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SULFATE DISORDER IN SCAPOLITE

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ABSTRACT

Sulfate scapolites show high-pressure stability and high entropy, a fact that has been tentatively related to positional disorder of the sulfate group. The exact location of sulfate anions was determined in a sulfate-rich scapolite crystal with cell content $(Ca_{5.87}Na_{1.82}Mg_{0.07}Fe^{3+}_{0.07}\square_{0.08}K_{0.04}Sr_{0.05})_{\Sigma=8}(Si_{14.20}Al_{9.80})_{\Sigma=24}O_{48}[(CO_3)_{1.36}(SO_4)_{0.58}Cl_{0.06}]_{\Sigma=2}$. Using 2280 symmetry-independent reflections the structure was refined in space group $I4/m$ to an unweighted R of 2.9% with Mo$K\alpha$ radiation. The tetrahedral SO_4 group is centered at (0, 0, 0), site symmetry $4/m$, with its $\bar{4}$ axis directed along c. The group occupies two orientations, as required by symmetry, related by a 90° rotation about $\bar{4}$. Equal occupancy of the two orientations leads to space group $I4/m$; unequal occupancy lowers the space group to $P4_2/n$. The carbonate groups lie in the (001) plane, confirming the results of Levien & Papike (1976).

SOMMAIRE

Sous haute pression, les scapolites sulfatées sont stables et possèdent une entropie élevée, fait d'observation qu'on a déjà tenté d'expliquer par un désordre de position des groupes SO_4 et peut-être leur rotation à haute température. Nous nous sommes proposés de déterminer la position exacte des anions SO_4^{2-} dans un cristal dont la maille contient $(Ca_{5.87}Na_{1.82}Mg_{0.07}Fe^{3+}_{0.07}\square_{0.08}K_{0.04}Sr_{0.05})_{\Sigma=8}(Si_{14.20}Al_{9.80})_{\Sigma=24}O_{48}[(CO_3)_{1.36}(SO_4)_{0.58}Cl_{0.06}]_{\Sigma=2}$. Nous en avons affiné la structure en $I4/m$ sur 2280 réflexions indépendantes (en rayonnement Mo$K\alpha$) jusqu'au résidu non-pondéré R = 2.9%. Le centroïde du groupe tétraédrique SO_4^{2-} se situe en (0, 0, 0), point de symétrie $4/m$, et l'axe $\bar{4}$ est dirigé suivant c. Le tétraèdre se présente en deux orientations tournées l'une par rapport à l'autre de 90° autour de l'axe $\bar{4}$, satisfaisant ainsi à la symétrie de site. Selon que les tétraèdres des deux orientations sont en nombres égaux ou inégaux, le groupe spatial sera $I4/m$ ou $P4_2/n$. Les groupes CO_3 se trouvent dans le plan (001) et confirment donc les résultats de Levien & Papike (1976).

(Traduit par la Rédaction)

INTRODUCTION

Recent experimental studies on the stability of scapolite at high pressures and temperatures have led to a re-evaluation of the importance of this mineral under high-grade metamorphic conditions. Newton & Goldsmith (1975) have shown synthetic meionite to have a surprisingly high thermal stability at high pressures. Sulfate-bearing scapolite was found by Newton & Goldsmith (1976) to be stable at even higher pressures, and the observed high entropy of sulfate scapolite was ascribed by them to the assumed disordered arrangement of the anionic groups, the orientation of which was not known. Goldsmith (1976) summarized the scapolite studies and stressed that scapolite might be an important reservoir of CO_2 and SO_2 in the lower crust. The high-temperature field of stability of this mineral phase suggests that it may be a liquidus phase in appropriate magmas.

The sulfur content of scapolite in xenoliths of granulite-facies, deep-crustal origin was found to be high, and possibly a reflection of the high pressure of formation (Lovering & White 1964). However, Lovering and White could not explain why such a large ion as S^{2-} or a large complex like SO_4^{2-} would increase the stability of high-pressure scapolites. The increase in sulfur content of scapolite with increasing pressure of formation makes it a potential geobarometer.

The purpose of the present study is to obtain structural information concerning the anion location in the cavity and to elucidate the role of sulfate groups in stabilizing the scapolite structure at high temperatures and pressures.

PREVIOUS WORK

The chemical and structural variations of scapolites have already been the subject of numerous investigations (Shaw 1960, Papike &

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Stephenson 1966, Lin & Burley 1975, Levien & Papike 1976). However, with one exception, all the scapolites studied were sulfur-poor. Lin & Burley (1975) refined a 52% *Me* scapolite that contained 0.37 sulfate groups per unit cell, yet these sulfate ions were ignored in the structure refinements; also, the formula was incorrectly converted from wt.% to formula unit.

OCCURRENCE AND PHYSICAL PROPERTIES

Iiyama (1959) described an unusual scapolite occurrence from Chuquet Genestoux near Puy-de-Dôme, France; Professor R. F. Martin of McGill University supplied us with material from this locality. Large anhedral crystals, up to 3 cm long, are found as megacrysts in a basaltic scoria, and embayments in the crystals contain basaltic groundmass. All scapolites are mantled by very fine-grained plagioclase, and most large crystals contain small rods of apatite. The scapolite color varies from milky light grey to very dark grey to black. A Mössbauer study was carried out by Dr. Erika Hermon on a hand-picked sample of the darkest-colored megacryst from Professor Martin's collection. The powder sample was kept at 20°C; the source was ^{57}Co in Pd, 20 mC strong. A constant acceleration spectrometer was used in conjunction with a multichannel analyzer. As neither ferrous nor ferric iron lines were detected on the Mössbauer spectrum, the maximum iron content in scapolite from this locality seems to be well below 5 wt.%. No good cleavage exists in hand specimen, and a conchoidal fracture is the rule. This lack of the usual good cleavages ({110} and {100} in scapolite) is a characteristic of most minerals found as megacrysts in alkali basalt. The scapolite crystal under study here, CG–2, is uniaxial negative with ϵ 1.564(2), ω 1.591(2). Its density, measured on the Berman balance, is 2.73(3) g/cm³ at 20°C (Table 1).

CHEMISTRY

All elements except carbon (Table 2) were measured with standard X-ray fluorescence techniques by Ms. S. Horsky. The calculated cell content is based on Si + Al =24. Repeated attempts to determine carbon were based on (1) volumetric analysis of CO_2 evolved during heating in HCl and (2) an oxidation method at 1600°C in a LECO furnace. Both methods were unsuccessful and gave inconsistent results. Therefore the wt.% CO_2 was calculated

TABLE 1. CRYSTAL DATA AND CRYSTAL OPTICS ON SCAPOLITE CRYSTALS

Sample No.	CG-2	XXXIV*	XL	XXX*
Reference	Present work	Levien & Papike (1976)	Lin & Burley (1975)	Papike & Stephenson (1966)
Locality	Chuquet Genestoux near Puy de Dome, France	Monmouth Township, Ont.	Tsarasaotra, Madagascar	Greenville, P.Q.
Collector	R.F. Martin	D.M. Shaw	not given	D.M. Shaw
Analyst	S. Horsky	C.O. Ingamells	S.B. Lin	C.O. Ingamells
Method	X-ray fluorescence	Wet chemical	Electron microprobe	Wet chemical
Cell content	See below [a]	See below [b]	See below [c]	See below [d]
% meionite	77	33	53	70
ϵ; ω	1.564(2); 1.591(2)	1.547; 1.560+	1.549; 1.570‡	1.555; 1.587+
$\frac{1}{2}(\epsilon+\omega)$; σ	1.5775 ; 0.027	1.553 0.013	1.559 0.021	1.571; 0.032
% meionite**	85 ; 70	38 ; 29	50 ; 53	72 ; 81
a; c (Å)	12.158(2);7.5733(9);20°C	12.066(4);7.5812(3);24°C	12.116(1); 7.581(2)	12.169(4); 7.569(3)
V (Å³)	1,119.5(9)	1,104.2(4)	1,112	1,120
Space group	$I4/m$	$P4_2/n$	$P4_2/n$	$I4/m$
D_{obs}; D_{calc}	2.73(3); 2.75(g/cm³)	2.660; --- (g/cm³)	2.69; --- (g/cm³)	2.703; --- (g/cm³)
Refinement Method	4-circle diffractometer θ-2θ scan	4-circle diffractometer θ-2θ scan	normal-beam (Wbg-type) diffractometer	Integrating Weissenberg
μ_o (cm⁻¹)	16.66; MoKα	12.2; MoKα	--- ; MoKα	--- ; CuKα
Independent reflections (obs.)	2280	1660	1370	488
Final R	0.029 (unweighted)	0.072 (unweighted)	0.086 (unweighted)***	0.157 (unweighted)

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* Sample numbers taken from Shaw (1960, p. 241). ** From optics (Shaw 1960). + Data from Shaw (1960, p. 241). ‡ Data from Shaw (1960, p. 239, sample No. XXII), on a scapolite from the same locality. ***Extinction-affected reflections omitted.

a CG2 $(Ca_{5.87}Na_{1.82}Mg_{0.07}Fe^{3+}_{0.07}\square_{0.08}K_{0.04}Sr_{0.05})\ (Si_{14.20}Al_{9.80})O_{48}[(CO_3)_{1.36}(SO_4)_{0.58}Cl_{0.06}]$

b XXXIV $(Na_{4.94}Ca_{2.66}K_{0.40})\ (Si_{16.10}Al_{7.90})O_{48}[Cl_{1.18}(CO_3)_{0.74}(SO_4)_{0.08}]$

c XL $(Ca_{4.18}Na_{3.30}K_{0.46}\square_{0.06})\ (Si_{15.0}Al_{8.70}\square_{0.30})\ (O_{47.80}\square_{0.20})\ [(CO_3)_{0.88}Cl_{0.74}(SO_4)_{0.38}]$

d XXX $(Ca_{5.14}Na_{1.44}K_{0.86}Mg_{0.22}\square_{0.34})\ (Si_{13.92}Al_{10.08})\ (O_{23.93}\square_{0.07})\ [(CO_3)_{0.59}\square_{0.29}(SO_4)_{0.11}Cl_{0.01}]$.

TABLE 2. CHEMICAL ANALYSIS AND CELL CONTENT OF SCAPOLITE CG-2

	Wt. %	Elements and complex ions	No. of atoms in formula unit	
SiO_2	46.45	Si	14.20	Σ = 24*
Al_2O_3	27.20	Al	9.80	
CaO	17.93	Ca	5.87	Σ = 7.92
Na_2O	3.07	Na	1.82	
MgO	0.16	Mg	0.07	
Fe_2O_3	0.31	Fe^{3+}	0.07	
SrO	0.28	Sr	0.05	
K_2O	0.11	K	0.04	
CO_2	3.26	CO_3	1.36**	Σ = 2.0
SO_3	2.53	SO_4	0.58	
Cl	0.12	Cl	0.06	
	101.42			
O ≡ Cl	-0.03			
Sum	101.39	Charge imbalance:	+0.31	

* Assumed.

** Amount of C assumed to fill anion cavity.

assuming xCO$_3$ + ySO$_4$ + zCl in the anion cavity with $x + y + z = 1$. This led to both a reasonable charge balance and a percent-oxide sum near 100. As the (Na + K)/(Ca + Na + Fe^{3+} + Mg + Sr + K) ratio is 0.23, this scapolite is 77% meionite, in reasonable agreement with the compositional prediction based on refractive indices (Table 1).

OXIDATION STATE OF SULFUR

Chappell & White (1968) used peak shifts of the S $K\alpha_1$ X-ray fluorescence peak to obtain information on the oxidation state of sulfur. Using a Philips PW1220 XRF spectrometer, Cr tube (50 kV, 20 mA) and a graphite monochromator (00.2 reflection) as analyzing crystal, fluorescence intensities were collected from the powdered sample with 0.05° step scanning and a ten-second counting time.

Different 2θ angles (near 106°) of the S $K\alpha_1$ maximum intensity can be observed for the two different oxidation states, S^{6+} in sulfates and S^{2-} in sulfides. The angular shifts, $\Delta = 2\theta$ (pyrite) — 2θ (sample), have the following positive magnitudes: pyrite (Δ 0°2θ), chalcopyrite (Δ 0.0023°2θ), scapolite CG–2 (Δ 0.0826°2θ), celestite (Δ 0.0886°2θ) and anhydrite (Δ 0.0956°2θ). As the CG–2 scapolite thus gives a S $K\alpha_1$ peak position close to that of other sulfate-bearing minerals, we conclude that all S in the scapolite is present as SO_4^{2-}.

EXPERIMENTAL PROCEDURE

A single crystal of the Chuquet Genestoux scapolite was ground into a sphere of radius 0.21(2) mm and mounted on a solid glass fibre. A careful search by film and counter methods for reflections that obey $h + k + l = 2n + 1$ showed no measurable intensities, not even for the reflections 081, 054 and 135 reported as the strongest 'forbidden' ones in other scapolites (Lin & Burley 1973a); therefore, we accept $I4/m$ as the appropriate space group for CG–2. The data were collected using a FACS–1 Picker diffractometer, graphite-monochromatized Mo$K\alpha$ radiation and the θ–2θ scan method. Three standards with 20,000 to 30,000 decacounts were measured after every 18 reflections. Attenuators were inserted when the counting rate exceeded 10,000 c.p.s. Of the 2575 symmetry-independent reflections in the limiting sphere, 2280 had an observed intensity greater than three times the variance of the intensity based on counting statistics and were therefore classed as observed. The cell dimensions, determined by least-squares refinement using 12 high-angle reflections, are summarized (Table 1) together with crystal data and crystal optics for four other specimens to be discussed below.

STRUCTURE REFINEMENT

The collected intensities were corrected for Lorentz and polarization factors and converted to structure factors. Absorption corrections (Ibers & Hamilton 1974) were applied for the spherical sample with $\mu = 16.66$ cm^{-1}. The initial positional parameters for the framework atoms were those of Lin & Burley (1973b). Atomic scattering factors for neutral atoms from International Tables, Vol. IV, were employed. The anion groups in the central cavity were ignored in the initial stages. Five cycles of isotropic least-squares refinement with the X–RAY 70 computing program (Stewart *et al.* 1970) using unit weights resulted in an R of 0.16. A difference-Fourier summation allowed the assignment of the S, Cl and C atoms to the sites with $4/m$ symmetry at position $2(a)$. The diffuse electron-density clouds surrounding these sites were interpreted as due to a fourfold partly filled carbonate-oxygen position. The sulfate-oxygen atoms were placed at $z = 18/23$, below the carbonate-oxygen atoms. Four additional cycles of anisotropic least-squares refinement using the X-RAY 76 program (Stewart *et al.* 1976) led to an R of 0.035. The still-large diffuse electron-density clouds about the carbonate-oxygen sites induced us to divide the carbonate-oxygen position into three positions as was first done by Papike & Stephenson (1966). The site occupancies of O(7), O(8) and O(9) were each set equal to 0.16, one third the refined occupancy of the diffuse carbonate oxygen position of 0.48(3) prior to the distinction of carbonate-group disorder. This value agrees well with the calculated carbonate-oxygen occupancy of 0.17 based on the chemical formula and carbonate-disordering model, and was not refined further. Four more cycles of refinement including, as variables, the occupancy of the position 2(*a*) and the sulfate-oxygen coordinates, resulted in a reduction of R to 0.029. The carbon atoms were assumed to be equidistant from their three carbonate-oxygen atoms and coplanar with them; their locations were not refined. Observed and final calculated F_{hkl} values (Table 3) are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Tables 9 and 10 are also in the Depository.

TABLE 5. ANISOTROPIC THERMAL PARAMETERS (x100) AND TEMPERATURE FACTORS (x100) FOR SAMPLE CG-2

U11	Ca	1.24(1)	T1	0.49(1)	T2	0.78(1)
U22		1.62(1)		0.62(1)		0.77(1)
U33		3.51(2)		0.96(1)		0.66(1)
U12		0.39(1)		-0.17(9)		-0.012(3)
U13		0		0		0.018(7)
U23		0		0		0.071(7)
B		1.68		0.54		0.58
Bmizz*		1.13		-0.08		0.03
U11	O1	0.92(3)	O2	2.04(5)	O3	1.95(3)
U22		1.61(4)		1.31(4)		1.69(3)
U33		2.26(5)		1.05(4)		1.78(3)
U12		0.11(3)		0.49(3)		-0.01(3)
U13		0		0		-0.03(3)
U23		0		0		-0.45(3)
B		1.26		1.16		1.43
Bmizz		0.58		0.87		0.84
U11	O5	2.22(4)	O7	2.0(6)	O8	4.(2)
U22		1.52(5)		3.5(7)		1.6(6)
U33		3.08(5)		6.(1)		6.(1)
U12		0.46(3)		-1.9(7)		-1.4(7)
U13		-1.65(4)		0		0
U23		-0.40(3)		0		0
B		1.79		3.0		2.8
Bmizz		0.79		---		---
U11	O9	7.(2)	O10	3.2(3)	S,Cl	2.14(9)
U22		8.(2)		3.6(4)		2.14(9)
U33		12.(2)		4.3(4)		1.94(6)
U12		5.(2)		-0.2(3)		0
U13		0		-1.7(3)		0
U23		0		-0.4(4)		0
B		7.2		2.9		1.59
Bmizz		---		---		1.8

* Bmizz refers to sample XXX (Table 1).

COMPARISON OF CG–2 WITH SULFATE-RICH SCAPOLITES IN THE LITERATURE

A comparison of the positional (Table 4) and thermal (Table 5) parameters of our scapolite with those of the 70% meionite (Table 1) refined by Papike & Stephenson (1966) shows no significant difference in the positional parameters of the framework atoms. The standard deviations, however, are smaller by an order of magnitude for CG–2, and the temperature factors are more reasonable. The for-

TABLE 4. ATOMIC CO-ORDINATES OF A 77% MEIONITE (SAMPLE CG-2) COMPARED WITH THOSE OF A 70% MEIONITE (PAPIKE & STEPHENSON 1966)

1		77% Me	70% Me	2		77% Me
Ca,Na	x	0.35783(3)	0.3572(3)	O7	x	0.507(2)
	y	0.28298(3)	0.2830(3)		y	0.385(2)
	z	1/2	1/2			1/2
T1	x	0.33916(3)	0.3391(3)	O8	x	0.602(2)
	y	0.40831(3)	0.4084(3)		y	0.533(2)
	z	0	0		z	1/2
T2	x	0.66023(2)	0.6607(2)	O9	x	0.415(4)
	y	0.91311(2)	0.9134(2)		y	0.535(2)
	z	0.79306(4)	0.7931(4)		z	1/2
O1	x	0.45805(9)	0.4581(7)	O10	x	0.5996(6)
	y	0.3481(1)	0.3480(7)		y	0.5177(8)
	z	0	0		z	0.606(1)
O2	x	0.6867(1)	0.6880(8)	C	x	0.4925(9)
	y	0.87309(9)	0.8720(8)		y	0.5130(9)
	z	0	0		z	1/2
O3	x	0.34942(7)	0.3489(5)	S,Cl	x	1/2
	y	0.94961(7)	0.9461(5)		y	1/2
	z	0.7928(1)	0.792(1)		z	1/2
O5	x	0.26668(7)	0.2668(5)			
	y	0.36560(7)	0.3646(5)			
	z	0.8261(1)	0.826(1)			

Col. 1: Cations and framework oxygen atoms.
Col. 2: Atoms in cavity
Note. - O6 is not a separate position in I4/m.

TABLE 6. SCAPOLITE CG-2 INTERATOMIC DISTANCES AND ANGLES*

Atoms	Distance	Atoms	Angle
Ca-O5x2	2.887(1)Å	O1-T1-O5^{vii}x2	109.32(4)°
O5^{i}x2	2.700(1)	O1-T1-O1^{v}	113.01(7)
O2^{ii}	2.351(1)	O1-T1-O5^{vii} x2	110.25(4)
O3^{iii}	2.510(1)	O5^{xiv}-T1-O5^{vii}	104.33(5)
O10^{iv}	2.605(9)	O3^{x}-T2-O5^{xi}	104.28(4)
O10^{v}	2.541(9)	O2^{viii}-T2-O3^{x}	112.51(5)
O7	2.19(2)	O2^{viii}-T2-O3^{ix}	107.75(5)
O8^{v}	2.54(2)	O2^{viii}-T2-O5^{xi}	104.78(5)
O9^{vi}	2.07(4)		
O7^{v}	2.58(3)	O3^{ix}-T2-O3^{x}	113.88(4)
O8^{iv}	2.31(2)	O3^{ix}-T2-O5^{xi}	113.35(4)
		O10-S-O10^{iv}x4	113.7(5)
S -O10	1.472(8)	O10^{xiv}-S-O10^{vi}x4	107.4(5)
T1-O1	1.620(1)	O2^{ii}-Ca-O5^{i}x2	79.38(3)
O5^{vii}x2	1.667(1)	O2^{ii}-Ca-O5x2	59.89(2)
O1^{v}	1.628(1)	O3^{iii}-Ca-O3^{xii}	77.40(4)
Mean	1.646	O3^{iii}-Ca-O5^{i}x2	61.0(3)
T2-O2^{viii}	1.672(1)	O5^{i}-Ca-O3^{xii}x2	97.19(3)
O3^{ix}	1.673(1)	O3^{xii}-Ca-O5x2	81.89(3)
O3^{x}	1.675(1)	O5^{i}-Ca-O5^{viii}	58.39(4)
O5^{xi}	1.680(1)	O5^{i}-Ca-O5^{xiv}x2	66.44(3)
Mean	1.675		
		O7^{iv}-C-O8^{iv}	117(2)
C -O7^{iv}	1.25	O7^{iv}-C-O9^{iv}	119(3)
O8	1.25	O8^{iv}-C-O9^{iv}	125(3)
O9^{iv}	1.25		

*

Symmetry transformations:

i.	1/2-x, 1/2-y, z-1/2	viii.	x, y, 1+z
ii.	x-1/2, y-1/2, 1/2+z	ix.	1-x, 2-y, z
iii.	y-1/2, 1/2-x, z-1/2	x.	3/2-y, 1/2+x, 3/2-z
iv.	1-x, 1-y, z	xi.	1/2+x, 1/2+y, 3/2-z
v.	y, 1-x, z	xii.	y-1/2, 1/2-x, 3/2-z
vi.	1-y, x, z	xiii.	1/2-x, 1/2-y, 3/2-z
vii.	x, y, -1+z	xiv.	x, y, 1-z

mula (Table 2) of the Papike & Stephenson sample came from a wet chemical analysis by C. O. Ingamells in Shaw (1960, p. 241) and is given in Table 2. This analysis shows that our assumption concerning the full occupancy of the position of non-framework anions may not be justified and may well be a source of error in our final refinement.

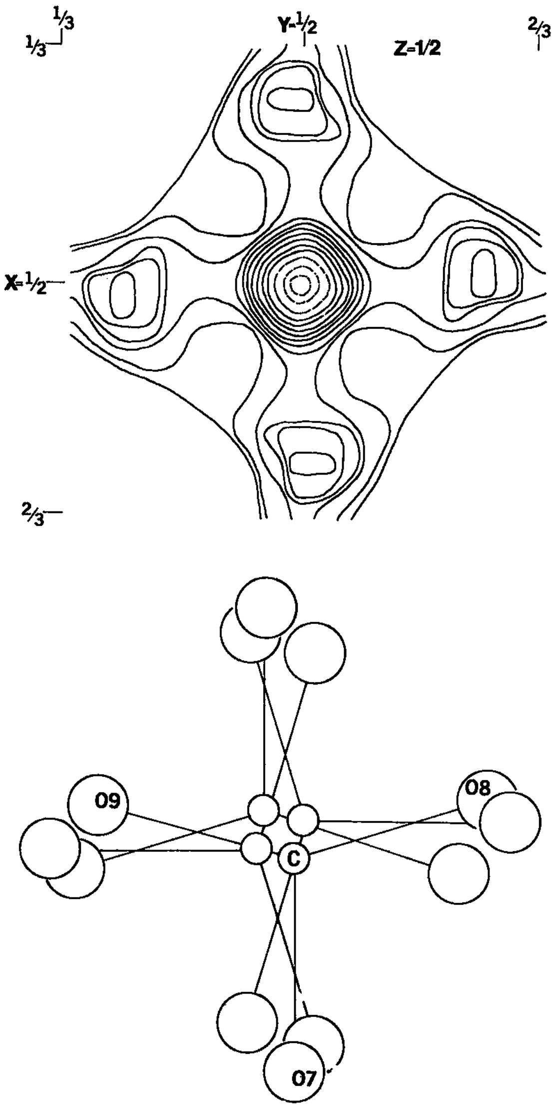

FIG. 1. (a) Section $z = \frac{1}{2}$ through Fourier-difference summation to which only framework atoms and (Ca,Na) contributed; (C,S,Cl) is at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and the diffuse carbonate-oxygen atoms are distributed in 4-fold symmetry in the mirror at $z = \frac{1}{2}$. Solid contours 1 $e/Å^3$, dot-and-dash 10 $e/Å^3$. (b) Disordering model of the carbonate group proposed by Papike & Stephenson (1966).

From the mean T–O lengths (Table 6) of $T1$ and $T2$ tetrahedra, the aluminum contents of the two positions were found to be 27 and 46 atomic % respectively, based on the equation of Jones (1968): $y = 6.4116x - 10.282$, where x is T–O and y is the atomic % Al. The framework structure of scapolite has been discussed in detail by Papike & Zoltai (1965).

ANION CAVITY

The orientation of the carbonate group in the cavity has been studied by several authors, most recently by Levien & Papike (1976). In all refinements, except that of Lin & Burley (1975), the carbonate group is placed in the

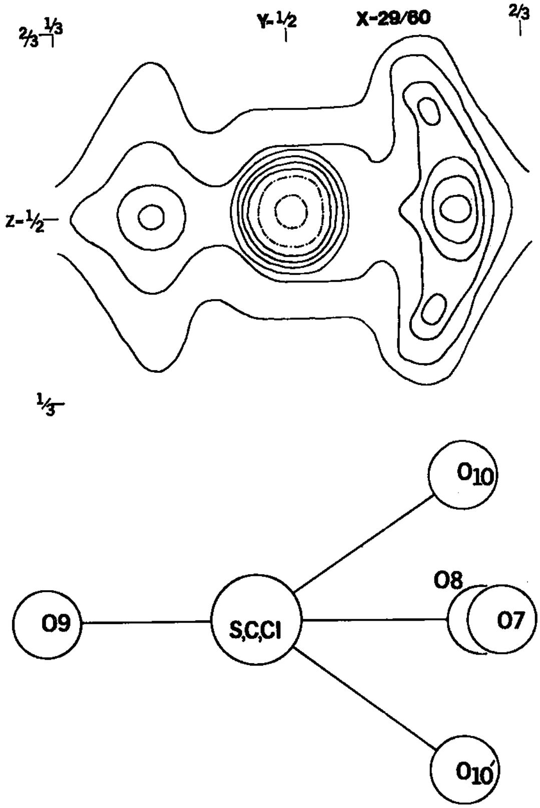

FIG. 2. (a) Section $x = 29/60$ through Fourier-difference summation to which only framework atoms and (Ca,Na) contributed, showing (C,S,Cl) at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), the carbonate oxygens in the $z = \frac{1}{2}$ plane and the electron density due to the sulfate oxygens above and below the $z = \frac{1}{2}$ plane. (b) Disordering model of sulfate and carbonate groups, showing only one fourth of the 24 atomic sites: one cationic site, three CO_3 oxygens O(7), O(8), O(9), and two SO_4 oxygens O(10), O(10′).

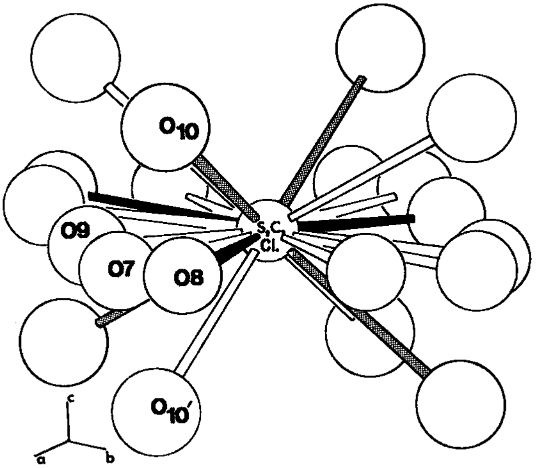

FIG. 3. ORTEP drawing of the anion site showing the two sulfate tetrahedra and four carbonate-group positions which were assigned in the refinement of scapolite CG–2. The carbonate groups lie in the mirror plane at $z = ½$. Note that the labeled oxygens O(7), O(8), O(9) belong to three CO_3 groups and that atoms O(10) and O(10′) belong to two SO_4 groups. Three dark bonds belong to one CO_3, four lighter bonds, to one SO_4.

plane $z = ½$. The difference-Fourier summation through the central anion cavity at $z = ½$ shows the electron density due to the disordered carbonate groups (Fig. 1a). Only the framework atoms were allowed to contribute to the F_{calc} terms.

However, in scapolite, there is considerable electron density above and below the $z = ½$ plane (Fig. 2a). The 1.472(8)Å distance between these maxima and the centre of the cavity at ½, ½, ½, where sulfur is located, is consistent with S–O distances obtained in various sulfates (Christidis & Rentzeperis 1975). The corresponding O–S–O angles are also within the range expected for tetrahedral groups: 107.4°(5), 113.7°(5). Thus we conclude that the tetrahedral sulfate group is positionally disordered in two equivalent orientations related by a 90° rotation about the $\bar{4}$ axis of the group (Fig. 3). The expected occupancy of the sulfate-oxygen position is one half the atomic percentage of $(SO_4)^{2-}$ as determined by chemical analysis (0.29/2 = 0.145) (Table 2). The independent least-squares refinement of the site occupancy gave 0.177(3).

RE-REFINEMENT OF SCAPOLITE XL

Lin & Burley (1975) refined scapolite XL with a formula (Table 1) that corresponds to 53% meionite but is of dubious accuracy as (1) the Si + Al content is 0.15 atoms less than the required 12 needed to fill the tetrahedral positions and (2) the charges do not balance (there is an excess of 0.32 negative charge per formula unit). In their observed space group, $P4_2/n$, using 1370 observed reflections and isotropic temperature factors, they achieved a final R of 0.083. Their carbonate groups are placed in two tilted orientations about position 2(*a*), not parallel to (001). This was done to account for the observed electron density above and below the planes $z = 0$ and $z = ½$. However, their final difference-Fourier map revealed remaining electron density in that region. The 0.38 SO_4^{2-} groups in the cell were ignored in the refinement.

TABLE 7. ATOMIC CO-ORDINATES OF A 53% MEIONITE, SAMPLE XL RE-REFINED FROM DATA OF LIN & BURLEY (1975)

Cations & framework oxygen atoms

		1975	Present			1975	Present
Ca	x	0.3603(2)	0.3606(1)	02	x	0.6902(5)	0.6902(2)
	y	0.2841(2)	0.2842(1)		y	0.8757(5)	0.8760(2)
	z	0.5126(3)	0.5120(2)		z	0.0088(7)	0.0098(5)
T1	x	0.3390(1)	0.3391(1)	03	x	0.3498(4)	0.3501(3)
	y	0.4092(1)	0.4093(1)		y	0.9420(4)	0.9418(3)
	z	0.9978(3)	0.9979(2)		z	0.7947(6)	0.7941(5)
T2	x	0.6593(2)	0.6593(1)	04	x	0.5459(5)	0.5457(3)
	y	0.9155(2)	0.9155(1)		y	0.8472(5)	0.8470(3)
	z	0.7967(2)	0.7972(2)		z	0.7160(7)	0.7161(5)
T3	x	0.4125(1)	0.4126(1)	05	x	0.2677(5)	0.2679(3)
	y	0.8363(1)	0.8364(1)		y	0.3667(5)	0.3668(3)
	z	0.7103(2)	0.7106(2)		z	0.8307(7)	0.8300(5)
01	x	0.4576(3)	0.4578(2)	06	x	0.3703(5)	0.3703(3)
	y	0.3503(3)	0.3505(2)		y	0.7287(5)	0.7294(3)
	z	0.0019(7)	0.0019(5)		z	0.8256(7)	0.8262(5)

Atoms in cavity

		1975	Present	Intermediate
07	x	0.398(5)	0.400(2)	0.405(4)
	y	0.479(5)	0.478(2)	0.479(2)
	z	0.460(8)	0.507(3)	0.463(5)
	occ.	0.16	0.27(3)	0.28(2)
08	x	0.401(3)	---	0.399(1)
	y	0.482(3)	---	0.481(2)
	z	0.587(5)	---	0.602(4)
	occ.	0.28	---	0.24(2)
010	x	---	0.401(2)	---
	y	---	0.481(2)	---
	z	---	0.612(3)	---
	occ.	---	0.17(3)	---
011	x	---	0.399(4)	---
	y	---	0.483(4)	---
	z	---	0.386(6)	---
	occ.	---	0.11(3)	---
Cl,C,S	x	½	½	½
	y	½	½	½
	z	½	½	½
R		0.083	0.041	0.043

Col. "1975": Coordinates from Lin & Burley (1975)
Col. "Present": CO_3 groups in (001); SO_4 groups included
Col. "Intermediate: CO_3 groups tilted

We used the intensity data of Lin & Burley

TABLE 8. TEMPERATURE FACTORS (x 100) OF SCAPOLITE XL RE-REFINED FROM DATA OF LIN & BURLEY (1975)

Framework atoms

U11	Ca	1.83(5)	T3	0.65(5)	O3	2.2(2)	O6	1.3(2)
U22		1.97(5)		0.72(6)		1.2(1)		1.7(2)
U33		3.57(7)		0.63(4)		2.0(2)		2.4(2)
U12		0.77(4)		-0.01(5)		0.2(1)		-0.5(2)
U13		0.09(6)		-0.05(4)		-0.2(1)		-0.4(1)
U23		0.11(7)		0.02(4)		-0.3(1)		1.3(1)
U11	T1	0.41(3)	O1	0.74(9)	O4	1.2(1)		
U22		0.53(3)		1.31(9)		1.9(2)		
U33		0.86(3)		2.0(1)		1.9(1)		
U12		-0.02(2)		0.22(7)		-0.4(1)		
U13		-0.04(5)		0.0(2)		-0.4(1)		
U23		-0.00(6)		-0.1(1)		-0.0(1)		
U11	T2	0.72(6)	O2	1.9(1)	O5	1.7(2)		
U22		0.78(6)		1.4(1)		1.4(2)		
U33		0.70(5)		0.95(9)		2.5(2)		
U12		0.02(5)		0.52(8)		0.3(2)		
U13		0.04(5)		0.0(1)		-1.4(2)		
U23		0.05(5)		0.1(1)		-0.3(1)		

Anion cavity atoms

		1		2	3	4
U11	Cl,S,C	3.3(2)	O7 B	5.(1)	8.(3)	2.2(6)
U22		3.3(2)	O8 B	3.9(6)	3.(1)	---
U33		2.7(2)	O10 B	---	---	9.(1)
			O11 B	---	---	4.(1)
U12		0				
U13		0				
U23		0				

Col. 1: Temperature factors for conditions of col. 4.
Col. 2: From Lin & Burley (1975).
Col. 3: Carbonate ions re-refined.
Col. 4: Sulfate ions added; carbonate ions re-refined.

TABLE 11. BOND LENGTHS FOR ANION-CAVITY ATOMS AFTER RE-REFINEMENT OF SCAPOLITE XL

1		2	
Ca - O7	2.45(4)Å	Ca - O10	2.55(2)Å
O8	2.52(2)	O10'	2.56(2)
$O8^{i}$	2.52(2)	O11	2.63(5)
$O7^{i*}$	2.44(4)	O11'	2.48(5)
		O7	2.40(3)
		O7'	2.41(3)
C - O7	1.21(4)	C,S- O10	1.49(2)
O8	1.47(2)	O11	1.51(5)
		O7	1.24(3)

* Symmetry operation i) 1-y, x, 1-z
Col. 1: Re-refinement for $R = 4.3\%$
Col. 2: Re-refinement for $R = 4.1\%$.

(1975), as well as their final positional and thermal parameters, in a scale-factor refinement which confirmed their published R value of 0.083. Two cycles of least-squares refinement with anisotropic temperature factors for all atoms, followed by two cycles of refinement of both positional and thermal parameters and, finally, two cycles of refinement of the occupancy of O(7), O(8) and (C,S,Cl) positions reduced R to 0.043 (Tables 7, 8). The original F_{obs} and the above F_{calc} data are given in Table 9 (deposited). Our refinement is based on the Ca and framework atom positions of the above 0.043 refinement and on the disordered arrangement of sulfate and carbonate groups developed for CG–2. However, the carbonate-group-oxygen position was not subdivided as it was in the CG–2 refinement. After two such cycles and a further two-cycle refinement of the occupancies of O(7), O(10), O(11) and (C,S, Cl), the R dropped to the final value of 0.041. This reduction in R of 0.02 is significant at a level of 0.005, according to the significance test of Hamilton (1965), provided, of course, that there are no systematic errors in the Lin & Burley data. The final F_{calc} values, together with the original F_{obs} data, are listed in Table 10 (deposited). Table 11 shows the interatomic distances between Ca and its nearest-neighbor oxygen atoms, as well as the C–O and S–O bond lengths in CO_3 and SO_4 groups, which were obtained in the refinements leading to $R = 0.043$ and 0.041, respectively.

CONCLUSIONS

From the refinement of two sulfate-rich meionites, a disordered arrangement of sulfate groups is derived, which offers an understanding of the observed stability of sulfate scapolite at high temperature and pressure.

The (001) disordered orientation of the carbonate groups obtained by Levien & Papike (1976) is confirmed. The sulfate groups are centred at (0,0,0) in two orientations related by a 90° rotation about the $\bar{4}$ axis of the SO_4^{2-} tetrahedron, thus statistically obeying the $4/m$ site symmetry required by space group $I4/m$. In $P4_2/n$, the site symmetry being $\bar{4}$, the positional disorder is not required; it is nevertheless observed on the difference-Fourier map and with a 2:3 occupancy ratio for the two orientations. The less-preferred position shows two Ca–O(11) bond lengths of 2.63(2) and 2.48(2)Å, whereas the preferred one has two statistically equal Ca–O(10) bonds of length 2.55(2)Å (Table 10).

With increasing temperature the scapolite structure suffers a rotation of the strings of tetrahedra along c (Pauling 1930), which is accompanied by an increase in a while c remains constant (Levien & Papike 1976). Thus, increasing the temperature moves the (Ca,Na) position away from the centre of the anion cavity, without change in its z coordinate for crystals with space group $I4/m$ and with small changes from $z = 0.500$ for crystals in space group $P4_2/n$. The x and y dimensions of the anion cavity, which can be described as an oblate ellipsoid, increase whereas the z dimension remains nearly constant, and the cavity becomes better suited to carbonate occupancy.

The opposite effect must take place with increasing pressure: the cavity shape will become more nearly spherical and more suited to sulfate occupancy. Specifically, the Ca–O(CO_3) bonds in scapolite XL (2.40(2)Å) lie near the plane $z = ½$ and would be more shortened with increasing pressure than would the Ca–O(SO_4) bonds (2.55(2)Å), which are at an angle of approximately 35° to the plane $z = ½$.

Comparison of the above two sulfur-rich scapolite crystals, samples CG–2 and XL, with space groups $I4/m$ and $P4_2/n$ respectively, shows significant structural difference between the two. In $P4_2/n$, both sites (0,0,0) and (½, ½,½) of point-position $2(a)\bar{4}$ are related by the n glide reflection. Each is occupied by both orientations of the SO_4 tetrahedra, but in inverse ratios (say, 3:2 and 2:3 respectively), so that the site occupancies *are* different. The ratios can be equal only for the special case 1:1, where the two sites become translation-equivalent and acquire site symmetry $4/m$, thus simulating space group $I4/m$. (Note that the 1:1 ratio is *required* by the site symmetry $4/m$.) The unit ratio cannot be expected to be rigorous or to occur frequently. For the end-members where it has been reported (Lin & Burley 1975), the structure assigned to $I4/m$ could as easily be described in $P4_2/n$ in view of the close relationship between the two space groups and the relevant point-positions. That the ratio tends toward unity as the composition approaches an end member is to be expected. Without the variation in composition from cell to cell, all the cells, and consequently the anionic cavities, tend to become identical, thus promoting the equality of the two site occupancies by the two orientations of the SO_4 ions, which results in the disappearance of the "sum-odd" reflections.

Similar considerations can be applied to the occupancy of the four carbonate orientations in the plane (001), but they were not studied in detail. Lin & Burley (1973a) ascribed the appearance of weak "sum-odd" reflections to "order-disorder of Al and Si in the tetrahedral framework," and this may well be a contributor. Another reason for favoring the lower $P4_2/n$ space-group symmetry over the body-centred $I4/m$ is that growth conditions prevent equal occupancies of (0,0,0) and (½,½,½) by the two observed orientations of the sulfate groups where conditions are far from equilibrium. Thus, such factors as growth velocity from the melt or from metamorphic pore fluids and pH of those fluids, which control the concentrations of CO_3 and HCO_3, SO_4 and HSO_4, Cl and molecular HCl (Donnay *et al.* 1978), will determine the intensities of the "forbidden" reflections and, in the limiting case where the intensities become too weak to be observed, will determine the reported space group. The oxygen atoms of the sulfate groups can contribute more intensity to the "sum-odd" reflections than those of the carbonate groups, because their coordinates differ more from one another. In general, crystals grown close to equilibrium conditions will tend towards the more symmetrical space group.

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