

THE CRYSTAL STRUCTURE OF GEORGECHAOITE $\text{NaKZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$

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ABSTRACT

Georgechaoite $\text{NaKZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (see preceding paper) is orthorhombic, space group $P2_1nb$, with a 11.836(4), b 12.940(6), c 6.735(4) Å; $Z = 4$. Its crystal structure has been refined to a residual $R = 0.053$, based on 1840 reflections measured on an automatic single-crystal X-ray diffractometer. It consists of sinusoidal single silicate chains, with six-tetrahedron repeat, running parallel to [101] and [101] directions, which are cross-linked by regular $[\text{ZrO}_6]$ octahedra and highly distorted $[\text{NaO}_4(\text{H}_2\text{O})_2]$ and $[\text{KO}_4(\text{H}_2\text{O})_2]$ octahedra. The average Si-O distances within the three crystallographically different tetrahedra are 1.624, 1.632 and 1.623 Å, and the average Na-O, K-O, and Zr-O distances are 2.557, 2.752, and 2.092 Å, respectively. All four hydrogen atoms belonging to the two water molecules participate in hydrogen bonding. Georgechaoite is isostructural with gaidonnayite, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (Chao 1973, 1985). The ordered replacement of Na by K in georgechaoite mostly affects the positions of the water molecules, with respect to those in gaidonnayite.

Keywords: georgechaoite, crystal-structure analysis, single chains, six-tetrahedron repeat, gaidonnayite, zirconium silicate, New Mexico.

SOMMAIRE

La georgechaoïte $\text{NaKZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (voir article précédent) appartient au groupe orthorhombique $P2_1nb$, avec maille a 11.836(4), b 12.940(6), c 6.735(4) Å; $Z = 4$. Sa structure cristalline, déterminée sur 1840 réflexions obtenues sur monocristal au diffractomètre automatique, a été affinée jusqu'au résidu $R = 0.053$. Elle consiste en chaînes anioniques simples, sinusoidales, de période égale à six tétraèdres, dirigées suivant [101] et [101] et reliées entre elles par des octaèdres réguliers (ZrO_6) ou difformes $[\text{NaO}_4(\text{H}_2\text{O})_2]$, $[\text{KO}_4(\text{H}_2\text{O})_2]$. La distance Si-O moyenne est de 1.624, 1.632, et 1.623 Å, dans trois types de tétraèdre cristallographiquement différents, et les distances moyennes Na-O, K-O, Zr-O sont respectivement égales à 2.557, 2.752, et 2.092 Å. Les atomes d'hydrogène de l'eau d'hydratation participent tous quatre aux liaisons hydrogène. La georgechaoïte est isotype de la gaidonnayite $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (Chao 1973, 1985). La substitution de K au Na qui fait passer la gaidonnayite à la georgechaoïte affecte surtout la position des molécules d'eau.

(Traduit par la Rédaction)

Mots-clés: georgechaoïte, structure cristalline, chaînes simples, période de six tétraèdres, gaidonnayite, silicate de zirconium, Nouveau Mexique.

INTRODUCTION

Georgechaoite $\text{NaKZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ is a new mineral species discovered by Mr. Robert Boggs in the Wind Mountain laccolith, Otero County, New Mexico (Boggs & Ghose 1985). It occurs in miarolitic cavities in an analcime nepheline syenite, associated with nepheline, analcime, K-feldspar, aegirine, catapleite, chlorite and monazite. The crystals of georgechaoite are white to colorless, have a maximum size of 1 mm and are almost always twinned. The morphology, optical properties, chemical composition, and X-ray-diffraction data have been reported by Boggs & Ghose (1985). From the morphology, chemical composition and mineral association, we suspected that the new mineral is the Na-K-ordered variety of gaidonnayite, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, described from Mont St. Hilaire, Quebec by Chao & Watkinson (1974). The structure determination reported in this paper confirms this view. We also report on the differences between these two structures due to (Na,K) substitution.

CRYSTAL DATA

An untwinned crystal was made available for the structure determination through the courtesy of Mr. Robert Boggs. It is approximately a parallelepiped in shape, measuring $0.32 \times 0.30 \times 0.41$ mm. The crystal was mounted on a Syntex P1 automatic single-crystal X-ray diffractometer, and the unit-cell dimensions were determined through least-squares refinement of 15 reflections with 2θ values ranging from 30 to 40° measured with monochromatized $\text{MoK}\alpha$ radiation. Georgechaoite is orthorhombic, space group $P2_1nb$, with a 11.836(4), b 12.940(6) and c 6.735(4) Å, and four formula units per cell (Boggs & Ghose 1985). The unit-cell volume is 1031.5(1) Å³, and the measured and calculated densities are 2.70(2) and 2.679 g/cm³, respectively. The linear absorption-coefficient $\mu(\text{MoK}\alpha)$ is 20.073 cm⁻¹. Owing to the replacement of Na by K, the unit-cell dimensions of georgechaoite are slightly larger than those of gaidonnayite [a 11.740(3), b 12.820(3), c 6.691(1) Å; Chao & Watkinson (1974)].

COLLECTION OF INTENSITY DATA

The X-ray-intensity data were collected from the

same crystal as described above, on the Syntex P1 diffractometer using $\text{MoK}\alpha$ radiation monochromatized by reflection from a graphite "single" crystal and a scintillation counter. The intensities were measured by the 2θ - θ method using a variable scan-rate, the minimum being $2^\circ/\text{min}$ (50 kV, 15 mA). All reflections with $2\theta \leq 65^\circ$ were measured. Out of a total of 1891 independent reflections, 51 had intensities below $2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity as determined by counting statistics. The intensity data were corrected for Lorentz and polarization factors, and approximately for absorption, assuming the crystal to have a spherical shape with a diameter of 0.34 mm.

STRUCTURE DETERMINATION AND REFINEMENT

The atomic position parameters of gaidonnayite were made available through the courtesy of Professor George Y. Chao (priv. comm. 1983) and used as starting parameters. Two different structure-factor calculations were made, assuming one of the two different sodium sites in gaidonnayite to be occupied by potassium. The R factors for the two models were found to be 18% and 17.7%; these were reduced by least-squares refinement using isotropic temperature-factors to 9.5 and 10.4%. The model with the lower R factor was taken as the correct trial structure, where K occupies the Na(1) site, which is the larger of the two sodium sites in gaidonnayite. The Na and K atom distribution was also confirmed from the Fourier and difference-Fourier syntheses; a much higher electron-density was found at the K site and, in addition, somewhat different atomic position for the water molecules. The new atomic parameters de-

rived from the difference-Fourier synthesis were used for block-diagonal least-squares refinement using first isotropic and then anisotropic temperature-factors, and a weighting scheme $W = 1/\sigma^2(F)$; σF is the standard derivation of the observed structure-factor. To fix the origin, the x_{Na} parameter was held constant. The refinement converged to an R factor of 0.053, where all the ratios of parameter shifts to standard deviations were less than 0.1. Site-occupancy refinement of Na and K converged to full occupancy by Na or K at these sites. A difference-Fourier map calculated at this stage revealed no residual density at the Na and K sites. The positions of all four hydrogen atoms belonging to the two water molecules were found from this map. Attempts, however, to refine the positions of the hydrogen atoms failed. Subsequently, two cycles of least-squares refinement using anisotropic temperature-factors for all atoms (except hydrogen) and fixed positions of the hydrogen atoms, with an isotropic temperature-factor of 3.0 \AA^2 , resulted in a final residual R of 0.053 for 1840 observed reflections. The atomic scattering factors for Na, K, Zr, Si, O and H were taken from Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman 1970). The least-squares program incorporated in the X-RAY SYSTEM (Stewart *et al.* 1972) was used for the refinement. The final atomic position and thermal parameters are listed in Table 1, and the bond lengths and angles with their standard deviations in Table 2. The observed and calculated structure-factors are listed in Table 3, which can be obtained at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 1. GEORGECHAQITE $\text{NaKZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$: POSITIONAL AND THERMAL PARAMETERS*

Atom	x	y	z	u ₁₁	u ₂₂	u ₃₃	u ₁₂	u ₁₃	u ₂₃
Na	-0.0041	0.3891(4)	0.3287(8)	1.3(2)	3.1(3)	4.2(3)	0.3(2)	0.3(2)	-0.6(2)
K	0.7515(4)	0.1499(2)	0.4136(5)	4.8(2)	3.2(1)	4.4(1)	-0.1(2)	-1.0(2)	1.0(1)
Zr	0.2499(1)	0.0521(1)	0.1468(1)	0.88(2)	0.68(2)	1.41(2)	0.0(3)	-0.02(4)	-0.03(2)
Si(1)	0.2820(2)	0.2869(2)	0.3883(4)	0.42(9)	0.14(9)	0.86(10)	-0.10(8)	0.02(8)	0.15(8)
Si(2)	0.4981(2)	0.4165(2)	0.3911(4)	0.19(9)	0.21(9)	1.06(10)	0.00(8)	-0.06(9)	-0.05(8)
Si(3)	0.7116(2)	0.3910(2)	0.1459(4)	0.60(9)	0.48(9)	0.80(10)	-0.06(8)	0.18(9)	-0.13(9)
O(1)	0.2163(6)	0.3939(5)	0.3627(11)	1.2(3)	0.2(2)	2.4(4)	-0.2(2)	-0.2(3)	0.4(3)
O(2)	0.4160(6)	0.3150(5)	0.4196(12)	0.5(3)	0.4(3)	3.0(4)	-0.0(2)	-0.5(3)	0.6(3)
O(3)	0.7424(8)	0.2709(5)	0.0940(10)	1.5(3)	1.8(3)	1.3(3)	0.4(3)	0.5(4)	0.2(2)
O(4)	0.2693(6)	0.2083(5)	0.2052(9)	1.9(4)	0.3(3)	1.1(3)	-0.3(2)	0.8(3)	0.2(2)
O(5)	0.4200(6)	0.0155(6)	0.1542(10)	0.8(3)	0.8(3)	1.8(3)	-0.0(2)	0.1(3)	0.1(3)
O(6)	0.5761(6)	0.3910(6)	0.1953(11)	0.6(3)	1.8(3)	1.9(4)	0.2(3)	0.2(3)	-0.8(3)
O(7)	0.0756(6)	0.0706(5)	0.0882(11)	0.7(3)	0.7(3)	1.7(3)	0.1(2)	-0.3(3)	-0.2(2)
O(8)	0.2347(7)	0.0378(5)	0.4549(10)	2.5(5)	0.3(3)	1.1(3)	0.2(3)	0.6(3)	-0.1(2)
O(9)	0.7786(6)	0.4273(6)	0.3411(9)	0.7(3)	1.4(3)	1.1(3)	-0.3(2)	-0.1(3)	-0.5(2)
O(10)W1	0.5265(11)	0.1271(8)	0.4753(19)	5.5(7)	2.7(5)	5.9(7)	1.7(5)	-2.7(6)	-1.1(5)
O(11)W2	0.9718(13)	0.2061(10)	0.3714(13)	7.0(9)	5.5(8)	2.6(5)	4.6(7)	-1.4(5)	-0.4(5)
H(1)	0.484	0.190	0.425	3.0					
H(2)	0.498	0.063	0.406	3.0					
H(3)	0.016	0.184	0.490	3.0					
H(4)	0.00	0.170	0.255	3.0					

* with standard deviations in parentheses.

DESCRIPTION OF THE STRUCTURE

The crystal structure of georgechaoite consists of sinusoidal six-tetrahedron-repeat single silicate chains running parallel to $[10\bar{1}]$ and $[101]$ directions (Fig. 1). These chains are cross-linked by corner-sharing with fairly regular ZrO_6 octahedra and distorted Na and K octahedra and hydrogen bonds into a three-dimensional framework (Fig. 2).

The sodium octahedron

Within the distorted $[NaO_4(H_2O)_2]$ octahedron, the water molecules occur in a *cis* configuration (Fig. 3a). The average Na–O distance is 2.628 ± 0.050 Å; however, the average Na–OH₂ distance (2.414 ± 0.005 Å) is much shorter than the average of the other four Na–O distances (2.628 ± 0.047 Å). The octahedral O–Na–O angles range from 54.9 to 113.3°, as opposed to the expected value of 90°. The Na octahedron shares two edges, O(1)–O(7) and O(5)–O(9), with two adjacent ZrO_6 octahedra and one edge, O(1)–O(10)(W1), with an adjacent K octahedron.

The potassium octahedron

Within the distorted $[KO_4(H_2O)_2]$ octahedron, the water molecules occur in a *trans* configuration (Fig. 3b). If we ignore the long K–O(1) distance, the other K–O bond distances range from 2.60 to 2.70 Å (av. 2.680 Å), with no distinction between K–O and K–OH₂ bond distances. This short average K–O distance yields a nominal value of 1.28 Å as the radius of the K⁺ ion, assuming the radius of the O²⁻ ion to be 1.40 Å, which is 0.1 Å shorter than the radius of octahedrally co-ordinated K⁺ according to Shannon & Prewitt (1969). However, the average of all six K–O distances (2.752 Å) yields at K⁺ radius of 1.352 Å, which is closer to the Shannon–Prewitt value (1.38 Å). The angular distortion in the K octahedron is comparable to that in the Na octahedron, the O–K–O angles ranging from 54.9 to 111.1°.

The zirconium octahedron

The ZrO_6 octahedron is fairly regular, with an average Zr–O distance of 2.092 Å; the octahedral O–Zr–O angles range from 85.4 to 97.2°. It is comparable to a similar ZrO_6 octahedron found in gaidonnayite (av. Zr–O 2.078 Å) (Chao 1985), petarasite $Na_5Zr_2Si_6O_{18}(Cl, OH) \cdot 2H_2O$ (av. Zr–O 2.091 Å) (Ghose *et al.* 1980) and zektzerite $NaLiZrSi_6O_{15}$ (av. Zr–O 2.074 Å) (Ghose & Wan 1978).

Configuration of the silicate tetrahedra and the six-tetrahedron-repeat single silicate chain

There are three crystallographically distinct sili-

cate tetrahedra, with average Si–O distances of 1.624, 1.632 and 1.623 Å. By corner-sharing, these tetrahedra form a sinusoidal six-tetrahedron-repeat single silicate chain (Fig. 2) previously found in stoke-

TABLE 2. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GEORGECHAOITE*

Na Polyhedron		K Polyhedron	
Na–O(1)	2.620(9)	K–O(1)	3.110(8)
Na–O(5)	2.675(9)	K–O(3)	2.667(7)
Na–O(7)	2.597(9)	K–O(4)	2.700(7)
Na–O(9)	2.621(9)	K–O(8)	2.599(7)
Na–O(10) (W1)	2.419(14)	K–O(10) (W1)	2.713(14)
Na–O(11) (W2)	2.408(15)	K–O(11) (W2)	2.723(16)
Mean	2.557	Mean	2.752
Zr Octahedron			
		distance	angle
Zr–O(1)	2.092(7)	O(1)–O(5)	2.885(10)
Zr–O(4)	2.076(6)	O(1)–O(7)	2.853(10)
Zr–O(5)	2.070(7)	O(1)–O(8)	2.850(9)
Zr–O(7)	2.115(7)	O(1)–O(9)	3.149(10)
Zr–O(8)	2.094(7)	O(7)–O(8)	3.137(10)
Zr–O(9)	2.106(6)	O(9)–O(5)	2.795(10)
Mean	2.092	O(4)–O(5)	3.091(10)
		O(4)–O(7)	3.012(10)
		O(4)–O(8)	2.809(9)
		O(4)–O(9)	3.021(9)
		O(7)–O(9)	2.925(10)
		O(8)–O(5)	3.002(11)
		Mean	2.961
			90.19
Si(1) Tetrahedron			
		distance	angle
Si(1)–O(1)	1.599(7)	O(1)–O(2)	2.605(10)
Si(1)–O(2)	1.642(7)	O(1)–O(3)	2.663(9)
Si(1)–O(3)	1.645(7)	O(1)–O(4)	2.704(9)
Si(1)–O(4)	1.608(7)	O(2)–O(3)	2.616(11)
Mean	1.624	O(2)–O(4)	2.650(10)
		O(3)–O(4)	2.655(9)
		Mean	2.656
			109.4
Si(2) Tetrahedron			
		distance	angle
Si(2)–O(2)	1.648(7)	O(2)–O(5)	2.649(10)
Si(2)–O(5)	1.611(8)	O(2)–O(6)	2.618(10)
Si(2)–O(6)	1.645(8)	O(2)–O(7)	2.658(10)
Si(2)–O(7)	1.624(8)	O(5)–O(6)	2.656(10)
Mean	1.632	O(5)–O(7)	2.704(10)
		O(6)–O(7)	2.696(10)
		Mean	2.664
			109.4
Si(3) Tetrahedron			
		distance	angle
Si(3)–O(3)	1.637(8)	O(3)–O(6)	2.602(11)
Si(3)–O(6)	1.638(8)	O(3)–O(8)	2.654(9)
Si(3)–O(8)	1.608(7)	O(3)–O(9)	2.660(10)
Si(3)–O(9)	1.608(7)	O(6)–O(8)	2.646(10)
Mean	1.623	O(6)–O(9)	2.636(10)
		O(8)–O(9)	2.694(9)
		Mean	2.648
			109.4
Si–O–Si Angles			
Si(1)–O(2)–Si(2)	137.0(5)		
Si(2)–O(6)–Si(3)	135.5(5)		
Si(3)–O(3)–Si(1)	132.6(4)		
Hydrogen bonds			
Water molecule, W1			
O(10)–H(1)	1.02	H(1)–O(10)–H(2)	109.8
O(10)–H(2)	1.01	O(10)–H(1)–O(2)	160.8
H(1)–H(2)	1.66	O(10)–H(2)–O(5)	142.3
H(1)–O(2)	1.81		
H(2)–O(5)	2.03		
O(10)–O(2)	2.791		
O(10)–O(5)	2.893		
Water molecule, W2			
O(11)–H(3)	1.00	H(3)–O(11)–H(4)	107.9
O(11)–H(4)	0.98	O(11)–H(3)–O(6)	163.8
H(3)–H(4)	1.60	O(11)–H(4)–O(7)	162.9
H(3)–O(6)	1.83		
H(4)–O(7)	1.92		
O(11)–O(6)	2.807		
O(11)–O(7)	2.871		

* with standard deviations in parentheses.

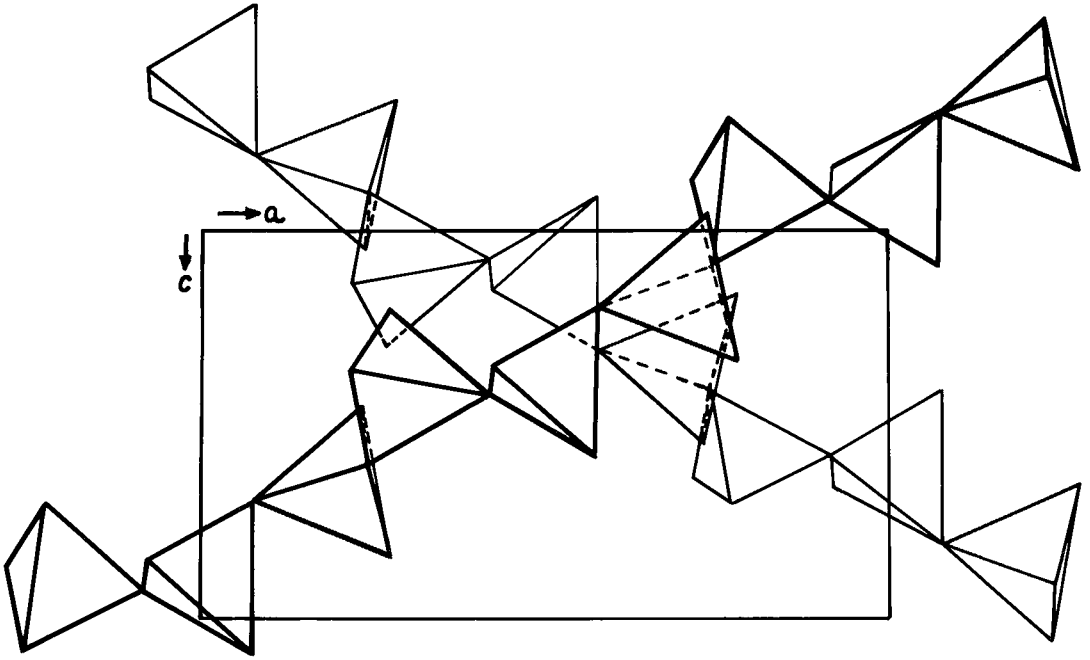


FIG. 1. Six-tetrahedron-repeat single silicate chains in georgechaoite.

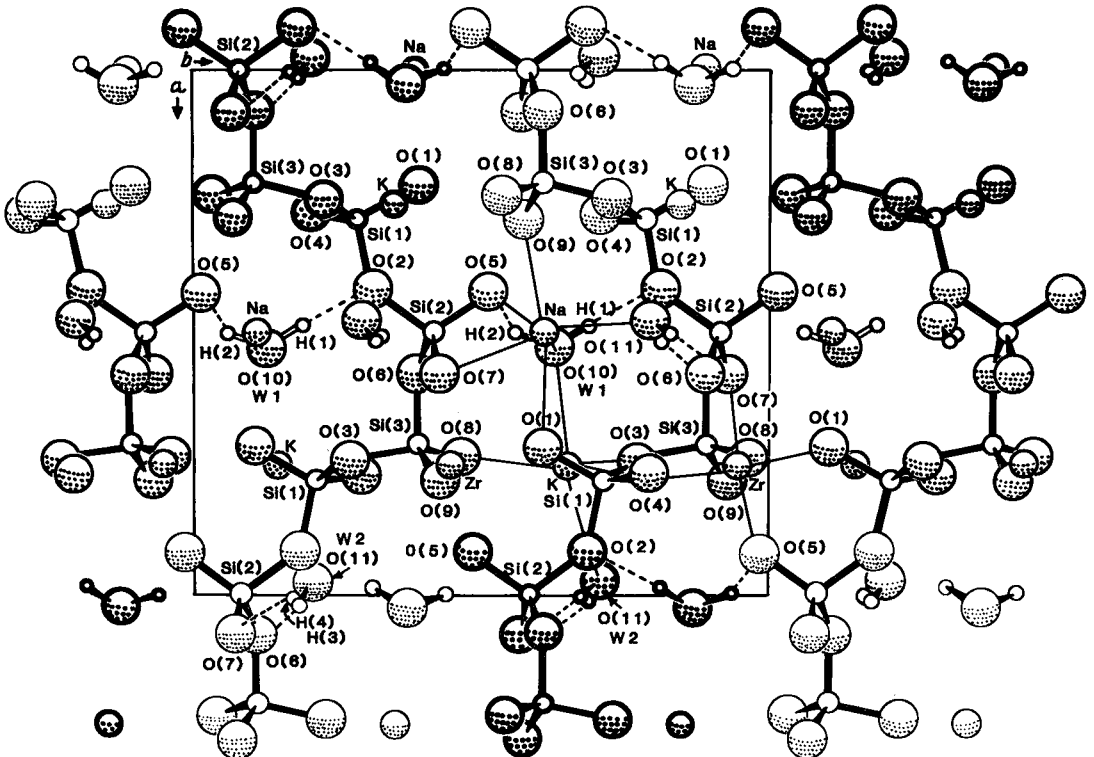


FIG. 2. A view of the crystal structure of georgechaoite, as viewed down the *c* axis.

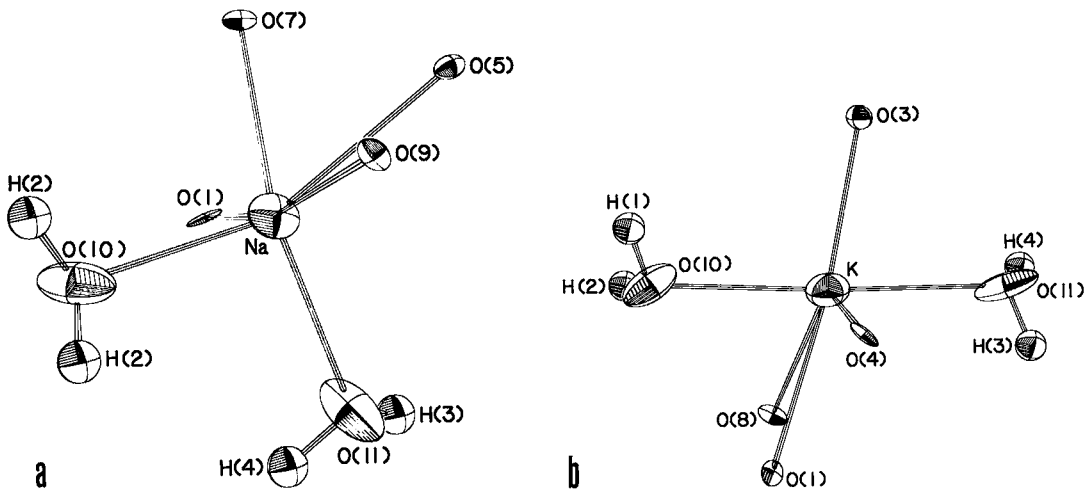


FIG.3. The configuration of (a) the $[\text{NaO}_4(\text{H}_2\text{O})_2]$ octahedron and (b) the $[\text{KO}_4(\text{H}_2\text{O})_2]$ octahedron in georgechaoite.

site $\text{CaSnSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ (Vorma 1963) and gaidonnayite (Chao 1973, 1985). Each silicate tetrahedron shares two corners with two adjacent silicate tetrahedra and the other two corners with Zr, Na or K octahedra. The average bridging Si–O bonds are significantly longer (1.643 Å) than the average non-bridging bonds (1.610 Å). Furthermore, the O–Si–O angles involving the bridging bonds are always significantly smaller (av. 105.3°) and remarkably constant, whereas the O–Si–O angles involving the non-bridging bonds are much larger (av. 114.1°) in all three tetrahedra. This trend in Si–O bond lengths and angles, which is very similar in gaidonnayite (Chao 1985), was first reported in the structure of Na_2SiO_3 (McDonald & Cruickshank 1967) and subsequently in Na_2GeO_3 (Völlenklee *et al.* 1971). McDonald & Cruickshank (1967) explained the difference between the bridging and nonbridging Si–O bonds in a silicate chain by the *d*–*p* π bonding theory of Cruickshank (1961) and the distortion in the O–Si–O angles by repulsion of the nonbridging oxygen atoms, which have more negative charge than the bridging oxygen atoms. An *ab initio* quantum-mechanical calculation incorporating both effects would be highly desirable (*cf.* Newton & Gibbs 1980). In georgechaoite, the difference between bridging and nonbridging oxygen atoms is less pronounced than in Na_2SiO_3 owing to the presence of Zr^{4+} ions, which drain some of the negative charge from the silicate ion.

Hydrogen bonds

Each of the two water molecules is bonded to one Na and one K. All the four hydrogen atoms belonging to two crystallographically distinct water molecules participate in hydrogen bonding. The O–H

distances range from 0.98 to 1.02 Å, and the H–O–H angles are 108° and 110° . The water molecule W1 donates H(1) to O(2), which is shared by Si(1) and Si(2), and H(2) to O(5), which is shared by Si(2), Zr and Na. The O–H . . . O angles are 161° and 142° for H(1) and H(2), respectively, the latter being a considerably bent hydrogen bond. The water molecule W(2) donates H(3) to O(6), which is shared by Si(2) and Si(3); the other hydrogen atom H(4) is donated to O(7), which is shared by Si(2), Zr and Na. The O–H . . . O angles are 164° and 163° for H(3) and H(4). These hydrogen bonds help bind the alkali-bearing octahedra to the silicate chains in a three-dimensional framework. From DTA and TGA experiments, Chao & Watkinson (1974) concluded that in gaidonnayite, dehydration begins immediately above room temperature and is completed at 400°C , at which point the structure collapses; at higher temperatures, a compound related to wadeite $\text{K}_2\text{Si}_3\text{O}_9$ is obtained. On the basis of the crystal structure, a similar behavior is expected for georgechaoite, with no great distinction between the two water molecules with respect to their dehydration behavior.

THE CRYSTAL-CHEMICAL EFFECTS OF Na–K SUBSTITUTION

The replacement of Na by K in georgechaoite mostly affects the positions of the water molecules compared to those in gaidonnayite, whereas the configuration of the other polyhedra and silicate chains remains practically undisturbed. In georgechaoite, the two K–OH₂ distances are comparatively larger by 0.25 and 0.19 Å, and the corresponding Na–OH₂ distances shorter by 0.05 and 0.08 Å. The other sig-

nificant increase occurs in the K-O(4) distance, which is 0.17 Å longer than the Na(1)-O(4) distance in gaidonnayite. The average K-O distance (2.752 Å) in georgechaoite is only slightly larger than the corresponding Na(1)-O distance (2.719 Å) in gaidonnayite, which explains the relatively minor structural change due to the substitution of K for Na.

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