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STRUCTURE OF DAVYNE AND IMPLICATIONS FOR STACKING FAULTS

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ABSTRACT

Crystal structures of two davyne specimens have been refined in space group $P6_3$ to R factors of 0.048 and 0.118, respectively, for observed reflections measured on an automated single-crystal X-ray diffractometer using Mo$K\alpha$ radiation. The Al and Si atoms have a 1:1 ratio; in the specimen with the higher R-factor, these atoms show a disordered arrangement that may arise from stacking faults, but Transmission Electron Microscopy (TEM) revealed no stacking faults, indicating that they are rare or absent in some crystal fragments. Subsequently, the structure of a davyne crystal free of stacking faults was refined; the Al and Si atoms were found to be completely ordered. The cage in davyne is occupied by $[\mathrm{Ca{\cdot}Cl}]^+$ clusters, in contrast to $[\mathrm{Na{\cdot}H_2O}]^+$ clusters, which occur in other members of the cancrinite group.

Keywords: cancrinite group, davyne, crystal structure, stacking faults.

SOMMAIRE

La structure cristalline de deux échantillons de davyne a été affinée dans le groupe spatial $P6_3$ jusqu'à un résidu R de 0.048 et 0.118, respectivement; les réflexions observées ont été mesurées sur cristal unique au moyen d'un diffractomètre automatisé utilisé avec rayonnement Mo$K\alpha$. Les atomes Al et Si sont présents dans une proportion 1:1; dans l'échantillon ayant le résidu plus élevé, ces atomes ont une distribution désordonnée qui pourrait résulter de défauts d'empilement. Toutefois, un examen par microscopie électronique par transmission n'a révélé aucun défaut, ce qui indique qu'ils sont rares ou absents dans certaines parties du cristal. Par la suite, la structure d'un échantillon de davyne dépourvu de tels défauts a été affinée; ce cristal montre une distribution complètement ordonnée de Al et Si. Ce sont des groupements de $[\mathrm{Ca{\cdot}Cl}]^+$ qui occupent la cage dans cette structure, plutôt que $[\mathrm{Na{\cdot}H_2O}]^+$, comme dans les autres membres du groupe de la cancrinite.

(Traduit par la Rédaction)

Mots-clés: groupe de la cancrinite, davyne, structure cristalline, défauts d'empilement.

INTRODUCTION

Deer *et al.* (1963) discussed the naming of minerals in the cancrinite group. The carbonate end-member is cancrinite, ideal formula $\mathrm{Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_2{\bullet}2H_2O}$; the sulfatic end-member is vishnevite, ideal formula $\mathrm{Na_8[Al_6Si_6O_{24}]SO_4{\bullet}2H_2O}$ (Hassan & Grundy 1984). These end members form a solid-solution series. The names *microsommite* and *davyne* refer to species of cancrinite rich in potassium and chlorine; more precisely, the term *davyne* must be used, as in the present paper, to indicate a mineral that is isostructural with cancrinite, whereas the term *microsommite* is associated with a mineral having a unit-cell translation c similar to that of cancrinite, but with $a_m = \sqrt{3}a_c$; the unit-cell content of microsommite is, therefore, three times ($Z = 3$) that of cancrinite (Bariand *et al.* 1968, Klaska & Jarchow 1977).

Except for microsommite, all the members of the cancrinite group, as well as the newly discovered cancrinite-like minerals, have similar values for a (Merlino 1984). Moreover, the values for c are similar for cancrinite-group minerals, but cancrinite-like minerals have values of c that are integral multiples of the c of cancrinite. However, the cancrinite-group minerals commonly contain superstructures that are characterized by integral multiples of c (Foit *et al.* 1973, Brown & Cesbron 1973). Cancrinite-like minerals have aluminosilicate frameworks topologically distinct from that of cancrinite, although closely related to it. These features make the distinction between cancrinite-group minerals and cancrinite-like minerals extremely difficult.

Microsommite is the only cancrinite-group mineral that shows a superstructure affecting the a^* axis; thus $a_m = \sqrt{3}a_c$. Synthetic microsommite $\mathrm{Na_5K_3[Al_6Si_6O_{24}](SO_4)_{0.7}(OH)_{0.7}{\bullet}2.3\text{-}2.7H_2O}$ studied by Klaska & Jarchow (1977) has $\mathrm{SO_4}$ in one third of the channels, and the remaining channels contain $\mathrm{H_2O}$ and OH. These chemically distinct channels are distributed in an ordered pattern and give rise to a unit cell that is three times that of cancrinite. The structure of a microsommite specimen from Pitigliano, Italy, of chemical composition

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$Na_{5.7}K_{2.3}(Al_6Si_6O_{24})(SO_4)_{1.0}$ ($Z = 3$), was refined by Mellini & Merlino (unpublished results in Merlino 1984) using the structural model of Klaska & Jarchow (1977). The two specimens had similar chemical compositions and gave similar results in both studies. However, microsommite from Vesuvius, Italy is chemically different from the above specimens because it is rich in chlorine and calcium. A chemical composition $Na_{3.3}K_{2.2}Ca_2(Al_6Si_6O_{24})(SO_4)_{0.5}Cl_{2.3}$ was obtained for a specimen from Vesuvius by Bariand *et al.* (1968; see Table 7, anal. no. 12). Merlino (1984) gave possible interframework distributions of cations for this specimen in the larger unit cell of microsommite.

The recent refinements of crystal structures of cancrinite (Smolin *et al.* 1981, Grundy & Hassan 1982), synthetic basic (hydroxy) cancrinite (Pahor *et al.* 1982, Hassan & Grundy, in prep.), and vishnevite (Hassan & Grundy 1984) showed that (i) the three-dimensional aluminosilicate framework is fully ordered, with a regular alternation of Al and Si atoms; (ii) the cage contains $[Na{\bullet}H_2O]^+$ clusters, and (iii) the channel contains the anion groups (CO_3, SO_4, OH, H_2O) and all remaining cations (Na, Ca, K). In the channel, the anion groups are disordered over distinct sets of positions, and because of space limitations, such sites are not fully occupied. The channel cation site, Na(2), does not show any positional disorder. The commonly observed superstructure reflections in the cancrinite-group minerals have been attributed to positional and substitutional ordering of the ions and vacancies in the channels (Grundy & Hassan 1982, Hassan & Grundy 1984).

TABLE 1. CHEMICAL ANALYSIS OF DAVYNE BM1907,210

Oxide	wt. percent[1]	No of ions[2] per unit cell	
Si_2O	33.89	Si	6.12
Al_2O_3	27.62	Al	5.88
Na_2O	8.34	Na	2.92
K_2O	5.09	K	1.17
CaO	12.48	Ca	2.41
SO_3	0.81	S	0.11
Cl	6.34	Cl	1.94
CO_3	n.d.		–
H_2O	n.d.		–
	94.56	Chemical formula from analysis	
O=Cl	−1.43	$Na_{2.9}K_{1.2}Ca_{2.4}(Al_{5.9}Si_{6.1}O_{24})(SO_4)_{0.1}Cl_{1.9}(?OH)_{1.0}$	
Total	93.13		
		Chemical formula from refinement	
		$Na_{3.3}K_{1.7}Ca_{2.0}(Al_6Si_6O_{24})Cl_{2.0}(?OH)_{1.0}$	

[1] Electron microprobe analysis determined by F. C. Hawthorne, University of Manitoba. n.d. = not determined; [2] based on Al + Si = 12; ?OH = estimated OH content.

TABLE 2. CRYSTALLOGRAPHIC DATA FOR DAVYNE

Parameter	Davyne BM1469	Davyne BM1907,210
a (Å)	12.793(3)	12.854(1)
c	5.367(3)	5.357(1)
Vol (Å^3)	760.69	766.53
Space Group	$P6_3$	$P6_3$
Z	1	1
Crystal size (mm)	sphere d=0.30	0.14×0.12 x0.10
Radiation/Monochromator	MoKα/C	MoKα/C
Total no. of intensities	2147	2168
No. of unique reflections	1012	1022
No. of non-equiv. $\|F_o\| > 3\sigma\|F\|$	862	688
Final R (obs) = $\Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$	0.048	0.118
Final $R_{w=1}$(obs) = $[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.050	0.128

Considering the overall charge of the cage ions, we can describe a model structure for the Cl-rich end-member *davyne* wherein each cage contains $[Ca{\bullet}Cl]^+$ clusters, instead of $[Na{\bullet}H_2O]^+$ clusters found in other members of the cancrinite group. To verify this model, and to obtain detailed structural information, we refined the crystal structure of davyne. Two davyne specimens were studied, because the structure of the first specimen did not refine satisfactorily.

EXPERIMENTAL

The davyne specimens [BM1469 and BM1907,210] used in this study were donated by the British Museum of Natural History. Localities for both specimens were given as Mount Vesuvius, Italy; however, the latter sample was labeled microsommite and was collected from the eruption of April, 1906. Crystals on specimen BM1907,210 occur as small, milky white needles (diameter 0.12 mm) in cavities, whereas crystals from specimen BM1469 are equidimensional, clear, and larger in size.

The chemical composition of only specimen BM1907,210 was determined by electron-microprobe analysis (Table 1) because only a minute amount of BM1469 was available, and the crystal used for X-ray data collection was lost, subsequently. However, a chemical composition reported by Bariand *et al.* (1968) for a sample of microsommite from the same locality is $Na_{3.3}K_{2.2}Ca_2(Al_6Si_6O_{24})(SO_4)_{0.5}Cl_{2.3}$ (Z = 3; Table 7, no. 12); this composition is similar to that deduced from the present structure-refinement, which indicates a chemical formula of $Na_{3.1}K_{2.6}Ca_2(Al_6Si_6O_{24})(SO_4)_{0.5}Cl_2$ (Table 7, no. 8).

Single-crystal precession photographs displayed diffraction symmetry and lattice extinctions compatible with space group $P6_3$. For davyne BM1907,210, all reflections were found to be sharp; no weak or diffuse superstructure reflections were observed on precession photographs. Davyne BM1469 showed weak streaking parallel to a^* for many reflections, but no superstructure reflections were observed. The latter observation indicates that this material is not typical microsommmite. Moreover, the present structure-refinement was done in the smaller cancrinite cell, so the name *davyne* is preferred for this material.

Unit-cell parameters were obtained by least-squares refinement using 15 reflections between 2θ of 12° and 34°, which were automatically aligned on a computer-controlled Nicolet P3 4-circle single-crystal X-ray diffractometer and using graphite-monochromatized Mo*K*α radiation. Table 2 contains information pertinent to collection and refinement of X-ray crystallographic data. Intensities were measured for reflections from two equivalent sets ($hk \pm l$) to a maximum 2θ of 65°. The diffractometer operated in the θ–2θ scan mode, with 2θ scan range of ($K\alpha_1$ −0.85) to ($K\alpha_2$ +0.85) and variable scan-rates of 3° to 29.3° $\min^{-1}$, depending on the intensity of a prescan. No change was observed in long-term diffractometer performance, which was monitored by measuring two standard reflections after every 50 reflections in each sample. The data were corrected for Lorentz, polarization, and background effects. Equivalent reflections were then averaged to produce unique data-sets. Subsequent refinements were obtained using the resulting structure-factors for which $|F_{obs}| > 3\sigma(F)$. All crystallographic calculations were made using the XRAY 76 Crystallographic System (Stewart 1976), and the diagrams were prepared using CHEMX (Chemical Design Ltd., Oxford, England).

STRUCTURE REFINEMENT

Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968), and the starting framework-atom parameters were those of vishnevite (Hassan & Grundy 1984). Calcium and Cl were assigned to the positions of Na and H_2O in the cage, respectively, but the Cl atom was placed on the 3-fold axis, whereas in other cancrinite-group minerals H_2O is disordered about this axis because of hydrogen bonding (Grundy & Hassan 1982, Hassan & Grundy 1984). The Na(2) site in the channel was assumed to be fully occupied by Na atoms. This initial model was refined on $|F|$ by full-matrix least-squares method, using isotropic temperature-factors, unit weights, and a variable overall scale-factor. Difference Fourier syntheses were examined at various stages of the refinement.

Davyne BM1907, 210

The positions of the framework atoms were initially held constant. Subsequent refinements gave mean Al–O and Si–O distances that indicate disordering of Al and Si atoms. The magnitude of the *T*–O distances also indicated the need for interchanging the Al and Si positions at various stages of the refinement. In the final analysis, the temperature factors *U* for Al and Si were of large but similar mag-

TABLE 3a. ATOMIC POSITIONS, ISOTROPIC TEMPERATURE FACTORS ($\times10^3$), AND SITE OCCUPANCIES FOR DAVYNE BM1907,210

Atom	Site	Site Content		x	y	z	$U_{(iso)}$
				Framework atoms			
O1	6c	1.0	O	0.212(1)	0.424(1)	0.724(3)	19(3)
O2	6c	1.0	O	0.112(1)	0.554(1)	0.746(4)	25(3)
O3	6c	1.0	O	0.009(1)	0.340(1)	0.010(3)	7(2)
O4	6c	1.0	O	0.328(2)	0.346(2)	0.025(4)	39(5)
T1	6c	1.0	Al	0.338(1)	0.413(1)	0.751(2)	10(1)
T2	6c	1.0	Si	0.077(1)	0.414(1)	3/4	11(1)
				Non-framework atoms			
Cl	2b	1.0	Cl	2/3	1/3	0.711(7)	91(5)
Ca	2b	1.0	Ca	2/3	1/3	0.218(1)	9(1)
Na	6c	0.55	Na	0.153(1)	0.308(1)	0.258(5)	38(4)
K	6c	0.28	K	0.118(1)	0.228(2)	0.264(7)	49(5)

[1] Estimated standard errors refer to the last digit.

TABLE 3b. ATOMIC POSITIONS, SITE OCCUPANCIES, AND TEMPERATURE FACTORS[1] FOR DAVYNE BM1469

Atom	Site & occupancy			x	y	z	U_{equiv}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
							Framework atoms						
O1	6c	1.0	O	0.2128(3)	0.4266(4)	0.7284(18)	217	93(14)	220(18)	338(32)	111(13)	9(24)	43(27)
O2	6c	1.0	O	0.1045(3)	0.5588(3)	0.7479(16)	155	157(14)	83(13)	224(18)	80(12)	2(25)	−13(26)
O3	6c	1.0	O	0.0004(5)	0.3300(6)	0.0203(13)	185	224(24)	183(24)	147(32)	139(21)	124(18)	81(19)
O4	6c	1.0	O	0.3205(6)	0.3383(6)	0.0028(12)	169	143(23)	221(25)	143(34)	65(20)	−27(18)	81(19
T1	6c	1.0	Si	0.3289(1)	0.4101(1)	3/4	47	39(4)	54(4)	49(5)	29(4)	1(17)	13(7)
T2	6c	1.0	Al	0.0704(1)	0.4099(1)	0.7508(7)	50	38(5)	51(5)	59(6)	25(4)	-5(8)	0(8)
							Non-framework atoms						
Cl	2b	1.01(2)	Cl	2/3	1/3	0.7322(14)	993	1314	1314	172(21)	657(16)	0	0
Ca	2b	0.97(1)	Ca	2/3	1/3	0.2287(8)	150	114	114	221(13)	57(2)	0	0
Na	6c	0.51(1)	Na	0.1518(7)	0.3109(10)	0.2716(21)	821	507(42)	1600(87)	355(42)	826(56)	−19(57)	−83(90)
K	6c	0.43(1)	K	0.1106(4)	0.2264(4)	0.2564(21)	449	243(160)	470(20)	633(33)	232(16)	−7(30)	29(40)
O51	6c	0.23(2)	O	−.0511(36)	0.0462(36)	0.1384(82)	707(106)						
O52	6c	0.25(2)		0.0591(27)	0.1148(27)	0.3619(57)	448(64)						
S	2a	0.25(1)	S	0	0	0.2708(52)	297	156	156	579(98)	78(11)	0	0
O5	2a	0.26(3)	O	0	0	0.4964(221)	723(143)						

[1] anisotropic temperature factor = $\exp\left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} (U_{ij} a_i a_j h_i h_j)\right]$. Estimated standard errors refer to the last digit.

nitude; those for O1 and O2 were reasonable, that of O3 was unusually small, and *U* for O4 was large (Table 3a).

The positions of the cage ions refined rapidly, but *U* for Cl was large (Table 3a,b). The large *U* for Cl was expected because Cl is linearly coordinated by two Ca atoms that form ... Ca–Cl–Ca ... chains; thermal motion is thus expected to be large in the plane perpendicular to the chain length. The Na(2) site in the channel had a large temperature-factor, and difference Fourier sections showed that the electron density for this site is elongate. The chemical analysis indicates a significant amount of K, so that the Na(2) site was split into Na and K sites, and the refinement progressed successfully (Table 3a).

The chemical formula deduced from the refinement and results of the chemical analysis showed an excess of +1 v.u., which could be satisfied by one OH^- (Table 1). If this ion is positionally disordered over six positions in the channel, small values for electron density would result in the difference Fourier sections, which is the case for this specimen. This electron density could not be modeled.

The *R*-factor for the model based on isotropic

TABLE 4. FRAMEWORK INTERATOMIC DISTANCES (Å), ANGLES (°), AND BOND STRENGTH (V.U.)

BM 1907,210						BM1467					
SiO$_4$tetrahedra			AlO$_4$tetrahedra			SiO$_4$tetrahedra			AlO$_4$tetrahedra		
		v.u.			v.u.			v.u.			v.u.
T2–O1	1.68(2)	0.86	T1–O1	1.70(2)	0.82	T1–O1	1.605(5)	1.05	T2–O1	1.730(5)	0.76
–O2	1.63(2)	0.98	–O2	1.68(2)	0.86	–O2	1.607(5)	1.04	–O2	1.728(4)	0.76
–O3	1.66(1)	0.91	–O3	1.68(2)	0.86	–O3	1.611(11)	1.03	–O3	1.739(7)	0.74
–O4	1.68(3)	0.86	–O4	1.68(2)	0.86	–O4	1.612(7)	1.03	–O4	1.749(8)	0.72
Mean	1.66	Σ3.61	Mean	1.69	Σ3.40	Mean	1.609	Σ4.15	Mean	1.737	Σ2.98
TetrahedralEdges						TetrahedralEdges					
O1–O2	2.57(2)		O1–O2	2.61(2)		O1–O2	2.533(5)		O1–O2	2.670(7)	
–O3	2.74(2)		–O3	2.73(3)		–O3	2.626(14)		–O3	2.830(9)	
–O4	2.79(4)		–O4	2.71(3)		–O4	2.627(11)		–O4	2.830(13)	
O2–O3	2.77(2)		O2–O3	2.82(2)		O2–O3	2.689(10)		O2–O3	2.929(8)	
–O4	2.79(2)		–O4	2.80(4)		–O4	2.684(14)		–O4	2.949(8)	
O3–O4	2.61(3)		O3–O4	2.78(3)		O3–O4	2.597(10)		O3–O4	2.785(10)	
Mean	2.71		Mean	2.74		Mean	2.626		Mean	2.832	
TetrahedralAngles						TetrahedralAngles					
O1–T1–O2	102.1(7)		O1–T1–O2	102(1)		O1–T1–O2	104.1(3)		O1–T1–O2	101.1(2)	
–O3	110.2(8)		–O3	108(1)		–O3	109.5(4)		–O3	109.3(4)	
–O4	112(2)		–O4	107(1)		–O4	109.5(4)		–O4	108.8(6)	
O2–T1–O3	114.4(9)		O2–T1–O3	115(1)		O2–T1–O3	113.3(4)		O2–T1–O3	115.3(4)	
–O4	115(1)		–O4	113(1)		–O4	113.0(3)		–O4	116.0(4)	
O3–T1–O4	102.9(9)		O3–T1–O4	112(1)		O3–T1–O4	107.4(5)		O3–T1–O4	105.9(3)	
Mean	109.4		Mean	109.5		Mean	109.5		Mean	109.4	
BridgingAngles						BridgingAngles					
T1–O1–T2	167(1)					T1–O1–T2	164.9(4)				
T1–O2–T2	152(1)					T1–O2–T2	158.1(3)				
T1–O3–T2	144(1)					T1–O3–T2	141.5(6)				
T1–O4–T2	142(1)					T1–O4–T2	141.1(4)				
Mean	151					Mean	151.4				

TABLE 5. SELECTED CATION-ANION DISTANCES (Å) AND BOND STRENGTH (V.U.) FOR DAVYNE

BM 1907,210						BM1469					
		v.u.			v.u.			v.u.			v.u.
Na–O3	2.47(3)	0.16	K–O3	2.81(4)	0.13	Na–O3	2.470(14)	0.158	K–O3	2.709(11)	0.156
–O3	2.65(3)	0.11	–O3	2.81(3)	0.13	–O3	2.548(14)	0.133	–O3	2.791(9)	0.135
–O4	2.40(3)	0.19	–O4	2.67(3)	0.17	–O4	2.471(13)	0.158	–O4	2.721(9)	0.153
–O4	2.74(5)	0.09	–O4	2.98(5)	0.10	–O4	2.555(18)	0.131	–O4	2.783(15)	0.137
–O1	2.81(3)	0.08	–O1	3.29(3)	0.06	–O1	2.767(15)	0.084	–O1	3.331(12)	0.056
Mean	2.61	Σ0.62	Mean	2.91	Σ0.59	–O52	2.227(33)	0.283	–O5^a	2.789(53)	0.133
						Mean	2.506	Σ0.946	–O5^b	2.894(59)	0.112
									Mean	2.861	Σ0.882

BM 1907,210			BM1469		
		v.u.			v.u.
Ca–O1×3	2.70(1)	0.15×3+	Ca–O1×3	2.659(4)	0.160×3+
–O2×3	2.47(1)	0.25×3=1.18	–O2×3	2.538(4)	0.211×3=1.114
–Cl^a×3	2.65(4)	0.5	–Cl^a×1	2.702(9)	0.5
–Cl^b×1	2.71(4)	0.5	–Cl^b×1	2.664(9)	0.5
		Σ2.18			Σ2.114

S–O5^b×1	1.473(12)	S–O5^a×1	1.211(12)
–O52^a×3	1.363(32)	–O51^b×3	1.291(55)
Mean	1.391	Mean	1.271

a = above; b = below

temperature-factors was found to be 0.118; despite considerable efforts, which involved starting afresh a number of times, no improvement in the model was achieved. An attempt was made to refine anisotropic temperature-factors, but as the number of variables increases and as the errors for the anisotropic temperature-factors were quite large, the resulting *R*-factor of 0.091 indicates no significant improvement in the structural model. Structural parameters for the model based on isotropic temperature-factors are given in Tables 3a, 4 and 5.

Stacking faults

The disordered distribution of Al and Si atoms implied by the mean *T*–O distances (Table 4) was surprising, as structure refinements of vishnevite, cancrinite, and basic (hydroxy) cancrinite verified complete ordering of Al and Si atoms. Thus, the question of stacking faults in the cancrinite-group minerals was raised once again (Rinaldi & Wenk 1979). The framework of cancrinite consists of six-membered $[(Al,Si)_6O_{24}]$ rings, the centers of which are stacked in a manner analogous to closest packing of spheres. In cancrinite, the stacking sequence is *ABAB*... but the possibility exists for the occurrence of stacking faults that can interrupt the regular *ABAB*... sequence with a *C*-type layer. This effectively interchanges the occupancy of the framework cation sites, *T1* and *T2* (Hassan & Grundy 1984). Because of the averaging effect of the X-ray method, such material will show an apparent disorder of the framework, with the degree of disorder being directly proportional to the volume of each arrangement. This seems to be the case for davyne BM1907,210. More commonly, however, minerals in the cancrinite group grow in one of the two equally probable arrangements, one as in cancrinite (Grundy & Hassan 1982), and the other typified by vishnevite (Hassan & Grundy 1984), wherein the occupancy of the *T1* and *T2* sites is reversed with respect to that in cancrinite (Table 6).

The peculiarities of davyne BM1907,210 suggested that it would be useful for investigation by Transmission Electron Microscopy (TEM). The specimen was examined in a JEOL 200CX microscope at the Center for Solid-State Science, Arizona State University. Images similar to those for cancrinite were obtained (Grundy & Hassan 1982), but no stacking faults were observed. This suggests that stacking faults may be rare and only by chance would they be observed by TEM even if they are present in the much larger crystals used in X-ray single-crystal observation. To better determine the structure of davyne, another sample of Cl-rich davyne was selected for structural analysis.

Davyne BM1469

Refinement of the structural model for davyne BM1469 progressed rapidly to the model obtained for davyne BM1907,210. Difference Fourier sections through the channel showed SO_4 groups, which are in positions similar to those in vishnevite (Hassan & Grundy 1984). The isotropic temperature-factors were converted to the anisotropic form for the final cycles, during which the interframework site-populations were included as variables. The refinement finally converged to $R = 0.048$ and $R_w = 0.050$ for 862 observed reflections (Table 2). Final structural parameters are presented in Table 3b, 4 and 5. The structure factors for both davyne specimens are listed in Table 8, which is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 6. CRYSTALLOGRAPHIC DATA[1] FOR CANCRINITE-GROUP MINERALS

					Average		Si–O/Al–O	Occupancy		
Specimens	a	c	c/a	V	Al–O	Si–O		T1	T2	Reference
1 cancrinite	12.75(2)	5.14(3)	0.403	723.63	1.75	1.61	0.92	Al	Si	Jarchow (1965)
2 cancrinite	12.590(5)	5.117(1)	0.406	702.42	1.733	1.612	0.930	Si	Al	Grundy & Hassan (1982)
3 cancrinite	12.62(1)	5.138(2)	0.407	708.67	1.706	1.645	0.964	Si	Al	Emiraliev & Yamzin (1982)
4 basic cancrinite	12.664(2)	5.159(1)	0.407	716.54	1.727	1.621	0.939	Si	Al	Hassan & Grundy (1990)
5 basic cancrinite	12.678(1)	5.179(6)	0.409	720.91	1.742	1.615	0.927	Si	Al	Pahor et al. (1982)
6 basic cancrinite	12.736	5.1871	0.407	728.66	–	–	–	–	–	Klaska et al. (1979)
7 vishnevite	12.685(6)	5.179(1)	0.408	721.70	1.732	1.615	0.932	Al	Si	Hassan & Grundy (1984)
8 davyne BM1469	12.793(3)	5.367(3)	0.420	760.69	1.737	1.609	0.926	Si	Al	This study
9 davyne BM1907,210	12.854(1)	5.357(1)	0.417	766.53	1.68	1.66	0.99	Al	Si	This study
10 microsommite[2](syn)	12.781	5.248	0.411	742.43						Klaska & Jarchow (1977)
11 microsommite[2]	12.792(3)	5.237(2)	0.409	742.15						Leoni et al. (1979)
12 microsommite[2]	12.75(2)	5.33(2)	0.42	750.37						Bariand et al. (1968)

[1] Linear measure in Å; V in $Å^3$; [2] a and V of microsommite are normalised to that of cancrinite

DISCUSSION OF THE STRUCTURE

Framework

The aluminosilicate framework in davyne BM1469 is similar to that observed for cancrinite (Grundy & Hassan 1982), vishnevite (Hassan & Grundy 1984), and basic (hydroxy) cancrinite (Pahor *et al.* 1982, Hassan & Grundy, in prep.), wherein all framework atoms have similar relative positions. The mean *T*–O bond lengths of the AlO_4 and SiO_4 tetrahedra, and the charge balance of the framework cations, confirm the presence of complete ordering of Al and Si atoms (Table 4).

Davyne BM1907,210 shows an apparent disorder of the framework *T* cations that may arise from stacking faults. Because of this apparent disorder, no direct comparison of tetrahedral edges or angles for the two specimens can be made (Table 4). However, the bridging angles are similar in both specimens, and their values are considerably larger than those found in other members of the cancrinite group.

If the observed respective mean *T*–O bond lengths of 1.737 Å and 1.609 Å for the AlO_4 and SiO_4 tetrahedra in davyne BM1469 are taken as an indication of fully ordered *T*1 and *T*2 sites, the distances of 1.68 Å and 1.66 Å in davyne BM1907,210 correspond by interpolation to 0.63 Al + 0.37 Si in the *T*1 site and 0.60 Si + 0.40 Al in the *T*2 site (Tables 4, 6). These values are also indicated by the valence sums about Al and Si (Table 4), which were calculated using the method of Brown & Shannon (1973). The two types of *T*1 and *T*2 arrangements, therefore, occur in about a 3:2 ratio. A similar comparison of the two carbonate-rich cancrinite samples of Grundy & Hassan (1982) and Emiraliev & Yamzin (1982) shows that in the latter sample, the *T*1 site contains 0.78 Si + 0.22 Al, and the *T*2 site contains 0.73 Al + 0.27 Si; thus the two different arrangements in that crystal are in the ratio 3:1 (Table 6). Therefore, it seems likely that this cancrinite also contains stacking faults.

Cancrinite-group minerals, which have Al and Si atoms distributed in a fully ordered manner, have a ratio of Si–O to Al–O of 0.93 (Table 6). The cancrinite studied by Emiraliev & Yamzin (1982) and davyne BM1907,210 have values that depart significantly from 0.93. Their values suggest that these specimens probably have stacking faults.

Cage contents

The cage in davyne contains $[Ca{\cdot}Cl]^+$ clusters, in contrast to $[Na{\cdot}H_2O]^+$ clusters that occur in other members of the cancrinite group. Cancrinite, basic (hydroxy) cancrinite, and vishnevite have similar values for *c* and *a*, but those for davyne are significantly larger (Table 6). The increase in cell parameters for davyne results from the increase in the size of the cages that arise from the substitution of $[Ca{\bullet}Cl]^+$ for $[Na{\bullet}H_2O]^+$. This substitution causes a larger increase in *c* compared to *a*; thus davyne has a larger *c/a* value than other members of the can-

TABLE 7. CHEMICAL DATA FOR FORMULAE OF CANCRINITE-GROUP MINERALS

				Chemical Formula $C(Al_6Si_6O_{24})A$						
[1]Ref.	Na	Ca	K	ΣC	CO_3	SO_4	OH	H_2O	Cl	ΣA
				Cancrinite						
Ideal	6	2	–	8	2	–	–	2	–	4
1	6.3	0.91	–	7.21	1.47	–	–	2.47	–	3.94
2	6.0	1.52	–	7.52	1.52	–	–	1.75	–	3.27
3	7.6	0.4	–	8.00	1.0	–	–	2.2	–	3.20
				Basic(hydroxy) Cancrinite						
Ideal	8	–	–	8	–	–	2	2	–	4
4	8.0	–	–	8.00	–	–	2.0	2.68	–	4.68
5	7.4	–	–	7.40	–	–	1.4	5.0	–	6.4
6	8.0	–	–	8.00	–	–	2.0	5.0	–	7.0
				Vishnevite						
Ideal	8	–	–	8	–	2	–	2	–	4
7	6.5	0.1	1.0	6.7	–	0.9	–	2.0	–	2.9
				Davyne						
Ideal	3	2	3	8	–	–	2	–	2	4
8	3.1	2.0	2.6	7.7	–	0.5	–	–	2	2.5
9	2.9	2.4	1.2	6.5	–	–	–	–	1.9	1.9
				Microsommite						
Ideal	6	–	2	8.0	–	0.67	0.67	2	–	3.33
10	5.0	–	3.0	8.0	–	0.7	0.7	2.5	–	3.90
11	5.7	–	2.3	8.0	–	1.0	–	–	–	1.0
12	3.3	2.0	2.0	7.3	–	0.5	–	–	2.3	2.8

[1]See table 6

crinite group, and it also has the largest cell volume (Table 6).

The Ca atom on the 3-fold axis contributes about 1 v.u. to six framework oxygen atoms that form the six-membered rings (Table 5). The remaining charge on the Ca atom satisfies the charge deficiencies on two Cl atoms to which it is also coordinated. Each Cl atom is linearly coordinated by two Ca atoms forming ...Ca–Cl–Ca... chains. The bond-valence sums about Ca and Cl atoms and the refined occupancy-factors imply that these sites are fully occupied (Tables 3, 5).

Channel contents

The single Na(2) cation site in cancrinite is divided into two sites, Na and K, in davyne. The Na site closest to the wall of the channel is occupied predominantly by Na atoms and possibly small amounts of Ca, whereas the K site closest to the 6_3 axis is occupied by K atoms (Table 3). These sites show deficiencies, which are substantial in davyne BM1907,210.

No anions were found in the channel of davyne BM1907,210; however, the refinement and the chemical data suggest that one OH probably is present in the channel and is located just off the 6_3 axis in the plane of the channel cations. The deficiencies of bond-valence sums about Na and K also indicate the presence of anions that could be OH (Table 5). The channels in davyne BM1469 contain SO_4 groups, which prefer those configurations wherein the sulfur atom and the triangular array of channel cations are approximately coplanar, as in vishnevite (Hassan & Grundy 1984).

Chemical composition

The range of chemical composition in the cancrinite-type structure is further clarified by this work. Ideal end-member formulae and chemical formulae for cancrinite-group minerals are summarized in Table 7. With a full complement of eight interframework cations, as is almost the case with sample BM1469, the maintenance of local charge-balance becomes the predominant factor controlling the ordering of the interframework cations and anions. Chlorine in principle could occupy either the cage or channel sites; in the channel, Cl atoms have to fully occupy both of the symmetry-equivalent sites on the 6_3 axis for local neutralization of charges. Substantial overlap of Cl atoms along the 6_3 axis

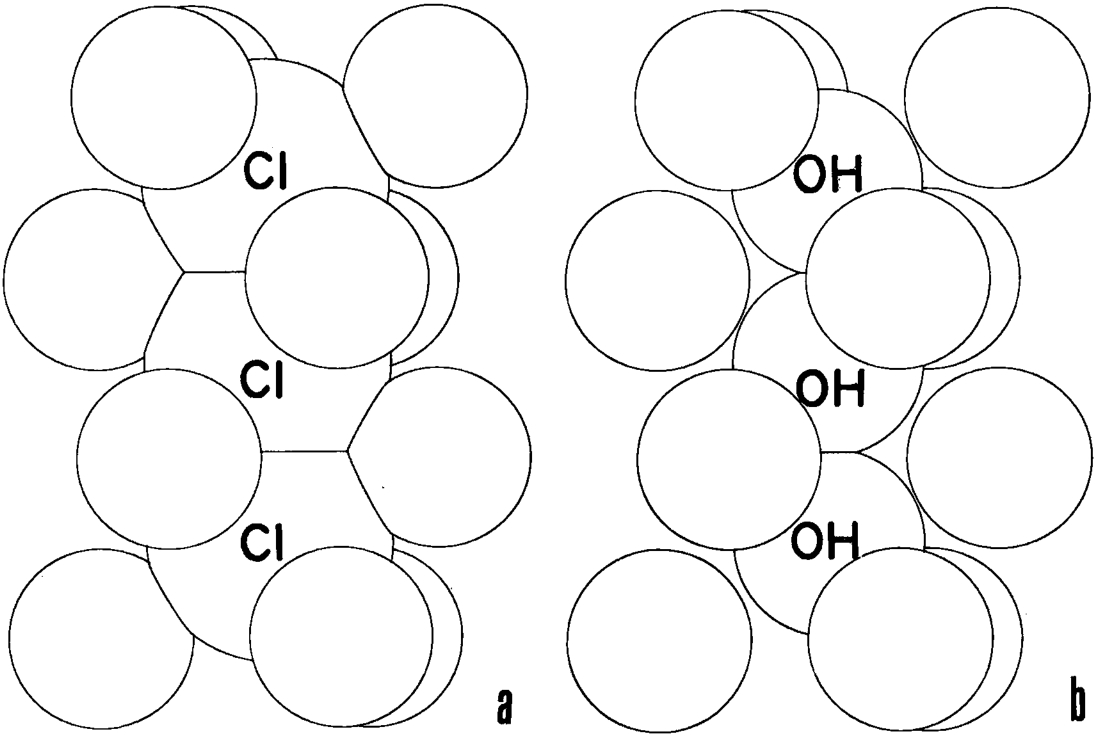

FIG. 1. Packing diagram viewed perpendicular to the 6_3 axis (vertical). All unlabeled atoms are K. (a) KCl clusters coordination (r_{Cl} = 1.82 Å, r_K = 1.35 Å), showing minor overlap of K and Cl atoms, but major overlap of Cl atoms. (b) KOH clusters coordination (r_O = 1.4 Å), showing no significant overlap of atoms.

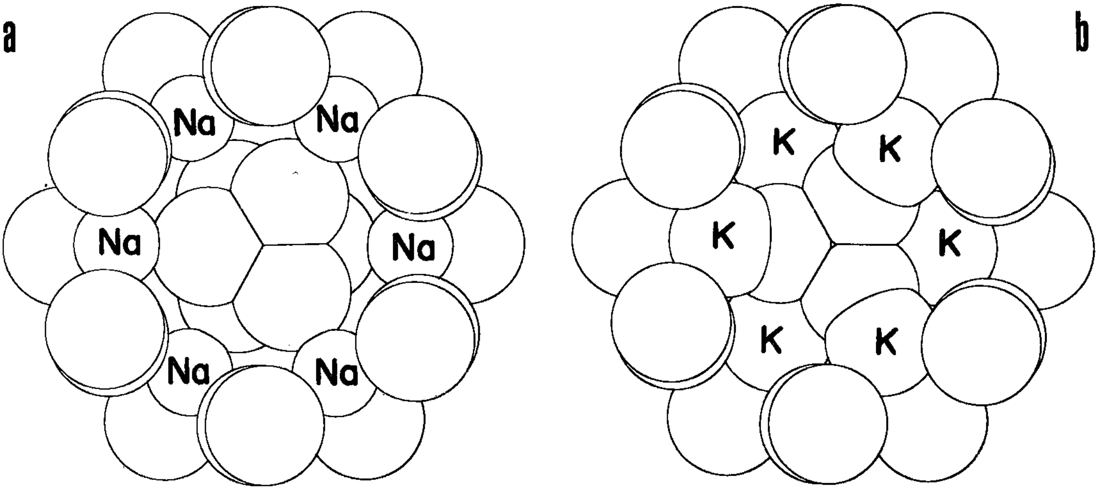

FIG. 2. Packing diagram viewed down the 6_3 axis. All unlabeled atoms are either O, H_2O, or OH (r_O = 1.4 Å). (a) $NaSO_4$ clusters coordination (r_{Na} = 1.02 Å), showing no significant overlap of atoms. (b) KSO_4 clusters coordination showing large overlap of K and O atoms.

precludes this arrangement (Fig. 1a), and so the only place for Cl is in the cage together with a suitably sized divalent cation, Ca. The OH can be located on the 6_3 axis and bond to K (Fig. 1b), but not to Na, which is further away, so we expect clusters of [K•OH]. Any excess OH will be located off the 6_3 axis and bond to Na in an irregular coordination similar to that found in basic (hydroxy) cancrinite (Hassan & Grundy, in prep.).

The SO_4 group, located in the channel of davyne, is associated with Na (Fig. 2a), as in vishnevite; the SO_4 group is too large to give reasonable bonding distances with K (Fig. 2b), so we expect clusters of [Na•SO_4]. Calcium in excess of cage requirements could be accommodated in the channel, but this substitution would have to be offset by vacant cation sites to balance charge.

In microsommite the smaller size of the cage (Klaska & Jarchow 1977) imposes spatial limitations on the structure such that each channel exclusively contains either [K•OH] or [Na•SO_4] clusters, which are fully ordered to reduce structural strain; this channel ordering is characteristic of the microsommite structure. In davyne, the much larger Cl-bearing cage expands the framework and creates enough space for the clusters to be mixed within each channel. The channels, therefore, are statistically similar in davyne and give rise to a low level of order that is indicated by the diffuse streaking on precession photographs, in contrast to the sharp superstructure reflections observed for microsommite.

Theoretically, a cage of the size found in davyne is large enough to accommodate [K•H_2O] clusters; with high K activities during crystallization, [K•H_2O] clusters could occupy the cages. As K and Cl fit together in the channel with minor overlap (Fig. 1a), clusters of this type also might occur; however, the vacant cation and anion sites, which are necessarily present if Cl resides in the channel, would promote rapid diffusion of Cl within the channel, leading to an unstable state. Stacking faults that systematically block the channels and give rise to elongate cavities, such as those found in the cancrinite-like minerals, could possibly stablize the [K•Cl] clusters.

Carbonate, CO_3, which is an important constituent of cancrinite, is notably absent from the davyne specimens described in this work. If present, CO_3 would compete for the available Ca and could result in the elimination of Cl from the structure and the formation of [K•H_2O]$^+$-containing cages.

In summary, the main chemical feature of the davyne structure is the presence of [Ca•Cl] clusters in the cage. This implies that Ca is available and that CO_2 is unlikely to be an important constituent. In cancrinite-group minerals, Cl is not normally a channel anion, and its presence could indicate stacking faults. The distinction between microsommite and davyne can be made on the basis of channel ordering, which is a direct consequence of difference in cage size caused by the substitution of [Ca•Cl]$^+$ for [Na•H_2O]$^+$.

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