0.03(3)	−0.07(3)
O(7)	1.02(4)	0.92(4)	0.87(4)	−0.26(3)	0.18(3)	−0.01(4)
OW(1)	2.5(1)					
OW(2)	3.6(2)	13.5(6)	4.8(3)	−2.6(3)	0.9(2)	−1.3(3)
Na(2)	3.5(1)					

* Site occupancy factor.

Final positional parameters, site symmetry, site occupancy factors and anisotropic displacement parameters are given in Tables 2 and 3. Listings of observed and calculated structure factor amplitudes and bond angles for the Ti octahedron and Na(1) polyhedron have been deposited.[1]

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[1] Additional material to this paper can be ordered referring to no. CSD 54241, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 3. Positional and displacement parameters (Å^2) for vinogradovite (LT).

Atom	Site symm.	s.o.f.*	x	y	z
Ti	1	1.014(1)	0.34962(1)	0.40362(3)	0.21244(5)
Si(1)	1	1.000	0.76688(2)	0.40830(6)	0.72484(9)
Si(2)	1	0.891(2)	0.43553(2)	0.89961(7)	0.7248(1)
Na(1)	1	1.000	0.64896(4)	0.1890(1)	0.7956(2)
O(1)	2	1.000	0.5000	0.8430(3)	0.7500
O(2)	1	1.000	0.42101(6)	0.9610(2)	1.0046(3)
O(3)	1	1.000	0.79185(5)	0.5119(2)	0.9839(2)
O(4)	1	1.000	0.61523(5)	0.5683(2)	0.4519(2)
O(5)	1	1.000	0.79233(5)	0.2392(2)	0.7824(2)
O(6)	1	1.000	0.69991(5)	0.4180(2)	0.6661(2)
O(7)	1	1.000	0.39548(6)	0.7510(2)	0.6234(3)
OW(1)	2	0.370(7)	0.0000	0.1413(9)	0.2500
OW(2)	1	0.534(7)	0.0078(3)	0.914(1)	0.642(1)
Na(2)	1	0.203(4)	0.4644(3)	0.4014(7)	0.963(1)

	B (iso)/ B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0.379(6)	0.356(7)	0.379(6)	0.008(7)	0.015(5)	0.032(7)
Si(1)	0.38(1)	0.31(1)	0.24(1)	0.02(1)	0.018(9)	0.00(1)
Si(2)	0.45(1)	0.37(2)	0.45(1)	−0.02(1)	0.02(1)	−0.01(1)
Na(1)	1.15(3)	0.81(2)	0.66(2)	0.25(2)	−0.04(2)	0.11(2)
O(1)	0.61(5)	0.74(6)	1.24(6)	0.00	0.13(5)	0.00
O(2)	0.78(4)	0.82(4)	0.96(4)	−0.07(3)	0.24(3)	−0.19(3)
O(3)	0.47(3)	0.49(3)	0.34(3)	0.02(3)	0.01(3)	−0.10(3)
O(4)	0.46(3)	0.54(3)	0.34(3)	0.07(3)	−0.01(2)	−0.04(3)
O(5)	0.53(3)	0.41(3)	0.47(3)	0.13(3)	0.02(3)	0.04(3)
O(6)	0.38(3)	0.44(3)	0.31(3)	−0.02(3)	−0.03(2)	−0.03(3)
O(7)	0.71(3)	0.59(4)	0.58(3)	−0.12(3)	0.07(3)	0.03(3)
OW(1)	1.8(1)					
OW(2)	3.3(2)	12.2(5)	3.8(2)	−2.7(3)	0.8(2)	−2.0(3)
Na(2)	2.5(1)					

* Site occupancy factor.

$\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ where a^*, b^* and c^* are the reciprocal lattice constants.

Results

A detailed description of the vinogradovite framework has been given previously by Rastsvetaeva et al. (1968) and Rastsvetaeva and Andrianov (1984). The vinogradovite structure consists of two types of infinite chains of tetrahedra of the two crystallographically distinct Si atoms. The Si(1) tetrahedra form single chains (Si_2O_6) and the Si(2) tetrahedra double chains $[(Si,Al)_4O_{10}]$. The double chain has its only natural occurrence in

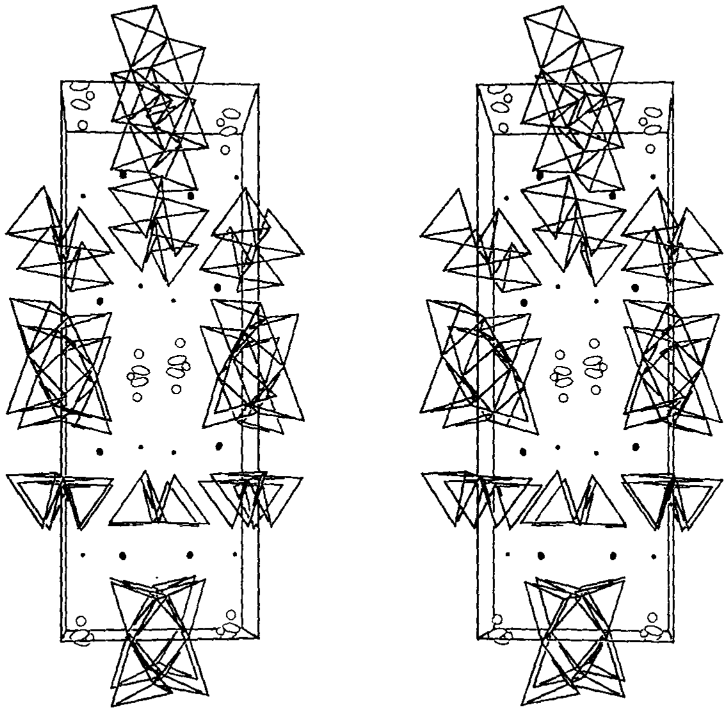

Fig. 1. Stereo drawing of vinogradovite seen along the *c*-axis. The *a*-axis is vertical and the *b*-axis horizontal. The Ti and Na(1) atoms are shown as filled ellipsoids and the OW(1), OW(2) and Na(2) atoms as open ellipsoids.

Table 4. Interatomic distances (Å) and angles (°).

	RT	LT
Ti Octahedron		
Ti–O(4^{i})	1.820(1)	1.822(1)
Ti–O(4^{ii})	1.943(2)	1.940(1)
Ti–O(5^{iii})	1.948(1)	1.952(1)
Ti–O(6^{i})	2.131(1)	2.127(1)
Ti–O(6^{ii})	2.130(1)	2.127(1)
Ti–O(7^{iv})	1.856(2)	1.857(1)
Average	1.971	1.971
Si(1) Tetrahedron		
Si(1)–O(3)	1.646(1)	1.645(1)
Si(1)–O(3^{iv})	1.641(2)	1.641(1)
Si(1)–O(5)	1.597(1)	1.599(1)
Si(1)–O(6)	1.615(1)	1.617(1)
Average	1.625	1.626

Table 4. (Continued)

	RT	LT
O(3)–Si(1)–O(3$^{\mathrm{iv}}$)	105.27(7)	105.17(7)
O(3)–Si(1)–O(5)	105.57(7)	105.65(6)
O(3)–Si(1)–O(6)	110.22(7)	110.17(7)
O(3$^{\mathrm{iv}}$)–Si(1)–O(5)	109.92(8)	110.06(7)
O(3$^{\mathrm{iv}}$)–Si(1)–O(6)	109.50(7)	109.62(6)
O(5)–Si(1)–O(6)	115.80(7)	115.60(7)
Si(2) Tetrahedron		
Si(2)–O(1)	1.6323(9)	1.6360(8)
Si(2)–O(2)	1.644(2)	1.646(2)
Si(2)–O(2$^{\mathrm{v}}$)	1.656(2)	1.659(2)
Si(2)–O(7)	1.645(2)	1.647(1)
Average	1.644	1.647
O(1)–Si(2)–O(2)	112.29(6)	112.43(6)
O(1)–Si(2)–O(2$^{\mathrm{v}}$)	111.05(9)	111.07(8)
O(1)–Si(2)–O(7)	108.0(1)	107.67(9)
O(2)–Si(2)–O(2$^{\mathrm{v}}$)	108.76(9)	108.82(8)
O(2)–Si(2)–O(7)	109.02(9)	109.03(8)
O(2$^{\mathrm{v}}$)–Si(2)–O(7)	107.56(8)	107.70(7)
Na(1) Polyhedron		
Na(1)–O(2$^{\mathrm{vi}}$)	2.533(2)	2.516(2)
Na(1)–O(2$^{\mathrm{vii}}$)	2.860(2)	2.886(2)
Na(1)–O(3$^{\mathrm{viii}}$)	2.417(2)	2.420(2)
Na(1)–O(3$^{\mathrm{ix}}$)	2.714(2)	2.704(2)
Na(1)–O(4$^{\mathrm{x}}$)	2.455(2)	2.448(2)
Na(1)–O(5$^{\mathrm{viii}}$)	2.495(2)	2.483(1)
Na(1)–O(6)	2.506(2)	2.497(2)
Na(1)–O(7$^{\mathrm{i}}$)	2.326(2)	2.318(2)
Average	2.538	2.534

i: $-x+1, -y+1, -z+1$; ii: $-x+1, y, -z+\frac{1}{2}$; iii: $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; iv: $x, -y+1, z-\frac{1}{2}$; v: $x, -y+2, z-\frac{1}{2}$; vi: $-x+1, -y+1, -z+2$; vii: $-x+1, y-1, -z+\frac{3}{2}$; viii: $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+2$; ix: $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; x: $x, -y+1, z+\frac{1}{2}$.

vinogradovite but has been described in the synthetic compound $Li_2(Si_{0.25}Ge_{0.75})O_5$ (Völlenkle, Wittmann and Nowotny, 1968). Figure 1 illustrates how the infinite chains run parallel to the *c* axis and how the big channels are populated.

The site occupancy factors (s.o.f.'s) of Ti and Si(2) account for the simultaneous presence of different elements on these sites. The chemical data (Rønsbo et al., 1990) indicate small amounts of Nb and Fe on the same site as Ti, this agrees with s.o.f. for $Ti > 1.00$ indicating that heavier elements also occupy this site.

Rastsvetaeva and Andrianov (1984) describe Al in the Si(2) site as the only substitution. The calculated value of s.o.f. for Si(2) from chemical analysis ($Si_{5.969}Al_{1.234}$) is 0.988, whereas the refined value 0.892, being considerably less than unity, indicates the presence of a lighter element in this site. This led to analysis for Be (Rønsbo et al., 1990), which was confirmed to be present. s.o.f. = 0.892 corresponds to 0.85 Be atoms/unit cell, in agreement with the calculated Be content 0.797 atoms/unit cell from chemical analysis.

The Al and Be substitution in the Si(2) site is reflected in the longer mean $\langle Si-O \rangle$ distance in the Si(2) tetrahedron (Smith and Bailey, 1963; Rastsvetaeva and Andrianov, 1984). The mean $\langle Si(1)-O \rangle$ distance is 1.625 Å (RT) and 1.626 Å (LT) compared to the mean $\langle Si(2)-O \rangle$ distance 1.644 Å (RT) and 1.647 Å (LT). Ti is octahedrally coordinated and Na(1) coordinated by 8 O atoms from the chains. The Ti octahedron is slightly distorted (Table 4). The largest deviations between RT and LT studies were observed in the polyhedron of Na(1).

The positions of the two water molecules in the channels agree fairly well with the ones reported by Rastsvetaeva and Andrianov (1984) whereas the displacement parameters and s.o.f.'s of the O atoms differ. We observe the OW(1) site to be less populated than the OW(2) site (1.4 and 4.4 atoms/unit cell respectively) and OW(1) having the smaller displacement parameter. The opposite was reported by Rastsvetaeva and Andrianov (1984).

The vinogradovite crystal contains small amounts of K located in the channels of the structure (Rastsvetaeva and Andrianov, 1984). From our analysis the K atoms are most likely situated in the OW(2) site. Normal $K-O$ distances are in the range 2.7 – 2.9 Å, excluding the Na(2) site for K atoms. The large displacement parameter for OW(2) could be due to two almost resolvable sites, but it could as well reflect the presence of a heavier element (K) not accounted for.

The s.o.f. for Na(2) = 0.200 corresponds to 1.6 Na atoms/unit cell. This agrees with the extra 1.97 Na atoms from chemical analysis (Rønsbo et al., 1990).

The results from RT and LT are so similar that it can be concluded that the disorder in the channels of vinogradovite is static.

Two differences are observed in the crystal structure of the vinogradovite sample compared to earlier work (Rastsvetaeva et al., 1968; Rastsvetaeva and Andrianov, 1984). The excess Na is located in the channels and the site occupancy factor for Si(2) showed Be in this crystallographic site.

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