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THE CRYSTAL STRUCTURE OF GAIDONNAYITE $Na_2ZrSi_3O_9{\cdot}2H_2O$*

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ABSTRACT

Gaidonnayite, $Na_2ZrSi_3O_9{\cdot}2H_2O$, from Mont St. Hilaire, Quebec is orthorhombic, $P2_1nb$, with a 11.740(3), b 12.820(3), c 6.691(1) Å and Z = 4. The structure was solved by a three-dimensional Patterson synthesis and refined by full-matrix least-squares method using anisotropic temperature-parameters. The final residual R is 3.92% for 1211 reflections collected on an equi-inclination single-crystal diffractometer. The structure is composed of sinusoidal single silicate-chains of tetrahedra, repeating at every six tetrahedra, along [101] and [10$\bar{1}$] and cross-linked by one Zr–O octahedron and two distorted Na–O octahedra. The mean Si–O distances in the three independent tetrahedra are 1.629, 1.617 and 1.623 Å. The mean Zr–O distance is 2.078 Å, and the mean Na–(O, H_2O) distances are 2.626 and 2.542 Å.

Keywords: gaidonnayite, structure determination, single chain, silicate, six-tetrahedron repeat, Mont St. Hilaire, Quebec.

SOMMAIRE

La structure de la gaidonnayite, $Na_2ZrSi_3O_9{\cdot}2H_2O$, du mont St-Hilaire (Québec), dont on connait la symmétrie ($P2_1nb$) et la maille [a 11.740(3), b 12.820(3), c 6.691(1) Å], a été résolue pour Z = 4 par synthèse Patterson à 3 dimensions et affinée par moindres carrés à matrice entière et paramètres thermiques anisotropes. Le résidu final est 0.0392 pour 1211 réflexions mesurées au diffractomètre à équi-inclinaison et cristal unique. La structure silicatée est en chaînes simples sinusoïdales, dont la période contient six tétrahèdres et qui alternent en direction entre [101] et [10$\bar{1}$]. Ces chaînes sont reliées par un octaèdre Zr–O et deux octaèdres Na–O difformes. La distance Si–O moyenne pour chacun des trois tétraèdres indépendants est 1.629, 1.617 et 1.623 Å. La distance Zr–O moyenne est égale à 2.078 Å; la moyenne des distances Na–(O, H_2O) pour l'un des octaèdres difformes est 2.626 Å; pour l'autre, elle est 2.542 Å.

(Traduit par la Rédaction)

Mots-clés: gaidonnayite, détermination de la structure, chaîne simple, silicate, période de six tétraèdres, mont St-Hilaire (Québec).

CRYSTAL DATA

Gaidonnayite ($Na_2ZrSi_3O_9{\cdot}2H_2O$, Chao & Watkinson 1974), a dimorph of catapleiite, is orthorhombic with a 11.740(3), b 12.820(3), c 6.691(1) Å, V = 1007.03 Å^3, Z = 4. Systematic extinctions are $h0l$ with $h + l = 2n + 1$ and $hk0$ with $k = 2n + 1$. The space group is $P2_1nb$ (#33, $Pna2_1$ with cab orientation). The observed density is 2.67 g/cm^3, and the density calculated from electron-microprobe data is 2.70 g/cm^3. The linear absorption-coefficient μ(Mo$K\alpha$) is 15.95 cm^{-1}.

EXPERIMENTAL

A crystal fragment of gaidonnayite from Mont St. Hilaire, Quebec, was ground to a sphere approximately 0.12 mm in diameter, and used for collection of intensity data on a manual Supper equi-inclination single-crystal diffractometer, with a scintillation counter and Mo$K\alpha$ radiation (λ = 0.7107 Å). The ω-scan method was used with a scanning speed of 2°/min. All hkl and $hk\bar{l}$ reflections with $2\theta \leq 55°$ were measured and averaged to yield a total of 1211 independent reflections. Of these, 18 reflections have net intensities less than $2 \times \sigma(I)$, where $\sigma(I)$ was obtained from counting statistics. These were considered unobserved and were arbitrarily assigned one behalf of the background intensities. The intensity data were corrected for Lorentz and polarization factors but not for absorption on account of the low absorption-coefficient and small size of the crystal (μr = 0.19).

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by a three-dimensional Patterson synthesis, from which the position of Zr, two Na and three Si atoms was determined. As the multiplicity of these positions in the centrosymmetric space-group $Pmnb$ is incompatible with the contents of the cell, the noncentrosymmetric space-group was assumed in calculating the initial trial Fourier map, using all F_{hkl} values. The Fourier map revealed the position of all nine oxygen atoms and two water molecules. Distances and angles calculated at this stage showed no unreasonable values, and the trial structure in the noncentrosymmetric space-

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TABLE 1. ATOMIC POSITIONAL AND THERMAL PARAMETERS-(x 10^4)

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	0.7466(3)	0.1567(2)	0.4307(4)	51(2)	45(2)	162(8)	7(4)	-19(8)	-5(6)
Na(2)	-0.0041(3)	0.3876(3)	0.3316(5)	47(2)	37(2)	180(10)	6(4)	-10(6)	-49(6)
Zr	0.2500	0.0531(1)	0.1510(1)	24(1)	15(1)	63(1)	0(1)	-4(1)	0(1)
Si(1)	0.2809(1)	0.2883(1)	0.3927(2)	21(1)	7(1)	59(4)	-1(1)	-4(3)	0(2)
Si(2)	0.4981(1)	0.4180(1)	0.3911(2)	20(1)	15(1)	58(4)	-1(1)	-5(3)	-1(3)
Si(3)	0.7144(1)	0.3918(1)	0.1501(2)	20(1)	15(1)	51(4)	1(1)	4(3)	-8(2)
0(1)	0.2116(5)	0.3952(3)	0.3644(7)	25(3)	8(2)	90(10)	7(5)	-3(9)	-21(7)
0(2)	0.4173(4)	0.3155(3)	0.4186(7)	22(3)	9(2)	103(11)	-12(4)	-16(10)	15(8)
0(3)	0.7417(5)	0.2699(3)	0.1017(6)	29(3)	14(2)	56(8)	18(5)	21(11)	12(7)
0(4)	0.2654(5)	0.2096(3)	0.2065(7)	39(4)	17(2)	78(9)	-18(5)	36(12)	3(8)
0(5)	0.4225(4)	0.1940(4)	0.1562(7)	23(3)	14(3)	107(12)	12(5)	-16(9)	-23(8)
0(6)	0.5759(4)	0.3940(4)	0.1960(7)	22(3)	35(3)	60(9)	-1(5)	10(9)	-29(9)
0(7)	0.0743(4)	0.0706(4)	0.0898(7)	15(3)	23(2)	67(10)	2(4)	-5(9)	-3(9)
0(8)	0.2398(5)	0.0361(3)	0.4583(7)	27(3)	12(2)	6(8)	3(5)	11(10)	-6(6)
0(9)	0.7817(5)	0.4258(4)	0.3474(6)	31(3)	19(2)	47(10)	-11(5)	-20(9)	-18(7)
$H_2$0(1)	0.5397(5)	0.1326(4)	0.4739(10)	48(5)	32(3)	186(17)	11(6)	-30(15)	-32(12)
$H_2$0(2)	0.9558(7)	0.1991(5)	0.3821(10)	60(6)	35(4)	118(14)	26(7)	-18(14)	23(11)

The anisotropic temperature factors are expressed in the form: $\exp[-(h^2\beta_{11}.....+2hk\beta_{12}....)]$.
Estimated standard errors are in parentheses.

TABLE 2. BOND LENGTHS (Å) IN GAIDONNAYITE

Si(1)-0 Tetrahedron	
Si(1)-0(1)	1.606(6)
Si(1)-0(2)	1.647(6)*
Si(1)-0(3)	1.651(5)*
Si(1)-0(4)	1.613(5)
Mean	1.629
0(1)-0(2)	2.647(8)
0(1)-0(3)	2.671(7)
0(1)-0(4)	2.679(7)
0(2)-0(3)	2.636(7)
0(2)-0(4)	2.652(7)
0(3)-0(4)	2.671(7)
Mean	2.659
Si(2)-0 Tetrahedron	
Si(2)-0(2)	1.631(5)*
Si(2)-0(5)	1.631(6)
Si(2)-0(6)	1.623(6)*
Si(2)-0(7)	1.608(5)
Mean	1.617
0(2)-0(5)	2.661(7)
0(2)-0(6)	2.589(7)
0(2)-0(7)	2.615(7)
0(5)-0(6)	2.608(8)
0(5)-0(7)	2.687(7)
0(6)-0(7)	2.673(7)
Mean	2.639
Si(3)-0 Tetrahedron	
Si(3)-0(3)	1.628(5)*
Si(3)-0(6)	1.655(6)*
Si(3)-0(8)	1.611(5)
Si(3)-0(9)	1.597(5)
Mean	1.623
0(3)-0(6)	2.592(8)
0(3)-0(8)	2.665(6)
0(3)-0(9)	2.630(7)
0(6)-0(8)	2.651(8)
0(6)-0(9)	2.651(8)
0(8)-0(9)	2.694(7)
Mean	2.647
Na(1)-0 Octahedron	
Na(1)-0(1)	3.006(6)
Na(1)-0(3)	2.637(6)
Na(1)-0(4)	2.527(6)
Na(1)-0(8)	2.583(6)
Na(1)-$H_2$0(1)	2.465(8)
Na(1)-$H_2$0(2)	2.537(10)
Na(2)-0 Octahedron	
Na(2)-0(1)	2.545(7)
Na(2)-0(5)	2.622(6)
Na(2)-0(7)	2.575(6)
Na(2)-0(9)	2.563(7)
Na(2)-$H_2$0(1)	2.462(8)
Na(2)-$H_2$0(2)	2.485(8)
Zr-0 Octahedron	
Zr-0(1)	2.077(5)
Zr-0(4)	2.048(5)
Zr-0(5)	2.071(6)
Zr-0(7)	2.115(5)
Zr-0(8)	2.071(5)
Zr-0(9)	2.083(4)
Mean	2.078
0(1)-0(5)	2.947(8)
0(1)-0(7)	2.784(7)
0(1)-0(8)	2.835(7)
0(1)-0(9)	3.106(8)
0(4)-0(5)	3.076(8)
0(4)-0(7)	2.970(7)
0(4)-0(8)	2.807(7)
0(4)-0(9)	2.971(7)
0(5)-0(8)	2.955(8)
0(5)-0(9)	2.737(7)
0(7)-0(8)	3.170(7)
0(7)-0(9)	2.925(8)
Shortest $H_2$0-0 Distances	
$H_2$0(1)-0(2)	2.775(8)
$H_2$0(1)-0(5)	2.919(9)
$H_2$0(2)-0(6)	2.797(9)
$H_2$0(2)-0(7)	2.910(9)

* Bonds with bridging oxygen atoms

TABLE 3. SELECTED BOND-ANGLES (°) in GAIDONNAYITE

Si(1)-0 Tetrahedron	
0(1)-Si(1)-0(2)	108.9(5)
0(1)-Si(1)-0(3)	110.2(5)
0(1)-Si(1)-0(4)	112.7(6)
0(2)-Si(1)-0(3)*	106.1(5)
0(2)-Si(1)-0(4)	108.9(6)
0(3)-Si(1)-0(4)	109.9(5)
Mean	109.5
Si(2)-0 Tetrahedron	
0(2)-Si(2)-0(5)	110.6(6)
0(2)-Si(2)-0(6)*	105.4(5)
0(2)-Si(2)-0(7)	107.6(5)
0(5)-Si(2)-0(6)	107.8(5)
0(5)-Si(2)-0(7)	113.4(6)
0(6)-Si(2)-0(7)	111.7(6)
Mean	109.4
Si(3)-0 Tetrahedron	
0(3)-Si(3)-0(6)*	104.3(6)
0(3)-Si(3)-0(8)	110.7(5)
0(3)-Si(3)-0(9)	109.3(6)
0(6)-Si(3)-0(8)	108.6(6)
0(6)-Si(3)-0(9)	109.2(6)
0(8)-Si(3)-0(9)	114.3(6)
Mean	109.4
Si-0-Si Angles	
Si(1)-0(2)-Si(2)	136.4(8)
Si(2)-0(6)-Si(3)	134.8(8)
Si(3)-0(3)-Si(1)	131.2(7)

*Angles involving two bridging bonds.

group was accepted. In the subsequent least-squares refinement of the structure, the *x* parameter of Zr was fixed at ¼ to define the origin. Three cycles of full-matrix least-squares refinement using isotropic temperature-factors for all atoms reduced the residual R to 5.3%. The refinement was continued for three more cycles using anisotropic temperature-factors until no further significant shifts of parameters were encountered. The final unweighted residual R for all 1211 reflections is 3.92%. The final difference-map shows some spurious residual peaks, some of which may be due to the hydrogen atoms, but the refinement of their positions was not attempted.

The X-ray-scattering factors used were taken from the *International Tables for X-ray Crystallography* (1962). The scattering factor for Na^+ was adjusted to $0.905Na^+ + 0.095K^+$ on the basis of the empirical formula of the mineral (Chao & Watkinson 1974). No attempt was made to modify the scattering factor of Zr to compensate for the substitution of Nb for Zr in the mineral, as the scattering factors of Zr and Nb are very similar and the small difference is partly compensated by the presence of 2% Ti in substitution for Zr.

The final positional and thermal parameters for gaidonnayite are given in Table 1. Bond lengths and selected bond-angles are given in Tables 2 and 3, respectively. The observed and calculated structure-factors are given in Table 4, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The structure of gaidonnayite is composed of single chains of SiO_4 tetrahedra, repeating every six tetrahedra. The chains extend alternately along [101] and [10$\bar{1}$] and are cross-linked by a Zr–O octahedron and distorted Na–O octahedra (Figs. 1, 2).

There are three independent Si–O tetrahedra in each chain, with mean Si–O distances of 1.629, 1.617 and 1.623 Å. The bridging Si–O bonds in each Si–O tetrahedron are considerably longer than the non-

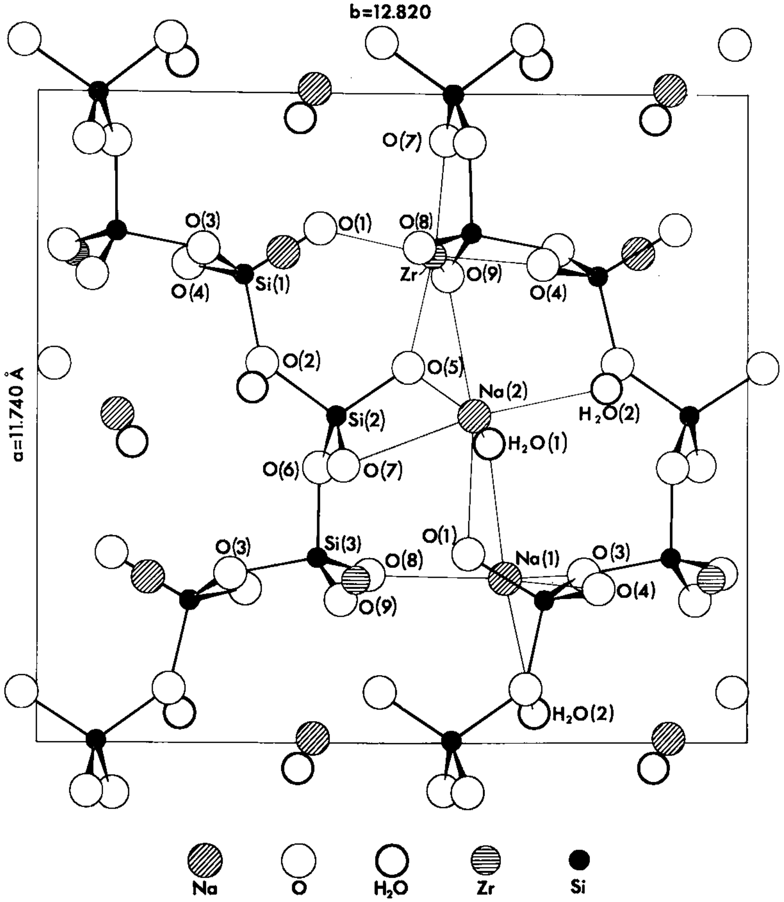

FIG. 1. The structure of gaidonnayite projected on (001).

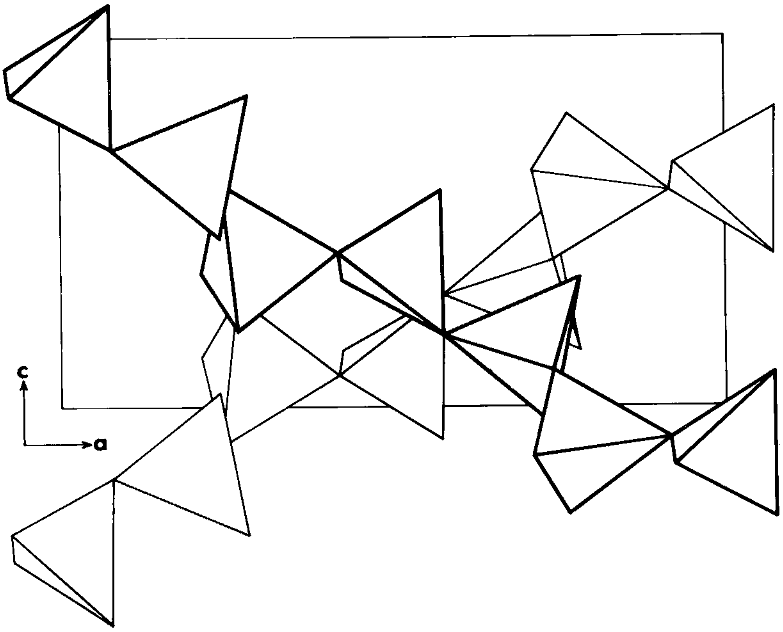

FIG. 2. The six-tetrahedron-repeat silicate chains in gaidonnayite projected on (010).

bridging Si–O bonds (Table 2); this is similar to what has been observed in many pyroxenes (Clark *et al.* 1969, Ribbe & Prunier 1977). In each Si–O tetrahedron, the distance between the bridging oxygen atoms is the shortest and that between the nonbridging oxygen atoms is the longest among the O–O distances (Table 2).

Both Na(1) and (Na(2) are co-ordinated with four oxygen atoms and two H_2O molecules to form a highly distorted octahedron. The water molecules are situated at opposite corners in the Na(1)–O octahedron and at adjacent corners in the Na(2)–O octahedron. The Na–H_2O bonds are significantly shorter than the Na–O bonds in both octahedra (Table 2). In both Na–O octahedra, the oxygen atoms are contributed from three different chains, two from one chain, and one each from two others. The distortion of the Na–O octahedra is revealed by the wide ranges of (O,H_2O)–Na–(O,H_2O) angles and (O,H_2O)–(O,H_2O) distances, 57.13–116.20° and 2.679–4.483 Å in the Na(1)–O octahdron, 62.24–105.51° and 2.687–4.066 Å in the Na(2)–O octahedron. The two Na–O octahedra share the O(1)–H_2O(1) edge. The Na(1)–O octahedron shares the O(1)–O(4) edge with the Si(1)–O tetrahedron, and the Na(2)–O octahedron shares the O(5)–O(7) edge with the Si(2)–O tetrahedron. This edge sharing is probably a major reason for the distortion of the Na octahedra. The Na(1)–O octahedron, with a stronger distortion and significantly larger Na–(O,H_2O) distances (Table 2), is probably the preferred site for the small amount of K found to substitute for Na in the mineral.

The zirconium atom is octahedrally co-ordinated with six oxygen atoms at a mean distance of 2.078 Å. The oxygen atoms are contributed from three different silicate chains (two from each). The O–O distances vary slightly (Table 2); the O–Zr–O angles range from 82.42° to 98.47° with a mean of 90.20°, close to the ideal value of 90°. The Zr–O octahedron shares the O(1)–O(5) edge with one Na(2)–O octahedron, the O(5)–O(9) edge with another and the O(1)–O(8) edge with a Na(1)–O octahedron.

The shortest H_2O–O approaches (Table 2) are H_2O(1)–O(2), H_2O(1)–O(5), H_2O(2)–O(6) and H_2O(2)–O(7), which are most likely hydrogen-bonded.

DISCUSSION

The single-chain silicate minerals may be divided into subgroups according to the number of SiO_4 tetrahedra within one repeat of the chain (*n*). The subgroups are represented by pyroxenes with $n = 2$, wollastonite (Buerger & Prewitt 1961) with $n = 3$, rhodonite (Peacor & Niizeki 1963) with $n = 5$, stokesite ($CaSnSi_3O_9 \cdot 2H_2O$, Vorma 1963) with $n = 6$, and pyroxmangite ($MnSiO_3$, Liebau 1959) with $n = 7$. The chain in gaidonnayite, with $n = 6$, is remarkably similar to that in stokesite in its sinusoidal shape, a feature not found in chains in minerals of other subgroups (Fig. 3). The unusual topography of the chains in gaidonnayite and stokesite is probably a result of the accommodation of the

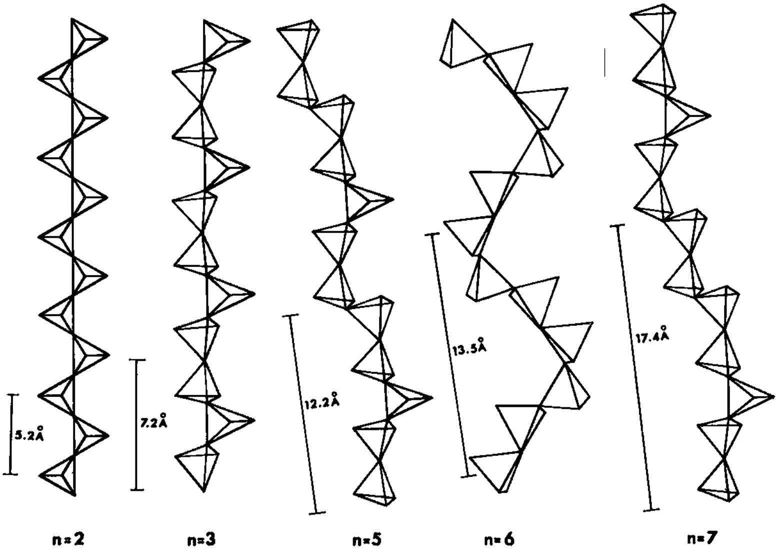

FIG. 3. The single silicate chains in pyroxenes ($n=2$), wollastonite ($n=3$), rhodonite ($n=5$), gaidonnayite ($n=6$) and pyroxmangite ($n=7$), expanded from Figure 5 of Liebau (1959).

tetravalent interchain cations Zr^{4+} and Sn^{4+}. The structure of gaidonnayite is unique in that the adjacent chains extend along different directions, whereas in other single-chain minerals the chains are parallel to one direction only. This unique arrangement, together with the presence of tetravalent interchain cations, explains why cleavages characteristic of the single-chain silicate minerals are absent in gaidonnayite.

Hilairite ($Na_2ZrSi_3O_9{\bullet}3H_2O$, Chao *et al.* 1974) is compositionally similar to but structurally different from gaidonnayite. The structure of hilairite is composed of infinite spiral chains cross-linked by Zr–O octahedra (Ilyushin *et al.* 1981).

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