Canadian Mineralogist
Vol. 22, pp. 333-340 (1984)

THE CHARACTER OF THE CANCRINITE–VISHNEVITE SOLID-SOLUTION SERIES

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ABSTRACT

Complete characterization of the cancrinite–vishnevite solid-solution series has been made possible by the determination of the crystal structure of vishnevite using X-ray-diffraction data. The final conventional residue R is 3.7% using space group $P6_3$. As expected, the structure shows great similarity to that of the carbonate-rich end member; however, owing to space limitations, the number of SO_4^{2-} radicals is limited to one per unit cell. Although the crystal fragment used in the refinement shows no superstructure, other fragments of the same crystal do. The superstructure can be attributed to the orientation of SO_4^{2-} groups and also slight changes in chemistry on unit-cell scale. The ideal formula for vishnevite is $Na_8Al_6Si_6O_{24}{\cdot}SO_4{\cdot}2H_2O$.

Keywords: cancrinite, vishnevite, crystal structure, HRTEM, superstructure, zeolite.

SOMMAIRE

La caractérisation complète de la série de solutions solides entre la cancrinite et la vishnévite est rendue possible par la détermination de la structure cristalline de la vishnévite, au moyen de données de diffraction X. Le résidu conventionnel final R est de 3.7% dans le groupe spatial $P6_3$. Comme il fallait s'y attendre, la structure ressemble beaucoup à celle du pôle carbonaté; toutefois, faute d'espace disponible, il n'y a qu'un seul groupe SO_4^{2-} par maille. Quoique la partie du cristal qui a servi à l'affinement ne possède aucune surstructure, d'autres fragments du même cristal en ont une. Cette surstructure serait due à l'orientation des groupes SO_4^{2-} et aussi à une légère variation de composition à l'échelle de la maille. La vishnévite répond à la formule chimique idéale $Na_8Al_6Si_6O_{24}{\cdot}SO_4{\cdot}2H_2O$.

(Traduit par la Rédaction)

Mots-clés: cancrinite, vishnévite, structure cristalline, microscopie électronique par transmission de haute résolution, surstructure, zéolite.

INTRODUCTION

The solid-solution series cancrinite–vishevite is defined in Deer *et al.* (1963) by two end members of composition $(Na,Ca)_{7\text{-}8}Al_6Si_6O_{24}(CO_3,SO_4,Cl)_{1.5\text{-}2.0}{\bullet}1\text{-}5H_2O$ and $(Na,Ca)_{6\text{-}7}Al_6Si_6O_{24}(CO_3,SO_4,Cl)_{1.0\text{-}1.5}{\bullet}1\text{-}5H_2O$, respectively; the range in chemical composition is determined by chemical analytical data and not in terms of the crystal-structure requirements. This work forms part of an ongoing study to systematize the chemistry of the cancrinite group of minerals; we describe here the crystal structures of those species that have CO_3^{2-}, H_2O and SO_4^{2-} as their only important volatile components; the role of Cl^- will be discussed in a later paper.

The recent refinement of the crystal structure of cancrinite (Grundy & Hassan 1982) showed 1) that its three-dimensional aluminosilicate framework is fully ordered, with a perfect alternation of the AlO_4 and SiO_4 tetrahedral components, 2) that the 'cancrinite' cage is occupied by Na and H_2O and 3) that the large continuous channel also characteristic of the cancrinite structure contains CO_3^{2-} groups up to an ideal maximum of two per cell and, in addition, all remaining cations. The CO_3^{2-} groups occur on two sites unrelated by symmetry (each of multiplicity two) with equal probability; owing to space restrictions and also a deficiency of the CO_3^{2-} anion, the sites are not fully occupied. The ordering of the vacant positions, together with a sympathetic ordering of the cations within the channel, gives rise to a superstructure based on a cell with the same a_0 and b_0 dimensions as the substructure but with a c translation equal to eight times that of c_0.

If we view the tetrahedral SO_4^{2-} group as a triangular base of oxygen atoms plus an apical atom of oxygen, we can describe a model structure based on that of cancrinite for the SO_4^{2-}-rich end-member *vishnevite,* with the triangular base substituting for the triangular CO_3^{2-} group and with the apical atom of oxygen pointing either up or down. In order to verify this model and also to obtain detailed structural information, we determined the crystal structure of vishnevite.

EXPERIMENTAL

The material used in this study was donated by the British Museum (no. 1974, 516) and comes from the type locality at Vishnevy Gory, Urals. Single-crystal X-ray-diffraction patterns of this mineral, recorded by precession camera, were often found to differ in detail. Three representative patterns from fragments of the same single crystal as shown in Fig. 1 indicate a variable development of the superstructure. A microprobe analysis of the single crystal from which the fragments were removed showed no detec-

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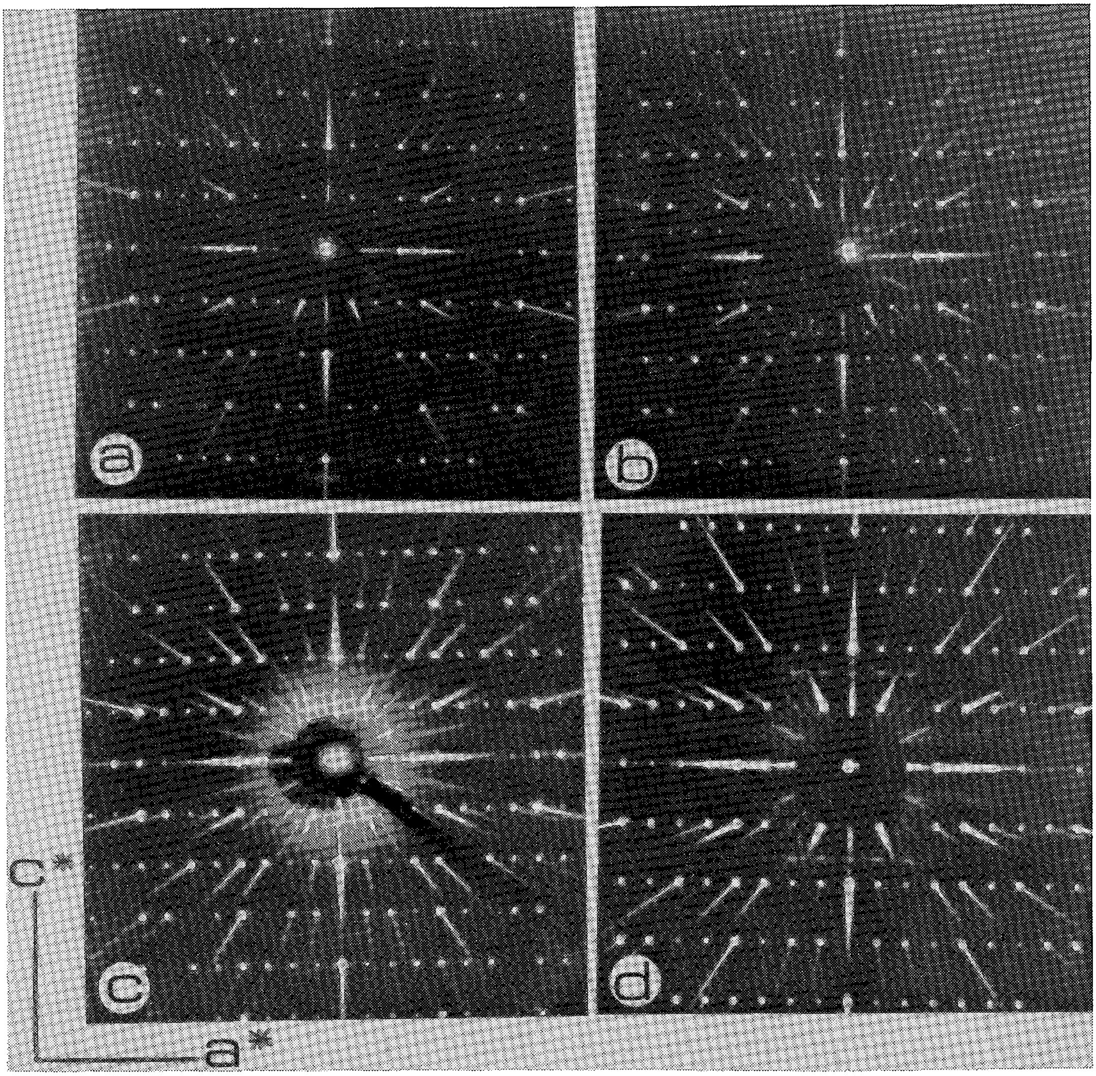

FIG. 1. Precession photographs down [100] (zero level, μ = 30°, Mo$K\alpha$). a) Vishnevite crystal used in the structural determination. b) Vishnevite from the same crystal fragments as (a) but showing a superstructure that doubles the c_0 translation (*i.e.*, $c = 2c_0$). c) Vishnevite from the same crystal fragment as (a) but showing a diffuse superstructure with $c \approx 7c_0$. d) Cancrinite (Chen 1970) that has been heat-treated, showing partly diffuse superstructure with $c \approx 7c_0$.

table variation in composition, and thus the origin of the superstructure must be due either to very subtle changes in chemistry or to differences in crystal structure (or to both).

Details pertinent to the particular fragment used for the structural analysis are given in Table 1. This material shows no superstructure, which is the usual case. The cell parameters were determined by the full-matrix least-squares method using 25 reflections automatically aligned on a 4-circle single-crystal diffractometer and monochromated Mo$K\alpha$ X radiation. Intensity data were collected out to a 2θ of 65° on a Syntex P2_1 4-circle diffractometer operating in the θ-2θ scan mode, with 2θ scan range ($K\alpha_1$ $-0.85°$ to $K\alpha_2$ $+0.85°$) and variable scan-rate between 3 to 29.3° min^{-1}, depending on a prescan. The two standard reflections, which were monitored after every 50 reflections collected, did not change in intensity. The data were corrected for Lorentz, polarization, background effects and spherical ab-

TABLE 1. CRYSTAL DATA FOR VISHNEVITE FROM VISHNEVY GORY, URALS†

Chemical composition*		Cell Contents**		Miscellaneous	
SiO_2	37.24	Si	6.194	a	12.685(6)Å
Al_2O_3	29.64	Al	5.806	c	5.179(1)Å
Na_2O	20.08	Na	6.471	V	721.70Å^3
K_2O	4.89	K	1.037	Space Group	$P6_3$
CaO	0.52	Ca	0.093	Z	1
SO_3	6.97	S	0.869	Density Calc.	2.37 g/cm^3
				μ	9.71 cm^{-1}
Cl	b.d.			Crystal Size	sphere diameter of 0.30 mm
CO_3	n.d			Radiation/Monochromator	MoKα/C
H_2O	n.d.			Total no. of I	955
wt. %	99.35			No. of Non equiv. $\|Fo\| > 3\sigma$	873
				Final R(obs)	= 3.7%
				Final R_w(obs)	= 4.6%
				w	= 1

† specimen courtesy of the British Museum (Natural History), no. 1974, 516. * Microprobe analysis determined by F. C. Hawthorne, University of Manitoba. b.d. below detection, n.d. not determined. ** based on Al + Si = 12.

sorption. Equivalent reflections were then averaged to produce a unique set; all those with intensities $< 3\sigma$ based on counting statistics were considered unobserved and not used in the refinement (Table 1). All calculations were made using the XRAY76 crystallographic system (Stewart *et al.* 1976).

STRUCTURE REFINEMENT

Refinement of the initial structural model using the full-matrix least-squares method and a starting composition of $Na_8Al_6Si_6O_{24}{\cdot}SO_4{\cdot}2H_2O$ progressed rapidly. Isotropic temperature-parameters were used in the early cycles, and these were converted to the anisotropic form for the final cycles. During the final cycles the chemistry was adjusted to match the observed chemical composition (Table 1), and the site populations were included as variables. The refinement converged and was consistent with the chemical analysis within the estimated error; the SO_4^{2-} group was found to prefer those configurations such that the sulfur atom and the triangular array of channel cations are approximately coplanar. The refinement finally converged with $R = 3.7\%$ using unit weights. Difference-Fourier sections of electron density prepared at this point are featureless and confirm the original assumption that the CO_3^{2-} component is insignificant. Table 2 lists the observed and calculated structure-factors together with their phase angles in millicycles. Table 2 is available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Final positional parameters and temperature factors are presented in Table 3, and selected interatomic distances and angles in Table 4.

DESCRIPTION OF THE STRUCTURE

The aluminosilicate framework is very similar to that observed for cancrinite (Grundy & Hassan 1982) both in size and relative position of the atoms; the mean bond-lengths of the AlO_4 and SiO_4 tetrahedra confirm the presence of complete order (Table 4). However, it must be noted that the occupancy of the *T1* and *T2* sites is reversed with respect to that in cancrinite, with Al occupying the *T1* site and Si the *T2*. Both arrangements are equally probable. There

TABLE 3. POSITIONAL PARAMETERS, POPULATION PARAMETERS AND ISOTROPIC TEMPERATURE-FACTORS (×10^4) AND ANISOTROPIC TEMPERATURE-FACTORS (×10^4) IN VISHNEVITE

atom	site	site content	x	y	z	$U_{(equiv)}$Å^2	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Framework atoms												
O1	c	1.0 O	.2017(3)	.4049(3)	.6698(8)	181	129(13)	247(15)	167(14)	123(12)	19(11)	27(13)
O2	c	1.0 O	.1175(3)	.5527(3)	.7278(11)	225	227(14)	133(20)	314(20)	106(11)	30(19)	13(18)
O3	c	1.0 O	.0406(3)	.3599(3)	.0393(7)	168	141(13)	259(16)	104(15)	85(12)	37(12)	43(13)
O4	c	1.0 O	.3255(3)	.3522(3)	.0561(7)	193	221(14)	265(16)	93(16)	171(13)	-1(12)	33(13)
T1	c	1.0 Al	.3380(1)	.4137(1)	.7506(5)	90	89(4)	102(4)	81(4)	57(4)	4(7)	11(7)
T2	c	1.0 Si	.0831(1)	.4124(1)	.7500	87	77(4)	104(4)	81(4)	48(3)	4(6)	11(6)
Non-framework atoms*												
O51	c	0.24 O+.76 []	.0615(18)	.1133(18)	.6725(39)	346	356(42					
O52	c	0.24 O+.76 []	.0496(28)	.1090(26)	.9541(63)	637	637(76)					
S	a	0.24 O+.76 []	0	0	.2918(35)	489	489(31)					
O7	a	0.24 O+.76 []	0	0	.0737(83)	454	454(81)					
O6	c	0.33 O	.6184(14)	.3043(35)	.6893(30)	564	598(102)	818(219)	278(81)	354(162)	51(61)	58(104)
NA1	b	1.0 Na	2/3	1/3	.1272(12)	357	253	253	566(31)	127(6)	0	0
NA2	c	0.75 Na+0.17K +.02 Ca+.06 []	.1319(3)	.2611(4)	.2885(6)	701	472(15)	1326(29)	305(17)	678(19)	-70(13)	-133(18)

* chemical symbol [] means vacancy.

TABLE 4. SELECTED INTERATOMIC DISTANCES AND ANGLES IN VISHNEVITE

Distances:			
Bond	Å	Bond	Å
T1-O1	1.728(4)	T2-O1	1.608(5)
-O2	1.719(7)	-O2	1.611(4)
-O3	1.744(7)	-O3	1.619(6)
-O4	1.736(4)	-O4	1.621(6)
Mean	1.732	Mean	1.615
Na-O1 × 3	2.884(4)	S-O7	1.460(46)
-O2 × 3	2.429(4)	-O51 × 3	1.391(21)
-O6^{a}	2.960(16)	Mean	1.408
-O6^{b}	2.330(16)		
Mean for 8	2.654	S-O7	1.130(46)
4	2.404	-O52 × 3	1.465(32)
		Mean	1.381
Trigonal bipyramid		Octahedral	
Na2-O1	2.529(5)	Na2-O1	2.529(5)
-O3	1.456(6)	-O3	2.456(6)
-O4	2.445(5)	-O4	2.445(5)
-O51^{a}	2.568(21)	-O52^{a}	2.573(66)
-O51^{b}	2.616(46)	-O52^{a}	2.705(35)
-O51^{b}	2.510(24)	-O52^{b}	2.407(31)
Mean	2.521	Mean	2.519
-O3	2.908(6)	-O3	2.908(6)
-O4	2.878(8)	-O4	2.878(8)
Mean	2.614	Mean	2.613
Angles:			
Tetrahedral			
O1-T1-O2	106.2(2)	O1-T2-O2	107.6(2)
-O3	107.6(2)	-O3	110.1(3)
-O4	109.2(2)	-O4	108.1(4)
O2-T1-O3	114.0(3)	O2-T2-O3	111.8(3)
-O4	113.9(2)	-O4	111.9(3)
O3-T1-O4	105.9(3)	O3-T2-O4	107.3(2)
Mean	109.5	Mean	109.5
Bridging			
T1-O1-T2	150.3(3)		
T1-O2-T2	149.8(2)		
T1-O3-T2	136.7(3)		
T1-O4-T2	136.7(3)		
Mean	143.4		

is the possibility, however, of the occurrence of a stacking fault or faults that can break the regular *ABAB* . . . alternation with a *C*-type layer. This would effectively reverse the occupancy of the *T*1 and *T*2 sites. Such materials will show apparent disorder of the framework owing to the averaging effect of the X-ray method, the degree of disorder being directly proportional to the volume of each arrangement present. A superstructure will not be observed if faults are randomly developed.

The cancrinite-type cage in vishnevite is identical to that in cancrinite; it contains one Na^+ and one water molecule which, as in cancrinite, is disordered about the axis of three-fold symmetry. The important differences are seen in the large channel, which contains the remaining cations chemically disordered over the six equivalent positions and the SO_4^{2-} groups. Theoretically, in a single cell there are four pairs of possible configurations for the SO_4^{2-} group. The individuals of each pair are related by the 6_3 axis. However, as noted previously, the results of the structure refinement show that only two orientations are preferred from those pairs that have the S atoms coplanar with the channel cations (Fig. 2). A possible explanation is that these arrangements allow the apical atom of oxygen of the SO_4^{2-} group to interact weakly with six cations; in the orientations that are not encountered, only three cations would be close enough for interaction.

The relative positioning of the base of the SO_4^{2-} group is, as expected, very similar to the positions of the CO_3^{2-} group in cancrinite and emphasizes the control exerted by the framework on the positions of the channel cations, which, in turn, regulate the position of the anion groups. Each cation in the channel is co-ordinated by either a trigonal bypyramidal or octahedral array of oxygen atoms contributed by both the framework and anion groups. The large mean cation–oxygen distance of 2.614 Å, compared to 2.550 Å for cancrinite, is due to the presence of K and the lower Ca content; this accounts for the modest increase in cell volume from 702.4 to 721.7 Å^3.

SOLID-SOLUTION SERIES

Owing to the similarity of the end members, the interchange of SO_4^{2-} for CO_3^{2-} should be complete. In the case of cancrinite, it can be readily seen that the ideal end-member composition should be $Ca_2Na_6Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$, but in the case of vishnevite, the replacement of CO_3^{2-} by SO_4^{2-} on a 1:1 basis has not been established by chemical analysis. Indeed the analytical data show that SO_4^{2-} is normally one or less, except in those cancrinite-type minerals with complex patterns of diffraction (Rinaldi & Wenk 1979). In order to explain the observed deficiency, the O–O distances of adjacent SO_4^{2-} groups within a unit cell can be examined. The van der Waals contact distance for oxygen atoms not bonded to the same cation is 2.8 Å. Consider the environment of a SO_4^{2-} group; it is clear that oxygen atoms associated with adjacent SO_4^{2-} groups are not allowed within the same unit-cell, as this would require contact distances much less than the minimum of 2.8 Å. Furthermore, as all these oxygen positions are controlled by the channel cations; other groups (CO_3^{2-}, H_2O, OH^-) are also precluded from this cell. Any sulfur in excess of one atom per cell must be present in a reduced state. Therefore, the ideal formula for vishnevite is $Na_8Al_6Si_6O_{24}{\cdot}SO_4{\cdot}2H_2O$, and a complete solid-solution series can be visualized as consisting of a mixture of CO_3^{2-} and SO_4^{2-} cells connected by a continuous framework.

The solid-solution series is shown in Figure 3. The analytical data plotted are taken from a variety of sources (Deer *et al.* 1963, Leoni *et al.* 1979, Hogarth 1979, Mazzi & Tadini 1981) and averaged on the unit cell of cancrinite. The dotted line represents the ideal compositional line for the series. Those points plot-

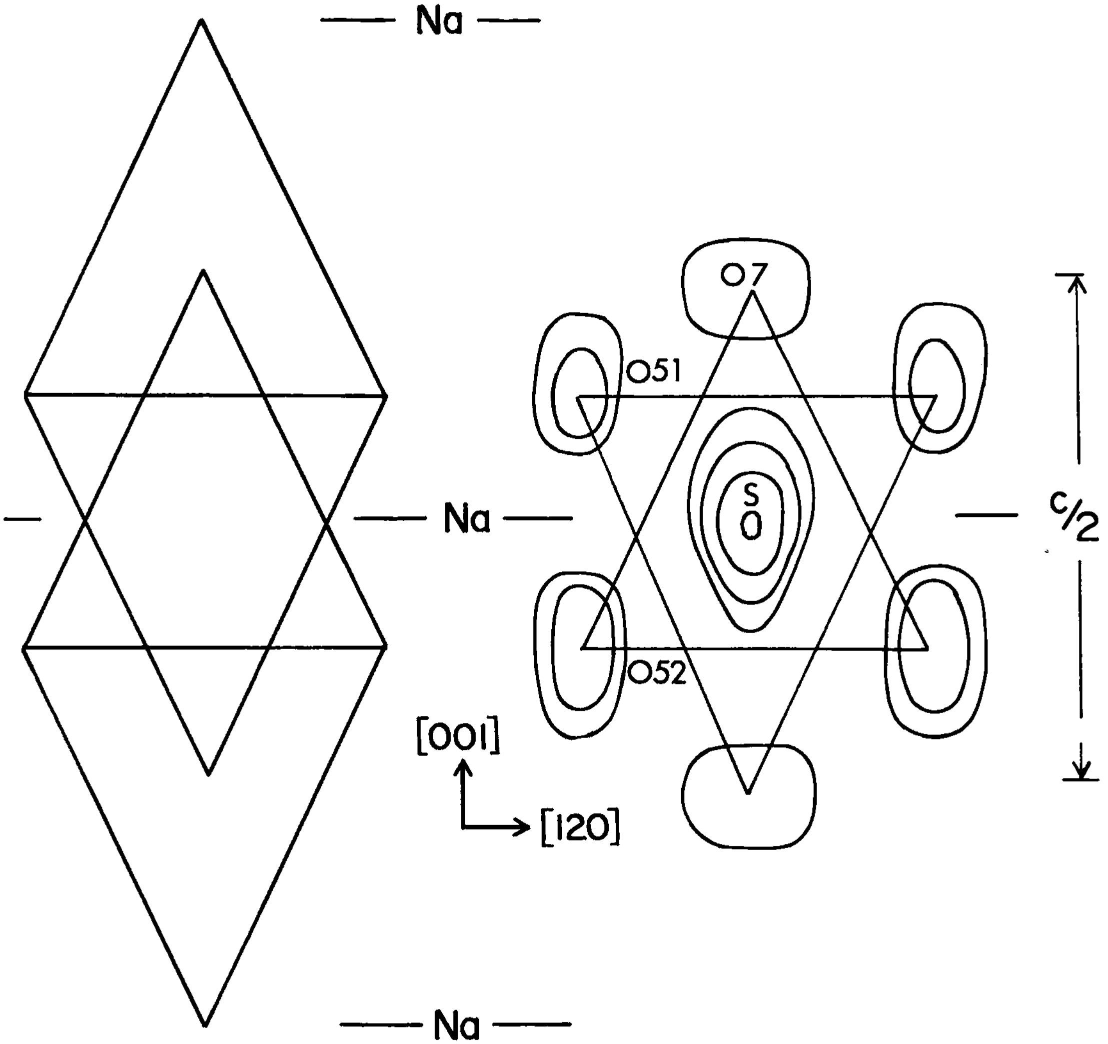

FIG. 2. Projection down [210] showing the atoms of the SO_4^{2-} group in the large channel. The third basal oxygen atom is omitted for clarity. Diagram at left is a schematic representation of all possible orientations of the SO_4^{2-} group; diagram at right is the observed density of electrons (contours at 1 eÅ^{-2} intervals), with the preferred orientations in outline. The position of the plane of Na atoms perpendicular to the *z* axis is also indicated and is approximately coplanar with the S atom.

ting below the line are indicative of stoichiometric deficiencies in excess of those for ideal solutions. The values plotted above pertain to those materials that are chemically distinct and considered to have different (although closely related) frameworks.

SUPERSTRUCTURE

The occasionally observed superstructure, diffraction patterns from which are shown in Figure 1, can now be rationalized in terms of the vishnevite structure. There are two observed symmetry-unrelated orientations of the SO_4^{2-} groups (apical atom of oxygen pointing either up or down) per cell. Equal occurrences of each would give a random pattern and no periodic features; however, if by chance some degree of correlation exists between channels, then any up-down residual would result in a doubling of the c_0 cell dimension and the appearance of extra reflections (Fig. 1b); the intensity of these reflections would depend on the extent of the correlation. We

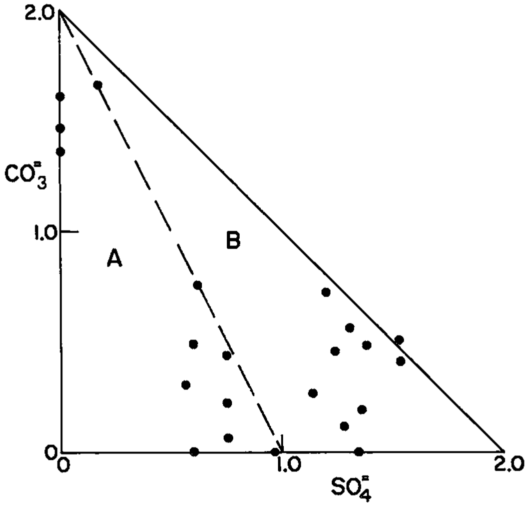

FIG. 3. The relationship between the number of CO_3^{2-} and SO_4^{2-} groups per unit cell (relative to cancrinite) for cancrinite-like minerals. Compositions used are taken from the literature (see text). The dashed line shows the ideal range in composition for members of the cancrinite - vishnevite solid-solution series. Those specimens plotting below this line (area A) have greater nonstoichiometry than is ideal, whereas those specimens lying above (area B) are cancrinite-type minerals with complex sequences of stacking.

are of course not limited simply to an up-down pattern; other patterns could be present also, *e.g.*, up-down-down-up, *etc.* However, owing to their complexity, it is very unlikely that such patterns would correlate between channels to give the periodicity necessary for observable extra reflections. As the CO_3^{2-} content of the vishnevite or departures from stoichiometry increase, then we can expect many varieties of superstructure due to the ordering of cancrinite cells, vishnevite cells and vacancies.

Figure 1c shows very weak and streaked diffraction maxima corresponding to the superstructure; these are similar, except for their degree of weakness, to those shown in Figure 1d, a precession photograph of a heat-treated crystal of cancrinite (Chen 1970). In this case the original sharp diffraction-maxima corresponding to the superstructure have moved and also weakened as a result of the heat treatment. In Figure 1c the superstructure shows a superperiod spacing of approximately $7c_0$. It is likely that for both these crystals the feature is due to small variations in chemical composition, which require long-range ordering in the channels to stabilize the structure. The position of the superstructure along the *z* direction probably results from ordering of vacancies, whereas the streaking perpendicular to the *z* axis is possibly due to the alternation of channels with either a high or low density of electrons, *i.e.*, cation plus anion contents, and reflects the extent of ordering of their distribution. In the case of the heat-treated cancrinite, this is probably due to the systematic loss of volatiles from the channels. Figure 4 is a HRTEM photomicrograph of cancrinite showing the variability of the channel contents. This particular sample (Grundy & Hassan 1982) has a superstructure, but the extra reflections show no streaking and, therefore, the channel contents are randomly distributed. For certain chemical compositions we can expect the degree of order to increase as, for example, in the case of synthetic microsommite studied by Klaska & Jarchow (1977). This specimen has channels with OH^-, H_2O and channels with SO_4^{2-} in the ratio of 1:2. These are distributed in a fully ordered pattern.

CONCLUSIONS

The specimen of vishnevite studied here is close to the ideal composition; the partial replacement of the channel Na^+ by K^+ and Ca^{2+} has no systematic effect on the structure except for a small increase in cell parameters. It has a fully ordered framework, and the channel anions may or may not be ordered. If they are ordered, a supercell is established with a characteristic doubling of the c_0 dimension, which is shown by the presence of sharp extra reflections on precession photographs. Streaked diffraction-maxima corresponding to a supercell have also been observed and can be rationalized by the nonrandom distribution of cations and anions over the channels in directions perpendicular to the *z* axis.

The solid-solution series cancrinite - vishnevite is completely characterized in terms of the crystal structures of the cancrinite and vishnevite end-members, which have ideal compositions of $Ca_2Na_6Al_6Si_6O_{24}\cdot 2H_2O(CO_3)_2$ and $Na_8Al_6Si_6O_{24}\cdot 2H_2O\cdot SO_4$, respectively. Those cancrinite-like materials with SO_4^{2-} in excess of one must have frameworks that are structurally different from cancrinite proper if sulphur is in a fully oxidized state.

ACKNOWLEDGEMENTS

Financial assistance came from NSERC operating grants to H.D. Grundy. Use of the X-ray facilities in the Materials Research Institute at McMaster University and of the central computing facility is greatly appreciated. The microprobe analyses were carried out courtesy of F.C. Hawthorne, University of Manitoba. We thank P.R. Buseck for access to the HRTEM facility at Arizona State University and financial support from his NSF grants EAR 7926375 and CHE 79-60980.

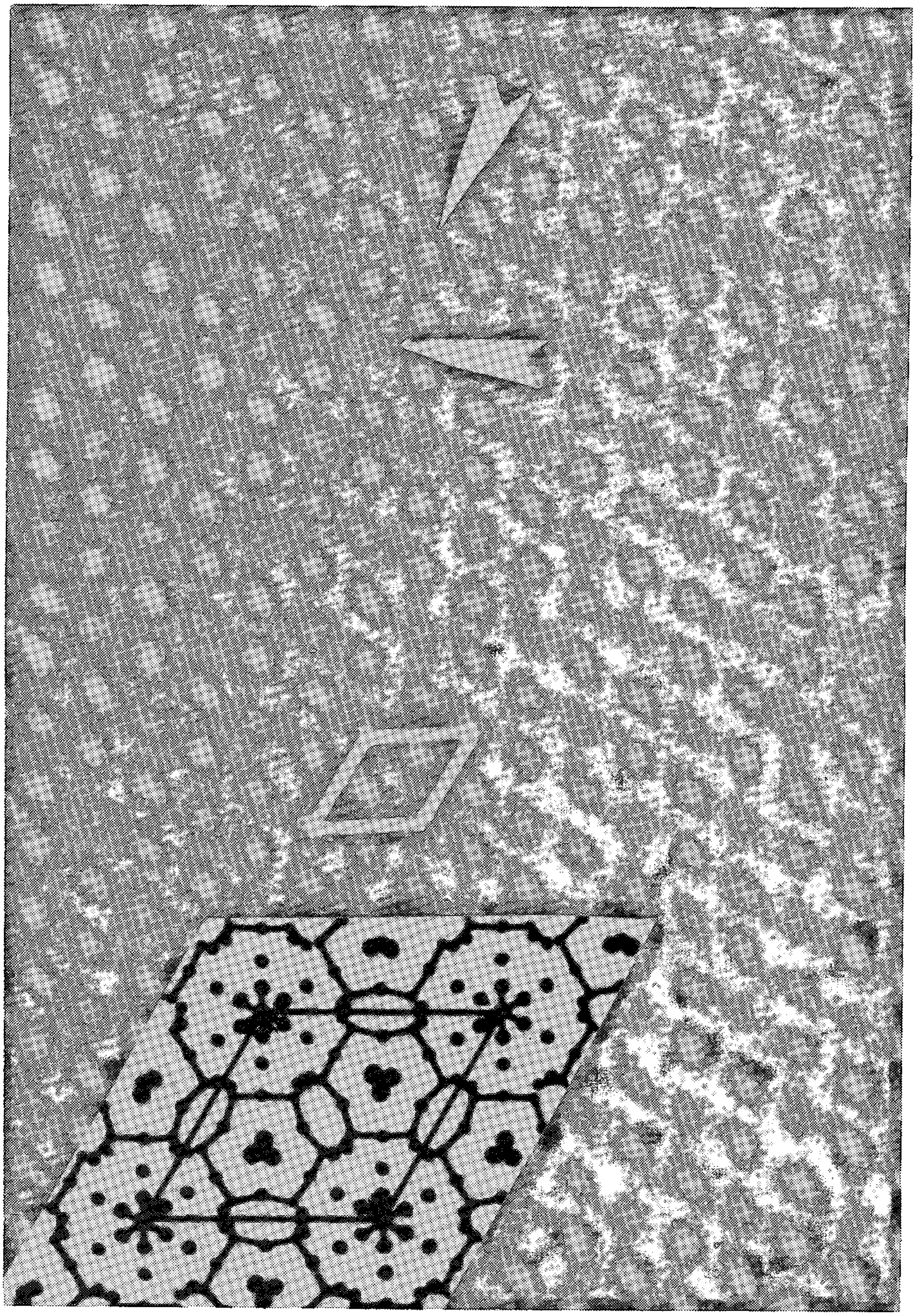

FIG. 4. Bright-field HRTEM micrograph of cancrinite (Grundy & Hassan 1982) down [001]. The cancrinite unit cell is shown in white outline; an equivalent cell is shown in black outline on the inset of the projected structure with correct orientation but at a scale × 2. The cell edge is 12.685 Å. Arrows point to changes in contrast that indicate variable chemical contents in the large channels; the light areas correspond to a relatively low density of electrons.

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Received January 10, 1983, revised manuscript accepted July 16, 1983.