

The crystal structure of voggite, a new hydrated Na–Zr hydroxide–phosphate–carbonate mineral*

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Abstract

The crystal structure of the new mineral voggite, $\text{Na}_2\text{Zr}(\text{PO}_4)(\text{CO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$, from the Francon quarry, Montreal, Quebec, Canada, has been solved in order to determine the correct chemical formula, as conventional electron microprobe methods were found unreliable. The unit cell is monoclinic, $I2/m$, with $a = 12.261(2)$, $b = 6.561(1)$, $c = 11.757(2)\text{\AA}$, $\beta = 116.19(2)^\circ$. The structure consists of layers of edge-sharing Zr–O pentagonal bipyramids, separated by layers of Na–(O, H₂O) octahedra. The carbonate ion acts as a bidentate ligand in the Zr–O polyhedron, the third oxygen atom being bonded to the Na atom. The phosphate group is bonded to three different Zr atoms and to a Na atom. The Zr–O bond lengths vary from 2.067 to 2.283 (mean 2.140\AA), while Na–O are between 2.304 and 2.773, ($\sigma = 0.006\text{\AA}$, mean 2.480\AA). The carbonate and phosphate bonds are normal. It is inferred from the structure that the columns of octahedrally coordinated Na atoms can easily be broken apart when subjected to the heat generated by the electron microprobe beam, with the subsequent expulsion of water. This gives rise to 'mobile' Na atoms, which make quantitative electron microprobe analysis extremely difficult. The structure allows the 'liberated' Na atoms to move freely within planes parallel to $(10\bar{1})$.

KEYWORDS: voggite, hydrated Na–Zr hydroxide–phosphate–carbonate, crystal structure, Na-ion mobility, Francon quarry, Montreal, Quebec, Canada.

Introduction

THE new mineral voggite, $\text{Na}_2\text{Zr}(\text{PO}_4)(\text{CO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$, from the Francon quarry, Montreal, Quebec, Canada, has been described recently by Roberts *et al.* (1990). The quantitative determination of the precise chemical composition was not possible using conventional electron microprobe analysis due to severe crystal decomposition. Such a situation often occurs when a compound contains weakly bonded water molecules, and is even further impaired when these water molecules are coordinated to sodium atoms. It is well known that under normal conditions of electron microprobe analysis, sodium ions become 'mobile', and tend to migrate away from the heat generated by the electron beam.

The crystal structure was determined in place of a quantitative electron microprobe analysis of the mineral and, in order to relate, if possible, the structure to the apparently anomalous Na microprobe results. This structure determination, along with qualitative microprobe analysis, was the first case to be accepted by the Commission on New Minerals and Mineral Names, I.M.A. (C.N.M.M.N.) for acceptance of a 'new mineral' and 'new mineral name' status, based upon these two criteria (along with a physical description). The dearth of pure material had precluded bulk wet chemical analysis of the composition, and the very fine acicular habit (aspect ratio about 100:1, most crystals less than 1 mm in length) made all other analytical methods very difficult to carry out with any degree of accuracy. All relevant mineralogical data on voggite are reported in Roberts *et al.* (1990).

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Table 1. Crystal data

Name:	Voggite (named after Adolf Vogg, an amateur mineralogist, who first discovered the mineral).
Locality:	The Francon quarry, Montreal, Quebec, Canada.
Chemical formula:	$\text{Na}_2\text{Zr}(\text{CO}_3)(\text{PO}_4)(\text{OH})\cdot 2\text{H}_2\text{O}$
Formula weight:	345.22 Daltons.
Crystal system & space group:	monoclinic, $I2/m$ (No. 12).
Unit-Cell dimensions:	$a=12.261(2)$, $b=6.561(1)$, $c=11.757(2)\text{\AA}$, $\beta=116.19(2)^\circ$.
Unit-cell volume:	$848.71(22)\text{\AA}^3$
Density:	$D_{\text{calc}}=2.70(2)$, $D_{\text{obs}}=2.702\text{ g/cm}^3$, $Z=4$.
Linear absorption coefficient:	$\mu(\text{MoK}\alpha)=15.96\text{ cm}^{-1}$.
Crystal dimensions:	0.013 mm between $\{100\}$, $\{001\}$ and $\{10\bar{1}\}$, 0.4 mm long.
X-ray data:	Whole sphere of MoK α data ($\lambda=0.70930\text{\AA}$) to $2\theta=60^\circ$, absorption-corrected and averaged to give 1329 unique reflections, 1176 observed with $I_{\text{obs}} > 1.65\sigma(I)$.
Refinement:	converged to $R=4.57\%$, $R_w=3.1\%$.

Experimental

From a small voggite-bearing vug on one of the holotype specimens, the thickest needle (0.013 mm) which appeared megascopically to be single was selected. It was too long (about 1 mm) for diffraction work, yet also too thin. It was cut with a scalpel perpendicular to the needle axis (b) to a length of about 0.4 mm, thus giving an aspect ratio of about 30:1. This fibre length is still excessive, for it is larger than the homogeneous diameter of the X-ray beam (diameter 0.7 mm, homogeneous diameter about 0.3 mm), and this is a limiting factor in the overall quality of the X-ray diffraction data. However, due to the weak X-ray scattering obtainable from such a fine needle, it was accepted as a compromise between an even shorter crystal (and hence even weaker X-ray diffraction data), and the problems of inaccurate data due to inhomogeneity.

Precession single-crystal photographs were used for a preliminary examination of the crystal and, from a prior knowledge of the unit cell, the indices of the crystal faces in the $h0l$ zone were determined as $\{100\}$, $\{001\}$ and $\{10\bar{1}\}$. The crystal is morphologically hexagonal in cross-section. It was mounted on a CAD4 single-crystal diffractometer and 74 reflections were selected and used for least-squares refinement of the unit-cell parameters. These parameters are: I -centred monoclinic, with $a=12.261(2)$, $b=6.561(1)$, $c=11.757(2)\text{\AA}$, $\beta=116.19(2)^\circ$. A full sphere of Mo-K α X-ray data was collected to $2\theta=60^\circ$ using θ - 2θ scans at a speed of between 0.24 and $1.65^\circ/\text{min}$ in 2θ . After application of a Gaussian absorption correction (grid of $10\times 10\times 10$ points), the data were averaged to yield 1329 unique reflec-

tions, of which 1176 were considered 'observed' on the criterion that $I_{\text{obs}} > 1.65\sigma(I)$. When averaging is carried out in Laue symmetry $2/m$, the agreement factor between symmetry equivalent intensities in the whole sphere is $R=3.1\%$. Essential details of the crystal data are included in Table 1. All the software used in the structural analysis (including absorption correction) is part of the PC version of the NRCVAX crystal-structure determination package (Gabe *et al.*, 1989). The scattering curves are taken from International Tables, Vol. IV (1974). Real ($\Delta f'$) and imaginary ($\Delta f''$) components (*ibid.*) of these scattering curves were included in the structure factor calculation and least-squares analysis.

Structure solution and refinement

The structure was solved by a combination of direct, Patterson and Fourier methods. Intensity statistics were ambiguous, with a distribution of E 's somewhere between centric and non-centric. Non-centric space groups $I2$ and Im were initially tried in the structure determination until it became apparent that $I2/m$ (centric) was the true space group. All 13 unique non-hydrogen atoms were located and were refined initially isotropically, and finally anisotropically. The final Residual is $R=4.57\%$, $R_w=3.1\%$. Refinement of an extinction parameter was attempted, but gave an unreasonable (negative) value, and is not included. Examination of the final difference synthesis did not reveal clearly the positions of the five hydrogen atoms of the formula unit. Two of the expected hydrogen-atom positions were found in resolved positive areas of the map, but these were not the highest peaks (which were 'diffrac-

tion ripple' near the Zr atom position). The other three hydrogen-atom positions were not resolved. Therefore, none of the hydrogen atoms were included in the final calculations. There was no indication in the atomic thermal ellipsoids or in the difference synthesis of possible positional disorder, as might be found if the space group were truly non-centric (*I2* or *Im*), but refinement constrained in the centric *I2/m*. As the structure was determined in order to ascertain the correct chemical formula for the mineral, the population parameter of the Na atom was included in the refinement parameters. The change from unity to 1.01(2) is insignificant, and indicates full Na occupancy of the site. Refinement of the population parameters for the Zr, P and C atoms in turn, also showed no significant difference from complete site occupancy. From a bond valence analysis of the structure, it is possible to assign one of three bonded oxygen atoms as a hydroxyl and the other two as water molecules. The structure therefore gives the complete chemical formula, and provides a plausible explanation for the anomalous behaviour of the mineral when subjected to electron bombardment in the microprobe beam.

The presence of the above-mentioned somewhat ambiguous observed intensity statistics can be attributed to the fact that the phase-dominating atom (Zr) is so much heavier than the others in the structure. A centrosymmetric structure with a small number of very heavy atoms gives rise to an *E* distribution (Hargreaves, 1955) which does not follow the centrosymmetric curve given by Howells *et al.* (1950). The cause of an in-between distribution has been discussed by Szymański (1982) for the case of hydrodresserite ($\text{BaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$) where the presence of Ba caused a distribution which appeared perfectly non-centric in *P* $\bar{1}$. However, an approximately centric structure can give rise to an *E* distribution somewhere between centric and non-centric. It was with such a situation in mind that space groups *Im* and *I2* were made the initial refinement choices. Refinement of the model structure in these gave rise to matrix near-singularity (as often occurs when a centric structure is refined in a non-centric space group using full-matrix refinement; Ermer and Dunitz, 1970). There was no obvious reason to lower the symmetry at the end of the structure determination and attempt further refinement in either of the non-centric space groups.

Final positional parameters (with equivalent isotropic thermal parameter) are given in Table 2. The anisotropic thermal parameters (U_{ij} 's) are listed in Table 3. Observed and calculated struc-

Table 2. Atomic positional parameters.

Atom	x	y	z	B(iso)
Zr	.15686(6)	0	.04209(7)	.49(3)
P	.24436(17)	0	.12768(17)	.60(7)
Na	.5226(3)	.2434(5)	.1695(3)	2.85(15)
C	.2910(7)	0	-.0855(8)	.99(29)
O1	.1749(4)	.3135(6)	.0501(4)	1.03(15)
O2	.2624(5)	0	.2439(5)	.97(21)
O3	.3756(5)	1/2	.1445(5)	1.13(23)
O4	.6521(6)	0	.1516(6)	1.73(28)
O5	.3412(5)	0	.0378(5)	1.23(23)
O6	.1721(5)	0	-.1370(6)	1.49(26)
OH	.0181(5)	0	.1062(5)	.85(21)
OW1	.5085(6)	0	.3037(6)	1.90(28)
OW2	.6304(6)	1/2	.1030(6)	1.91(29)

E.S.D.s refer to the last digit printed.
B(iso) is the mean of the three principal axes of the anisotropic thermal ellipsoid, (Table 3).

ture factors are included in Table 4. The atomic bond lengths and bond angles are listed in Table 5. Tables 3, 4, and 5 have been deposited at the British Museum (Natural History).

Description of the structure

A projection of the structure on the *x-z* plane is shown in Fig. 1. Of the 13 unique non-hydrogen atoms, all except the Na atom and the oxygen (O1) atoms lie on mirror planes. The coordination of the Zr atom is a somewhat irregular pentagonal bipyramid, edge-sharing (OH-OH) to a second pentagonal bipyramid across a centre of symmetry. Hence, two Zr atoms and ten ligands lie in the mirror plane $y=0$ and, with the apical oxygen (O1) above and below each Zr atom, they form a coordination polyhedron which is centred at the origin. This figure is repeated at the centre of the cell by the *I*-symmetry operation. The seven Zr-O bonds vary in distance from 2.067(4) to 2.283(6)Å (mean 2.140Å). The P atom and the two coordinating oxygen atoms (O2,O3) are in the mirror plane; the other oxygen atom (O1) is off the mirror plane, and is repeated by the mirror plane to form a fairly regular tetrahedron around the P atom, with bond lengths of $2 \times 1.539(4)$, 1.547(6), 1.532(6)Å and bond angles of $2 \times 108.9(2)$, 105.3(2), 110.6(2)°. The phosphate anion (P,O1,O1,O2,O3) is bonded to three different Zr atoms and a Na atom. In the *y* direction, it bridges the Zr-O pentagonal bipyramids by means of an O1-P-O1 link. The carbonate anion (C,O4,O5,O6) acts as a bidentate ligand to the Zr atom via oxygen atoms (O5) and (O6), while the other oxygen atom (O4) is part of the coordination polyhedron around the Na atom. The latter is close to $y = \frac{1}{4}$, and is bonded to three oxygen

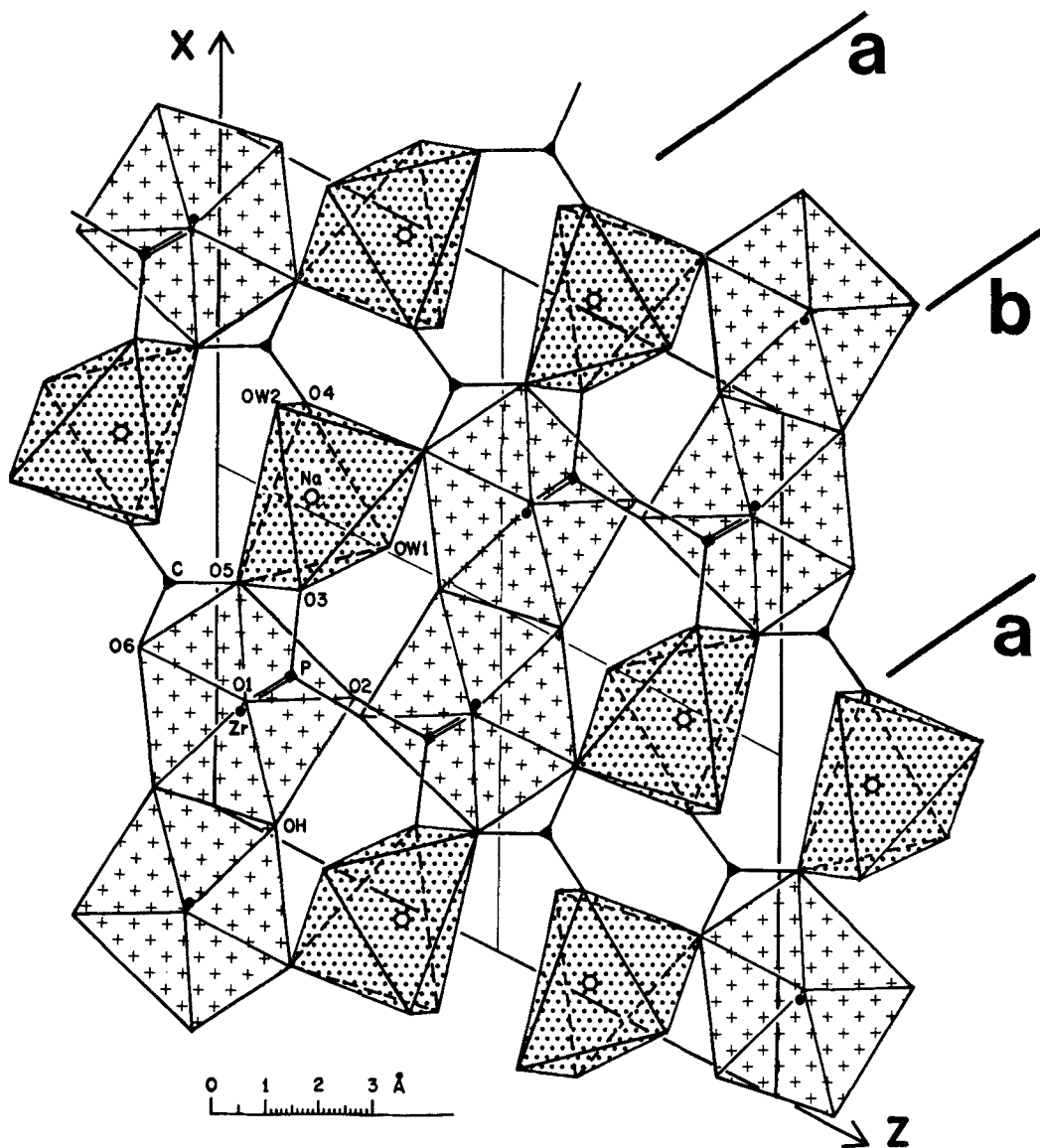


FIG. 1. The structure of voggite, projected on the x - z plane is shown, along with the unit cell and some surrounding atoms and polyhedra. The atoms of the asymmetric unit are labelled. The Na atom is drawn as open circles within the stippled octahedra. The large dashed triangle represents the three ligands in the plane $y=0$, and the large solid triangle around the Na atom represents the three ligands at $y=1/2$. The Zr atom is shown as a small solid circle within the pentagonal bipyramid (hatched with crosses), close to the centre of the five ligands, with which it is coplanar. The carbonate anion is shown as a small solid triangle, with three emanating bonds. The P atom is shown as a small solid square; the double bond originating from this atom is not a double bond in the chemical sense, but indicates single bonds to two (O1) oxygen atoms, one above and the other below the plane of (P, O2, O3). The planes of (Na, O, H₂O) octahedra are indicated by the solid lines (marked a), spaced with planes of edge-sharing (Zr, O) pentagonal bipyramids (marked b).

Table 6. Bond valence summary for voggite

	To Zr		To P		To C		To Na		Sum
	d(Å)	s	d(Å)	s	d(Å)	s	d(Å)	s	
O1	2.0666	.7068	1.5391	1.2524	--	--	--	--	1.959
	2.0666	.7068	1.5391	1.2524	--	--	--	--	
O2	2.1438	.5664	1.5476	1.2254	--	--	--	--	1.790
O3	--	--	1.5315	1.2793	--	--	2x 2.3877	.1904	1.660
O4	--	--	--	--	1.2524	1.4748	2x 2.3264	.2128	1.900
O5	2.2830	.3883	--	--	1.3006	1.2649	2x 2.6184	.1282	1.910
O6	2.1945	.4923	--	--	1.3085	1.2341	2x 2.7731	.1002	1.927
OH	2.1433	.5672	--	--	--	--	--	--	1.239
	2.0838	.6715	--	--	--	--	--	--	
OW1	--	--	--	--	--	--	2x 2.3043	.2217	0.443
OW2	--	--	--	--	--	--	2x 2.4716	.1641	0.328
Sum =	4.099		Sum =	5.007	Sum =	3.974	Sum =	1.017	

The parameters used are: for Zr, $R_1=1.950$, $N=6.00$; for P, $R_1=1.622$, $N=4.290$; for C, $R_1=1.378$, $N=4.065$; for Na, $R_1=1.622$, $N=4.290$. (Brown and Wu, 1976).

atoms in the plane $y=0$ (O4,O5,OW1) and three other oxygen atoms in the plane $y=\frac{1}{2}$ (O3,O6,OW2). These six oxygen atoms form a somewhat distorted octahedron, which contains the oxygen atoms of three different carbonate anions, and which has the other two positions occupied by water molecules (OW1,OW2) arranged *trans*. The mirror plane at $y=\frac{1}{2}$ generates a position for the Na atom at $1-y$ (i.e. close to $y=\frac{3}{4}$), and the three ligands at $y=0$ repeat at $y=1$. Columns of octahedrally coordinated Na atoms are formed, with sharing of the basal triangular face at $y=0$ and $y=\frac{1}{2}$. The bond lengths and bond angles about the C atom are somewhat distorted from regular geometry; the two larger bonds are part of the bidentate ligand, and the smallest angle is found between these two longer bonds; bond lengths and angles are: 1.252(10), 1.301(10), 1.308(10)Å; 124.9(8), 121.7(7), 113.5(6)°. The other bonds and angles within the structure are fairly typical, and do not deserve special comment.

Bond valence analysis (Brown and Wu, 1976) for voggite (Table 6) shows reasonable agreement for the expected valency of the Zr atom (4) and excellent agreement for the atoms of P(5), C(4) and Na(1). This is a confirmation that the Na atom site is fully occupied and that the problems encountered during electron microprobe analyses are not caused by partial site occupancy. The structure determination shows ten oxygen atoms within the formula unit, and a sum of the positive and negative charges for the cations and anion groups indicates that there are three unassigned oxygen atoms and one additional negative charge to be taken into account. One of these oxygen atoms must belong to a hydroxyl (1^-) and the

other two oxygen atoms must be part of water molecules (uncharged). The bond valence values in Table 6 clearly show that the oxygen atoms labelled OW1 (0.44 v.u.) and OW2 (0.33 v.u.) are the water-molecule oxygens, while the oxygen atom labelled OH (1.24 v.u.) is the hydroxyl oxygen. The bond valence for the other oxygen atoms varies from 1.96 to 1.66 v.u.; the difference from the ideal value of 2.0 v.u. is a measure of the extent to which a given oxygen atom is involved in hydrogen bonding.

Cause of voggite decomposition under the electron beam

Fig. 1 clearly shows alternating planes parallel to (10 $\bar{1}$); planes containing Zr-O and P-O polyhedra (shown cross-hatched and labelled **b**) are separated by planes containing Na-(O,OW) octahedra (shown stippled and labelled **a**). The Na-coordination octahedra are made up as follows: the triangle at $y=0$ has a corner-shared oxygen atom (O5), a carbonate-group oxygen atom (O4) and a water molecule (OW1); the triangle at $y=\frac{1}{2}$ has a corner-shared oxygen atom (O6), a phosphate-anion oxygen atom (O3) and a water molecule (OW2). Thermogravimetric analysis shows that water is easily driven off upon heating of the mineral. It can be seen in Fig. 1 that removal of these two coordinating water molecules will leave only two oxygen atoms from each of the basal coordination-triangles around the Na atom. With the two water molecules being *trans*, this leaves a square of coordinating oxygen atoms (O4,O5,O3,O6) from which the Na ion can easily escape into the enlarged vacant sheets. There it is free to move either along the fibre axis [010],

or along the $[10\bar{1}]$ direction, or in any direction within the plane of these two. The relative mobility of the Na ion along these directions may account for the different count rates reported by Roberts *et al.* (1990) for the electron microprobe analyses.

Conclusions

The precise chemical formula of voggite, $\text{Na}_2\text{Zr}(\text{PO}_4)(\text{CO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$, has been firmly established by crystal-structure methods in preference to quantitative microprobe analysis. The structure analysis has shown that the mineral has a stoichiometric composition, and this has taken the place of quantitative analysis to define this material as a 'new mineral' by the C.N.M.M.N. An explanation is also offered for the significant Na mobility, which occurs when the mineral is heated under the beam of the electron microprobe.

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