

Rosenhahnite, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$: crystal structure and the stereochemical configuration of the hydroxylated trisilicate group, $[\text{Si}_3\text{O}_8(\text{OH})_2]$

CHE'NG WAN, SUBRATA GHOSE

Department of Geological Sciences
University of Washington
Seattle, Washington 98195

AND G. V. GIBBS

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

Rosenhahnite, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$, is triclinic, with cell dimensions $a = 6.955(2)$, $b = 9.484(2)$, $c = 6.812(2)\text{\AA}$, $\alpha = 108.64(2)^\circ$, $\beta = 94.84(2)^\circ$, $\gamma = 95.89(2)^\circ$; space group PT , $Z = 2$. The crystal structure has been determined by the symbolic addition method and refined by the method of least-squares using anisotropic temperature factors for all atoms except hydrogens, for which isotropic temperature factors were used. The R factor is 0.035 for 3071 reflections measured on an automatic single-crystal diffractometer. The estimated standard deviation of Ca-O and Si-O bond lengths is 0.002\AA.

The crystal structure of rosenhahnite consists of $\text{Ca}(1)\text{O}_7$, $\text{Ca}(2)\text{O}_6$, and $\text{Ca}(3)\text{O}_7$ polyhedra and insular $[\text{Si}_3\text{O}_8(\text{OH})_2]$ groups. The trisilicate group with point symmetry 1 consists of a central SiO_4 tetrahedron sharing corners with two adjacent $\text{SiO}_3(\text{OH})$ tetrahedra. The Si-OH(nbr) bonds (av. 1.662\AA) are significantly longer than the Si-O(nbr) bonds (av. 1.603\AA); the Si-O(br) bonds average 1.656\AA. The two Si-O-Si angles are 146.1 and 128.0°. One hydrogen atom bonds the trisilicate groups in linear chains, and the other links adjacent trisilicate groups across symmetry centers into a three-dimensional array. The lack of symmetry in the trisilicate group, along with significant differences in the dimensions of the three silicate tetrahedra, is attributed to electrostatic interactions between the nonbridging oxygen atoms and Ca^{2+} ions, which are asymmetrically distributed around the trisilicate group. The bond length variations in the group are rationalized using a semi-empirical molecular orbital theory.

Introduction

The hydrous calcium silicate mineral rosenhahnite was first described by Pabst *et al.* (1967) from Mendocino County, California, where it forms narrow buff- to white-colored veins in brecciated fine-grained metagreywackes. In these veins, rosenhahnite occurs in association with pectolite, xonotlite, and datolite. Dunn (1975) has described rosenhahnite from Durham, Wake County, North Carolina, where it occurs in association with prehnite, gyrolite, okenite, and apophyllite.

Pabst *et al.* (1967) proposed the chemical formula of rosenhahnite as $(\text{CaSiO}_3)_3 \cdot \text{H}_2\text{O}$. They showed that

the complete dehydration of rosenhahnite crystals at 420°-540°C results in single crystals of β - CaSiO_3 (wollastonite), which maintain a perfect topotactic relation to the parent rosenhahnite. To clarify the structural basis for this topotactic thermal reaction, the structure determination of rosenhahnite was undertaken by us a few years ago. While this study was in progress, Jeffrey and Lindley (1973) published a short note indicating that the structure of rosenhahnite contains $\text{Si}_3\text{O}_8(\text{OH})_2$ groups and the chemical formula should be written as $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$. They further showed that the trisilicate groups are arranged as hydrogen-bonded linear chains in the struc-

ture, and the dehydration involves joining of these trisilicate groups in chains by splitting out water molecules. They did not publish atomic coordinates for rosenhahnite, nor the exact dimensions of the trisilicate group.

Because the hydroxylated trisilicate group $\text{Si}_3\text{O}_8(\text{OH})_2$ is relatively rare in silicates, and its exact configuration is of interest from the point of view of chemical bonding, we decided to complete our study and publish our results independently (Wan and Ghose, 1975).

Crystal data

The unit-cell dimensions of a small cleavage fragment of rosenhahnite from Mendocino County, California, were determined by least-squares refinement using 15 reflections with 2θ values between 35 and 45° measured with $\text{MoK}\alpha$ radiation on a single-crystal automatic diffractometer (Table 1). Pabst *et al.* (1967) could not distinguish between two possible triclinic space groups, $P1$ and $P\bar{1}$, from crystal morphology. The $N(z)$ test of the measured intensities indicated $P\bar{1}$ as the most probable space group, and this was subsequently confirmed through the determination and refinement of the structure.

Collection of intensity data

Intensity data on a cleavage fragment ($0.2 \times 0.2 \times 0.2$ mm) of rosenhahnite were collected by the $\theta - 2\theta$ method on a computer-controlled automatic single-crystal diffractometer (Syntex $P\bar{1}$). $\text{MoK}\alpha$ radiation

Table 1. Rosenhahnite: crystal data

Rosenhahnite, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$	
Buff-colored tabular crystals	
from Mendocino County, California	
$a = 6.955(2)\text{\AA}$	$\alpha = 108.64(2)^\circ$
$b = 9.484(2)$	$\beta = 94.84(2)$
$c = 6.812(1)$	$\gamma = 95.89(2)$
Cell volume: $420.25(14)\text{\AA}^3$	
Space group: $P\bar{1}$	
Cell content: $2[\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2]$	
D_m : 2.89 g cm^{-3}	
D_o : 2.895 g cm^{-3}	
$\mu(\text{MoK}\alpha)$: 23.32 cm^{-1}	
Crystal size: $0.2 \times 0.2 \times 0.2$ mm	

(50 kV, 12.5 mA), monochromatized by reflection from a graphite "single" crystal, and a scintillation counter were used for the data collection. All reflections within $2\theta \leq 65^\circ$ were measured. The minimum scan rate was $1^\circ/\text{min}$. A total of 3071 reflection intensities were measured, out of which 424 were below $3\hat{\sigma}(I)$, where $\hat{\sigma}(I)$ is the estimated standard deviation of the intensity I , as measured by the counting statistics. For I less than $0.7\hat{\sigma}(I)$, I was set equal to $0.7\hat{\sigma}(I)$, regardless of whether I was positive or negative. The intensities were corrected for Lorentz and polarization factors, and an approximate absorption correction was applied, assuming the crystal to be a sphere with a diameter of 0.2 mm.

Determination and refinement of the crystal structure

Since rosenhahnite is triclinic, space group $P\bar{1}$, and contains no heavy atoms, it is an ideal candidate for structure determination by direct methods. The structure has been determined by the symbolic addition method (Karle and Karle, 1966). E values were calculated for all reflections. The following three reflections with large E -values were assigned signs, so as to define the origin:

h	k	l	sign
0	3	0	+
9	-2	2	+
1	-8	-5	-

In addition, the following three reflections with large E -values were assigned symbols:

h	k	l	symbol
0	0	2	e
7	-4	6	f
4	3	-1	g

In addition to these six reflections, phases of 255 additional reflections were defined in terms of signs and symbols, from which eight E -maps were calculated. One E -map showed the correct structure, which yielded the positions of 3 Ca, 3 Si and 8 O positions. For this E -map, out of a total of 261 reflections used, signs of 131 were "+" and 130 "-." The three symbols e , f , g turned out to be -, -, and + respectively.

A difference Fourier map, calculated following a structure-factor calculation, yielded the positions of two missing oxygen and one of two hydrogen (H2) atoms. The position of the second hydrogen was

found from a subsequent difference Fourier map. At this stage, the *R* factor was 0.15 for 3071 reflections.

The refinement of the structure was carried out by the method of least-squares using the program RFINE (Finger, 1969). Atomic scattering factors for Ca, Si, O, and H were taken from Cromer and Mann (1968). Anomalous dispersion corrections were made according to Cromer and Liberman (1970). The observed structure factors (F_o 's) were weighted by $1/\hat{\sigma}^2(F_o)$, where $\hat{\sigma}(F_o)$ is the estimated standard deviation of F_o , as derived from counting statistics. Three cycles of refinement using isotropic temperature factors, followed by three more cycles using anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen, reduced the *R* factor to 0.035 for 3071 reflections. At this stage the average parameter shift/error was 0.01, the maximum being 0.04.

The atomic parameters are listed in Table 2. The estimated standard deviations in parameters of thermal ellipsoids, as well as in bond lengths and angles, have been calculated using the program ERROR (Finger, 1972, private communication). The thermal ellipsoids are listed in Table 3 and bond lengths and angles in Table 4. The average estimated standard deviation in Ca–O and Si–O bond lengths is 0.002Å and in O–Ca–O and O–Si–O angles 0.06 and 0.09°,

respectively. A list of observed and calculated structure factors is shown in Table 5.¹

Description of the structure

The crystal structure of rosenhahnite consists of hydroxylated trisilicate groups, $\text{Si}_3\text{O}_8(\text{OH})_2$, and three nonequivalent calcium polyhedra.

Stereochemistry of the $\text{Si}_3\text{O}_8(\text{OH})_2$ group

The trisilicate group consists of a silicate group sharing two of its corners with $\text{SiO}_3(\text{OH})$ groups. Although the maximal symmetry of the group is *mm2*, it is distorted and possesses point symmetry 1; the two $\text{SiO}_3(\text{OH})$ groups are quite different in terms of Si–O bond distances, and O–Si–O angles (Fig. 1).

The central $\text{Si}(2)\text{O}_4$ tetrahedron shares O(4) and O(7) with Si(1) and Si(3) tetrahedra respectively. The Si(1)–O(4)–Si(2) angle is 146.1°, whereas the Si(2)–O(7)–Si(3) angle is 128.0°. The $\text{Si}(2)\text{O}_4$ tetrahedron shows the maximum angular distortion, with the smallest O–Si–O angle being 99.8° and the largest 114.4°. The smallest O–Si–O angle involves the

¹ To obtain copy of this table, order Document AM-76-034 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit \$1.00 in advance for the microfiche.

Table 2. Rosenhahnite: atomic positional and thermal parameters (with standard deviations in parentheses). Form of anisotropic temperature factors ($\times 10^6$): $\exp \left\{ -\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right\}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B eq.*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	.27993(6)	.34503(5)	.18405(7)	0.669(7)	288(7)	207(4)	433(9)	16(4)	5(6)	53(5)
Ca(2)	.09599(6)	.68010(5)	.24285(7)	0.643(7)	272(7)	203(4)	388(9)	22(4)	2(6)	21(5)
Ca(2)	.84648(6)	.00858(5)	.26704(7)	0.698(7)	319(7)	236(5)	350(9)	23(5)	-55(6)	16(5)
Si(1)	.30412(8)	.04876(7)	.27718(9)	0.494(9)	187(10)	171(6)	282(12)	-11(6)	9(8)	14(7)
Si(2)	.62432(8)	.66151(7)	.32901(9)	0.482(9)	173(10)	175(6)	261(12)	-8(6)	-6(8)	4(7)
Si(3)	.80203(8)	.37614(7)	.27028(9)	0.506(9)	197(10)	185(6)	286(12)	10(6)	0(8)	31(7)
O(1)	.1928(2)	.0874(2)	.0902(3)	0.83(2)	493(29)	265(17)	357(33)	-14(18)	-119(24)	71(20)
O(2)	.5003(2)	.9696(2)	.2131(3)	0.99(3)	323(29)	298(19)	611(37)	66(18)	49(25)	-107(22)
O(3)	.1594(2)	.9480(2)	.3668(3)	0.75(2)	334(28)	226(17)	505(34)	-45(17)	34(24)	103(19)
O(4)	.3938(2)	.2132(2)	.4471(3)	0.80(2)	391(29)	211(17)	414(33)	-37(17)	56(24)	-74(19)
O(5)	.7694(2)	.7254(2)	.1969(3)	0.68(2)	287(27)	276(17)	401(32)	18(17)	67(23)	127(19)
O(6)	.4085(2)	.5931(2)	.2071(2)	0.67(2)	264(27)	227(16)	360(32)	-52(17)	-48(23)	15(19)
O(7)	.7211(2)	.5330(2)	.4128(2)	0.71(2)	406(28)	224(17)	355(32)	85(17)	14(24)	38(19)
O(8)	.6082(2)	.2950(2)	.0911(3)	0.82(2)	323(28)	287(18)	442(34)	-44(18)	-104(24)	42(20)
O(9)	.8560(2)	.2716(2)	.4015(3)	0.79(2)	474(30)	235(17)	438(34)	72(18)	8(24)	104(20)
O(10)	.9748(2)	.4193(2)	.1475(3)	0.73(2)	274(27)	301(18)	428(33)	11(17)	86(23)	116(20)
H(1)	.524(8)	.101(6)	-.122(8)	3.0(1.3)						
H(2)	.602(6)	.342(4)	-.020(6)	0.8(8)						

*Equivalent isotropic temperature factor calculated from β_{ij} 's.

bridging oxygens O(4) and O(7), which comprise a shared edge with the coordination polyhedron about Ca(1). Of the two bridging bonds, Si(2)–O(7) (1.677Å) is much larger than the Si(2)–O(4) bond (1.631Å). The Si–O(br) bonds are significantly longer than the two Si–O (nbr) bonds, which average 1.610Å.

Table 3. Rosenhahnite: thermal ellipsoids (with standard deviations in parentheses)

Atom	Axis r_z	rms amplitude (Å)	Angle (°) with respect to		
			+a	+b	+c
Ca(1)	1	0.081	158(7)	73(4)	72(4)
	2	0.090	120(7)	125(6)	108(3)
	3	0.104	84(3)	134(5)	27(5)
Ca(2)	1	0.077	142(11)	69(4)	61(6)
	2	0.085	51(11)	64(6)	71(4)
	3	0.106	85(2)	143(4)	35(4)
Ca(3)	1	0.073	128(4)	77(2)	44(2)
	2	0.094	47(4)	63(3)	76(3)
	3	0.111	105(3)	33(3)	137(4)
Si(1)	1	0.063	154(10)	69(6)	72(6)
	2	0.075	121(8)	105(4)	127(7)
	3	0.096	80(3)	27(4)	132(4)
Si(2)	1	0.060	150(9)	72(4)	65(6)
	2	0.074	125(8)	105(3)	124(6)
	3	0.097	84(3)	25(4)	131(4)
Si(3)	1	0.066	159(9)	81(4)	68(7)
	2	0.077	119(9)	107(4)	127(7)
	3	0.094	88(3)	22(5)	130(5)
O(1)	1	0.075	120(8)	86(6)	32(7)
	2	0.107	87(10)	170(8)	61(7)
	3	0.121	141(10)	100(9)	113(9)
O(2)	1	0.079	59(21)	61(11)	66(8)
	2	0.090	23(26)	107(13)	110(15)
	3	0.152	88(2)	143(5)	34(5)
O(3)	1	0.078	146(12)	50(12)	98(8)
	2	0.103	99(24)	88(25)	157(13)
	3	0.108	126(36)	137(36)	77(29)
O(4)	1	0.069	100(7)	52(5)	56(5)
	2	0.095	30(8)	93(6)	67(8)
	3	0.129	108(5)	143(7)	43(6)
O(5)	1	0.080	148(18)	78(9)	117(18)
	2	0.091	66(22)	77(12)	160(22)
	3	0.106	78(8)	26(10)	91(9)
O(6)	1	0.064	141(11)	66(7)	63(6)
	2	0.096	127(15)	95(11)	129(14)
	3	0.111	74(10)	26(12)	123(9)
O(7)	1	0.082	81(17)	64(17)	49(11)
	2	0.090	40(28)	58(26)	116(24)
	3	0.110	127(15)	44(12)	126(10)
O(8)	1	0.070	143(8)	74(5)	57(6)
	2	0.111	128(24)	99(19)	126(24)
	3	0.118	82(18)	20(23)	124(17)
O(9)	1	0.092	119(53)	130(58)	40(67)
	2	0.096	96(31)	132(51)	117(42)
	3	0.111	148(13)	71(12)	117(13)
O(10)	1	0.077	151(10)	81(5)	114(10)
	2	0.096	72(13)	89(10)	159(11)
	3	0.112	76(7)	21(8)	103(9)

The Si(1)O₃(OH) tetrahedron has two short Si–O(nbr) bonds averaging 1.601Å and two long bonds, one of which is a Si–O(br) bond, Si(1)–O(4), 1.639Å, and the other is a Si–OH(nbr) bond, 1.648Å. The O(2)–H(1) distance is 0.74 ($\hat{\sigma}$ = 0.05)Å, and the Si(1)–O(2)–H(1) angle is 111 ($\hat{\sigma}$ = 4)°.

The terminal Si(3)O₃OH group is slightly larger than the Si(1)O₃(OH) group, the average Si–O distances being 1.637 and 1.622Å respectively. Again, the two Si–O(nbr) bonds (av. 1.598Å) are much shorter than the other two Si–O bonds, one of which is a Si–O(br) bond 1.677Å, and the other is a Si–OH(nbr) bond 1.676Å. These two long Si–O bonds within the Si(3)O₃OH group are significantly longer (by 0.03Å) than their counterparts within the Si(1)O₃OH group. In each case, however, the Si–OH(nbr) bond is significantly longer than the Si–O(nbr) bonds. The angular distortion within the Si(3)O₃OH group is slightly larger than that within the Si(1)O₃OH group; in the former case, the O–Si–O angles range from 101.0 to 114.1°, and in the latter from 104.2 to 114.1°. The O(8)–H(2) distance is 0.99Å ($\hat{\sigma}$ = 0.04Å), and the Si(3)–O(8)–H(2) angle is 111 ($\hat{\sigma}$ = 2)°, which is close to the ideal tetrahedral angle.

Hydrogen bonding

The trisilicate groups are hydrogen bonded in linear chains through O(2)–H(1)···O(8) bonds [O(2)–O(8) 2.681Å] (Fig. 2). The hydrogen bond is nearly linear, the O(2)–H(1)···O(8) angle being 172($\hat{\sigma}$ = 6)°. The hydrogen-bonded linear silicate chains are cross-linked by nearly linear O(8)–H(2)···O(6) bonds [O(8)–O(6) 2.575Å and O(8)–H(2)···O(6) angle 176($\hat{\sigma}$ = 4)°] (Fig. 2). The hydrogen bond involving H(2) is much stronger than that involving H(1). This is consistent with the fact that the temperature factor for H(2) is much smaller than that for H(1) (Table 2).

Calcium polyhedra

The Ca(1) atom is seven-coordinated, the Ca–O bonds ranging from 2.319Å to 2.618Å, with an average Ca–O distance of 2.453Å. If the long Ca(1)–O(4) bond is neglected, the Ca(1)O₆ polyhedron can be considered as a distorted octahedron with octahedral O–Ca–O angles ranging from 77.9° to 112.3° (Fig. 3). The Ca(2)O₆ polyhedron is a distorted octahedron (Fig. 3); the Ca–O bonds range from 2.305Å to 2.507Å, with an average of 2.394Å. The octahedral O–Ca–O angles range from 73.0° to 110.9°. The Ca(3) atom is seven-coordinated, the Ca–O bond lengths ranging from 2.290Å to 2.917Å, with an aver-

Table 4. Rosenhahnite: interatomic distances (Å) and angles (°) (with standard deviations in parentheses)

<i>Ca(1) - Polyhedron</i>				<i>Si(1) - Tetrahedron</i>			
Ca(1) - O(1)	2.319(2)	O(1) - Ca(1) - O(4)	62.11(5)	Si(1) - O(1)	1.596(2)	O(1) - Si(1) - O(2)	112.89(10)
- O(4)	2.608(2)	O(1) - Ca(1) - O(5)	79.26(6)	- O(2)	1.648(2)	O(1) - Si(1) - O(3)	110.93(9)
- O(5)	2.448(2)	O(1) - Ca(1) - O(6)	166.15(6)	- O(3)	1.606(2)	O(1) - Si(1) - O(4)	104.24(9)
- O(6)	2.381(2)	O(1) - Ca(1) - O(7)	109.11(6)	- O(4)	1.639(2)	O(2) - Si(1) - O(3)	111.30(9)
- O(7)	2.618(2)	O(1) - Ca(1) - O(8)	87.8(6)	Mean	1.622	O(2) - Si(1) - O(4)	103.05(9)
- O(8)	2.472(2)	O(1) - Ca(1) - O(10)	100.07(6)	O(1) - O(2)	2.704(2)	O(3) - Si(1) - O(4)	114.06(9)
- O(10)	2.322(2)	O(4) - Ca(1) - O(5)	134.90(5)	O(1) - O(3)	2.637(2)	Mean	109.41
Mean	2.453	O(4) - Ca(1) - O(6)	123.87(5)	O(1) - O(4)	2.553(2)		
O(1) - O(8)	3.323(2)	O(4) - Ca(1) - O(7)	57.91(5)	O(2) - O(3)	2.687(2)		
O(8) - O(6)	3.179(2)	O(4) - Ca(1) - O(8)	78.25(5)	O(2) - O(4)	2.573(2)		
O(8) - O(10)	2.639(2)	O(4) - Ca(1) - O(10)	125.35(6)	O(3) - O(4)	2.722(2)		
O(10) - O(4)	4.381(2)	O(5) - Ca(1) - O(6)	89.57(6)	Mean	2.646		
O(4) - O(1)	2.553(2)	O(5) - Ca(1) - O(7)	166.53(5)				
O(5) - O(1)	3.042(2)	O(5) - Ca(1) - O(8)	77.89(5)				
O(5) - O(8)	3.093(2)	O(5) - Ca(1) - O(10)	81.47(6)				
O(5) - O(6)	3.402(2)	O(6) - Ca(1) - O(7)	83.44(5)				
O(5) - O(10)	3.114(2)	O(6) - Ca(1) - O(8)	81.83(6)	Si(2) - O(4)	1.631(2)	O(4) - Si(2) - O(5)	112.18(9)
O(5) - O(4)	2.684(2)	O(6) - Ca(1) - O(10)	86.20(6)	- O(5)	1.604(2)	O(4) - Si(2) - O(6)	109.01(9)
O(7) - O(1)	4.026(2)	O(7) - Ca(1) - O(8)	112.28(5)	- O(6)	1.615(2)	O(4) - Si(2) - O(7)	99.78(9)
O(7) - O(8)	4.228(2)	O(7) - Ca(1) - O(10)	86.57(5)	- O(7)	1.677(2)	O(5) - Si(2) - O(6)	114.38(9)
O(7) - O(6)	2.696(2)	O(8) - Ca(1) - O(10)	156.14(6)	Mean	1.632	O(5) - Si(2) - O(7)	110.62(9)
O(7) - O(10)	2.688(2)			O(4) - O(5)	2.684(2)	O(6) - Si(2) - O(7)	109.89(9)
O(7) - O(4)	2.530(2)			O(4) - O(6)	2.643(2)	Mean	109.31
O(10) - O(1)	3.557(2)			O(4) - O(7)	2.530(2)		
				O(5) - O(6)	2.706(2)		
				O(5) - O(7)	2.698(2)		
				O(6) - O(7)	2.696(2)		
				Mean	2.660		
<i>Ca(2) - Octahedron</i>				<i>Si(2) - Tetrahedron</i>			
Ca(2) - O(3)	2.388(2)	O(3) - Ca(2) - O(5)	82.77(6)	Si(2) - O(4)	1.631(2)	O(4) - Si(2) - O(5)	112.18(9)
- O(5)	2.368(2)	O(3) - Ca(2) - O(6)	106.16(6)	- O(5)	1.604(2)	O(4) - Si(2) - O(6)	109.01(9)
- O(6)	2.407(2)	O(3) - Ca(2) - O(9)	79.06(6)	- O(6)	1.615(2)	O(4) - Si(2) - O(7)	99.78(9)
- O(9)	2.305(2)	O(3) - Ca(2) - O(10)	168.87(6)	- O(7)	1.677(2)	O(5) - Si(2) - O(6)	114.38(9)
- O(10)	2.388(2)	O(3) - Ca(2) - O(10')	110.94(6)	Mean	1.632	O(5) - Si(2) - O(7)	110.62(9)
- O(10')	2.507(2)	O(5) - Ca(2) - O(6)	166.47(6)	O(4) - O(5)	2.684(2)	O(6) - Si(2) - O(7)	109.89(9)
Mean	2.394	O(5) - Ca(2) - O(9)	100.99(6)	O(4) - O(6)	2.643(2)	Mean	109.31
O(3) - O(5)	3.144(2)	O(5) - Ca(2) - O(10)	87.87(6)	O(4) - O(7)	2.530(2)		
O(5) - O(10)	3.300(2)	O(5) - Ca(2) - O(10')	79.37(5)	O(5) - O(6)	2.706(2)		
O(10) - O(6)	3.213(2)	O(6) - Ca(2) - O(9)	90.83(6)	O(5) - O(7)	2.698(2)		
O(6) - O(3)	3.833(2)	O(6) - Ca(2) - O(10)	84.15(5)	Mean	2.668		
O(10') - O(3)	4.033(2)	O(6) - Ca(2) - O(10')	87.84(5)				
O(10') - O(5)	3.114(2)	O(9) - Ca(2) - O(10)	96.92(6)				
O(10') - O(10)	2.912(2)	O(9) - Ca(2) - O(10')	169.88(6)				
O(10') - O(6)	3.409(2)	O(10) - Ca(2) - O(10')	79.197(6)				
O(9) - O(3)	2.988(2)						
O(9) - O(5)	3.606(2)						
O(9) - O(10)	2.682(2)						
O(9) - O(6)	3.357(2)						
<i>Ca(3) - Polyhedron</i>				<i>Si(3) - Tetrahedron</i>			
Ca(3) - O(1')	2.290(2)	O(1) - Ca(3) - O(1')	67.68(6)	Si(3) - O(7)	1.677(2)	O(7) - Si(3) - O(8)	101.02(8)
- O(1)	2.917(2)	O(1) - Ca(3) - O(9)	82.80(5)	- O(8)	1.676(2)	O(7) - Si(3) - O(9)	113.02(9)
- O(2)	2.377(2)	O(1) - Ca(3) - O(2)	143.62(6)	- O(9)	1.584(2)	O(7) - Si(3) - O(10)	109.61(9)
- O(3')	2.399(2)	O(1) - Ca(3) - O(5)	112.79(5)	- O(10)	1.612(2)	O(8) - Si(3) - O(9)	111.40(9)
- O(3)	2.405(2)	O(1) - Ca(3) - O(3)	58.48(3)	Mean	1.637	O(8) - Si(3) - O(10)	106.77(9)
- O(5)	2.563(2)	O(1) - Ca(3) - O(9)	114.05(6)	O(7) - O(8)	2.587(2)	O(9) - Si(3) - O(10)	114.08(9)
- O(9)	2.358(2)	O(1) - Ca(3) - O(2)	82.03(6)	O(7) - O(9)	2.720(2)	Mean	109.32
Mean	2.473	O(2) - Ca(3) - O(5)	77.41(6)	O(7) - O(10)	2.688(2)		
O(1) - O(1')	2.946(3)	O(2) - Ca(3) - O(9)	155.55(6)	O(8) - O(9)	2.694(2)		
O(1) - O(9)	3.513(2)	O(3) - Ca(3) - O(9)	108.12(6)	O(8) - O(10)	2.639(2)		
O(1) - O(2)	3.063(2)	O(3) - Ca(3) - O(2)	92.15(6)	O(9) - O(10)	2.682(2)		
O(1) - O(5)	3.042(2)	O(3') - Ca(3) - O(1')	103.91(6)	Mean	2.668		
O(1) - O(3)	2.637(2)	O(3') - Ca(3) - O(2)	165.93(6)				
O(1') - O(9)	3.900(2)	O(3') - Ca(3) - O(9)	77.80(6)				
O(9) - O(2)	3.410(2)	O(3') - Ca(3) - O(5)	78.46(5)				
O(2) - O(5)	3.105(2)	O(3') - Ca(3) - O(2)	90.22(6)				
O(5) - O(3)	3.144(2)	O(3') - Ca(3) - O(9)	89.51(5)				
O(3) - O(11)	2.637(2)	O(3') - Ca(3) - O(3)	78.11(6)				
O(3) - O(1')	3.698(2)	O(3') - Ca(3) - O(1)	123.30(5)				
O(3') - O(1')	2.637(2)						
O(3') - O(9)	2.988(2)						
O(3') - O(2)	2.687(2)						
O(3') - O(5)	3.496(2)						
O(3') - O(3)	3.027(3)						
				<i>Hydrogen Bonds</i>			
				H(1) - O(2)	0.74(5)	O(2) - H(1)...O(8)	172(6)
				H(1) - O(8)	1.94(5)		
				[O(2) - O(8)]	2.681(2)		
				H(2) - O(8)	0.99(4)	O(8) - H(2)...O(6)	176(4)
				H(2) - O(6)	1.58(4)		
				[O(8) - O(6)]	2.575(2)		
				H(1) - H(2)	2.16(6)		
				<i>Cation-Cation Distances <3.5Å</i>			
				Si(1) - Si(2)	3.1268(8)	Si(1) - Si(2) - Si(3)	127.17(2)
				Si(2) - Si(3)	3.0150(8)	Si(1) - O(4) - Si(2)	146.06(11)
				Ca(1) - Ca(2)	3.4644(6)	Si(2) - O(7) - Si(3)	128.02(10)
				Ca(1) - Si(1)	3.0895(8)		
				- Si(2)	3.4572(7)		
				- Si(2')	3.3494(8)		
				- Si(3)	3.4496(7)		
				Ca(2) - Si(2)	3.3778(7)		
				- Si(3)	3.4241(7)		
				Ca(3) - Si(1)	3.1588(7)		

age of 2.473Å. If the long Ca(3)-O(1) bond (2.917Å) is neglected, the Ca(3)O₆ polyhedron can also be described as a distorted octahedron. The Ca(3)O₇ polyhedron is then a distorted octahedron with an additional oxygen atom O(1) occurring above the octahedral face, O(1)-O(9)-O(3).

The three-dimensional framework

The Ca(2)O₆ octahedron shares two opposite edges O(6)-O(10) and O(3)-O(5), with two adjacent

Ca(1)O₇ and Ca(3)O₇ polyhedra, respectively, to form a linear polyhedral trimer (Fig. 3). Two such trimers are joined together into a hexamer by sharing additional polyhedral edges; thus Ca(1)O₇ and Ca(2)O₆ polyhedra belonging to one trimer share two O(5)-O(10) edges with the Ca(2')O₆ and Ca(1')O₇ polyhedra respectively, which belong to the other trimer (Fig. 3).

Such polyhedral hexamers are parallel to [110]. These hexamers are cross-linked by Ca(3)O₇ poly-

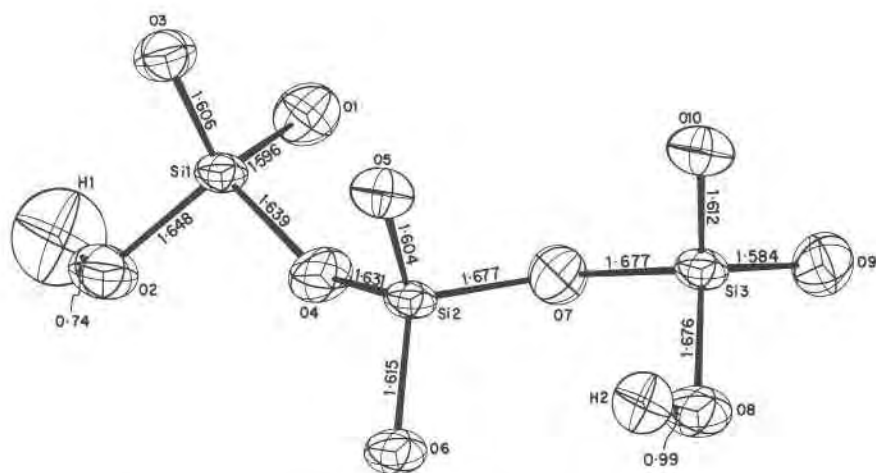


Fig. 1. The hydroxylated trisilicate group, $\text{Si}_3\text{O}_8(\text{OH})_2$ in rosenhahnite. The silicon and oxygen atoms are represented by thermal ellipsoids, and the hydrogen atoms by spheres.

hedra sharing two O(1)–O(1') edges on either side along the c direction (Fig. 3). The hexamers are cross-linked further by the $\text{Si}_3\text{O}_8(\text{OH})_2$ groups. The Si(3) O_3OH tetrahedron shares corners O(7) and O(9) with Ca(1)- and Ca(2)-polyhedra belonging to the hexamer above and the O(10) corner, which is common between Ca(1)- and Ca(2)-polyhedra below (Fig. 4). The Si(2) O_4 tetrahedron shares the tetrahedral edge O(4)–O(7) with Ca(1)-polyhedron above and O(5), a corner common between Ca(1)- and Ca(2)-polyhedra below. The Si(1)– O_3OH tetrahedron shares the tetrahedral edge O(4)–O(1) with

Ca(1)-polyhedron and edge O(1)–O(3) with Ca(3)-polyhedron. A stereoscopic view of the three-dimensional framework structure is shown in Figure 5.

Discussion

The trisilicate group, Si_3O_{10} , has been found in a number of synthetic and naturally-occurring silicates. Trisilicate groups with point symmetry m occur in ardenite, a manganese silicate (Donnay and Allmann, 1968), in kinoite, a copper-calcium silicate (Laughon, 1971), and in $\text{K}_3\text{YSi}_3\text{O}_8(\text{OH})_2$ (Maksimov *et al.*, 1968). T_3O_{10} groups with point symmetry m ,

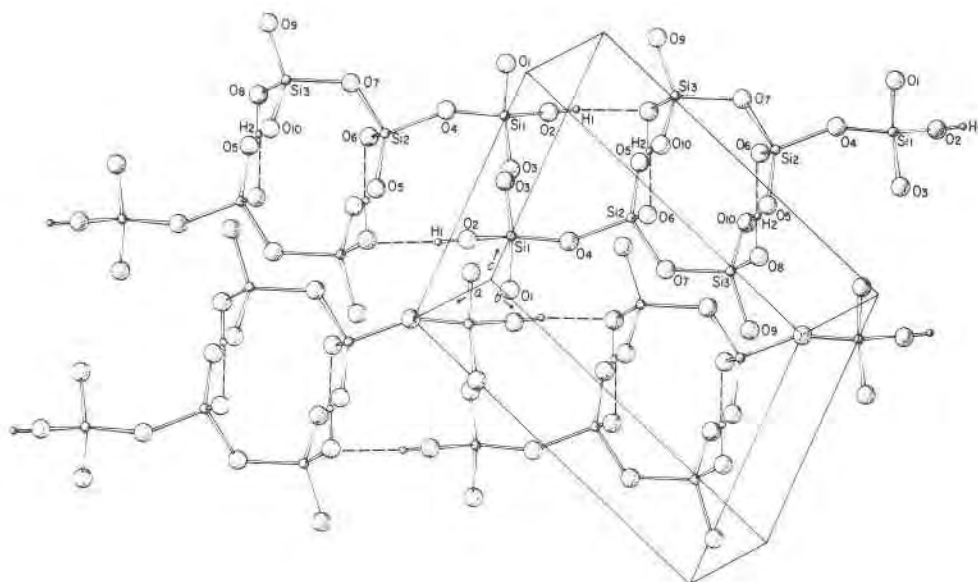


Fig. 2. A partial view of the structure, showing the trisilicate groups hydrogen bonded through H(1) into linear chains; the hydrogen atom H(2) bonds two adjacent trisilicate groups across a symmetry center into dimers.

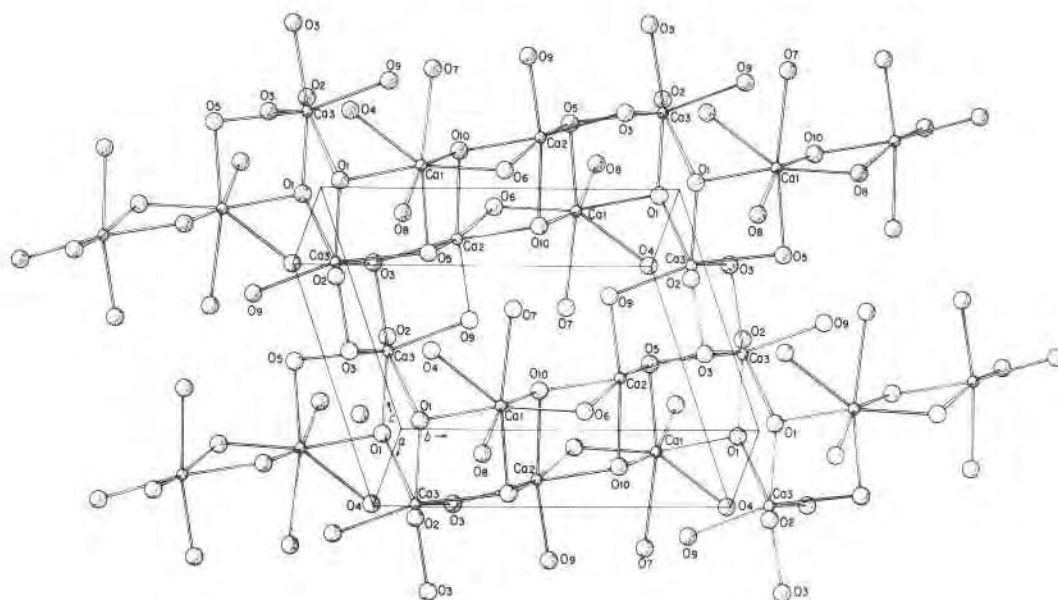


Fig. 3. A partial view of the structure, showing the calcium polyhedra.

consisting of a central SiO_4 tetrahedron sharing corners with two terminal $(\text{Si,Al})\text{O}_4$ tetrahedra, occur in kornerupine, a Mg,Al silicate (Moore and Bennett, 1968). On the other hand, Si_3O_{10} groups with point symmetry 2 have been found in $\text{Na}_4\text{Cd}_2(\text{Si}_3\text{O}_{10})$ (Simonov *et al.*, 1968) and in $\text{Na}_2\text{Ca}_3(\text{Si}_3\text{O}_{10})$ (Treuschnikov *et al.*, 1971). A Si_3O_{10} group with $mm2$ point symmetry has not to our knowledge been reported.

In thalenite, $\text{Y}_3(\text{Si}_3\text{O}_{10})(\text{OH})$ (Kornev *et al.*, 1972), the trisilicate group exhibits point symmetry 1 as in rosenhahnite. The electronegativity difference between the bonded atoms indicates that the bonding within the trisilicate group in rosenhahnite is considerably more covalent than that between the oxygen atoms of the group and the Ca ions. A similar situation probably obtains in thalenite. In both structures, the non-tetrahedral cations are asymmetrically distributed around the trisilicate ion. As a result, the ion is distorted from ideal $mm2$ conformation to satisfy the packing and bonding requirements of both the non-tetrahedral cations and the trisilicate ion. This distortion affects both the Si-O bond lengths and O-Si-O and Si-O-Si valence angles.

Molecular orbital theory predicts that the distortions in the valence angles should have an important effect on the electronic structure of the ion, *i.e.*, the wave-functions of the molecular orbitals characterizing the bonds involved in the wider valence angles should be stabilized relative to those involved in the narrower angles (Louisnathan and Gibbs, 1972). In

other words, the theory predicts larger Si-O bond overlap populations, $n(\text{Si-O})$, for the bonds involved in the wider valence angles. If we consider $n(\text{Si-O})$ as a crude measure of the electron density in the Si-O bond, then we may expect the shorter bonds to involve the wider angles. The Si-O bond lengths recorded for the trisilicate group in rosenhahnite con-

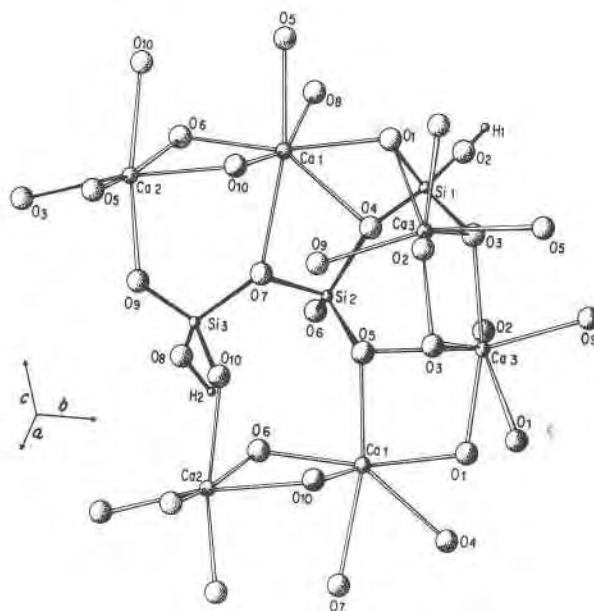


Fig. 4. A fragment of the structure, showing the bonding of the trisilicate group with the calcium polyhedra.

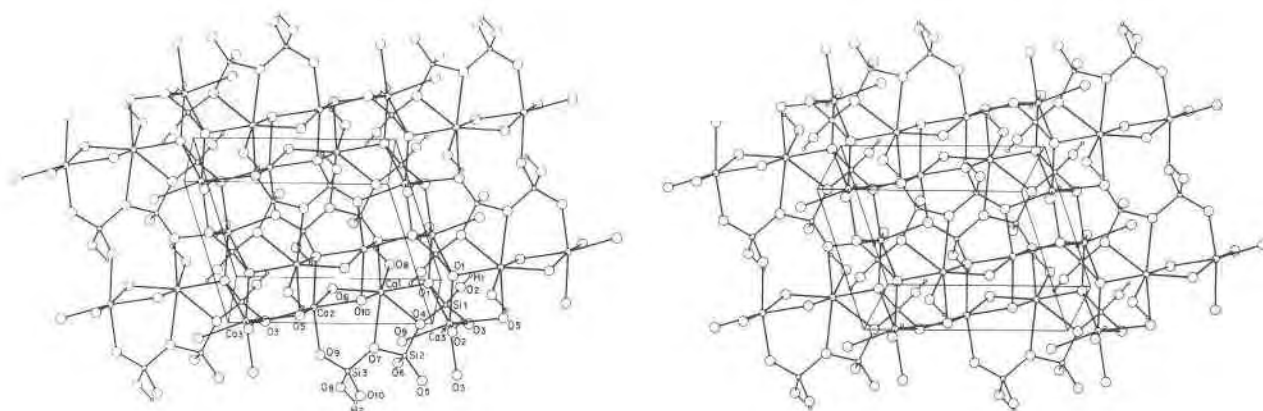


Fig. 5. A stereoscopic view of the three-dimensional framework, consisting of calcium polyhedra and hydroxylated trisilicate groups.

form with this prediction, as shown by Figure 6, where the shorter bonds are seen to involve the wider O-Si-O angles. We also observe that the two bonds involved in the wider Si(1)-O(4)-Si(2) angle (146.06°) are also significantly shorter (1.639, 1.631 Å) than those (1.677 Å) involved in the narrower Si(2)-O(7)-Si(3) angle (127.07°). To gain additional insight into the connection between the valence angles and bond lengths in the trisilicate group, extended Hückel molecular orbital (EHMO) calculations were completed for a $[\text{Si}_3\text{O}_{10}]^{6-}$ ion with all the Si-O bond lengths clamped at 1.63 Å and with the O-Si-O and Si-O-Si angles fixed as observed for

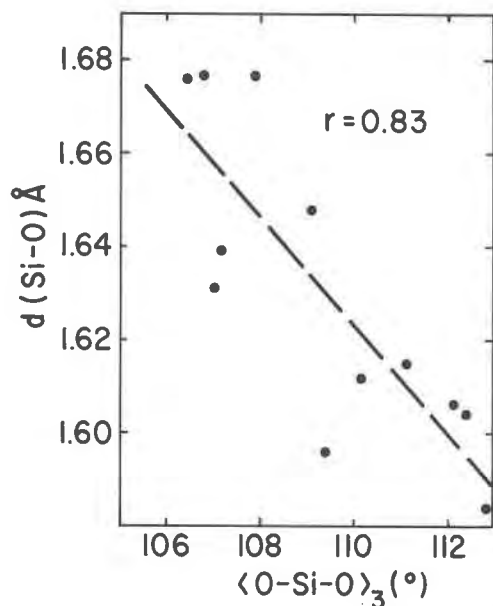


Fig. 6. Scatter diagram of the observed Si-O bond lengths, $d(\text{Si-O})$, plotted against $\langle \text{O-Si-O} \rangle_3$, the average of the three O-Si-O angles common to each bond.

rosenhahnite. Figure 7 shows that the resulting $n(\text{Si-O})$ values correlate with the observed Si-O bond lengths, shorter bonds tending to involve larger bond overlap populations. When calculations are made with the constraints that all Si-O bond lengths equal 1.63 Å, all the O-Si-O angles equal 109.47° , and both Si-O-Si angles equal 180° , the resulting $n(\text{Si-O})$ values predict that all the Si-O bond lengths should be nearly equal in length. Hence, by using the observed angles in the calculation, we believe that the resulting $n(\text{Si-O})$ values include some of the extrinsic effects of the non-tetrahedral Ca ions, which distort the ion by altering its valence angles. Studies by Smith (1953) and Baur (1961, 1970) show that the Si-O bond length variations in the tetrahedral portion of a silicate correlate with the bond strength sum to oxygen. In fact, the strong correlation found for the pyrosilicates led Baur (1971) to conclude that "it is not permissible to neglect the influence of the non-tetrahedral cations on the silicon-oxygen bond length." However, the results obtained for rosenhahnite and other silicates (Gibbs *et al.*, 1972, 1974) suggest as a first approximation that the non-tetrahedral cations may be neglected, provided the observed valence angles of the silicate are incorporated into the calculation.

As mentioned earlier, the Si-OH(nbr) bonds in the trisilicate group are ~ 0.03 Å longer than the Si-O(nbr) bonds. An EHMO calculation completed for $[\text{Si}_3\text{O}_8(\text{OH})_2]^{6-}$ gave $n(\text{Si-OH})$ values for the Si(1)-O(2)H and Si(3)-O(8)H bonds reduced by about 10 percent from the $n(\text{Si-O})$ values calculated for the Si(1)-O(2) and Si(3)-O(8) bonds in the $[\text{Si}_3\text{O}_{10}]^{6-}$ ion. Since the overlap populations for the Si-OH bond (~ 0.44) are less than those calculated for the Si-O(br) bonds (~ 0.47), theory predicts that

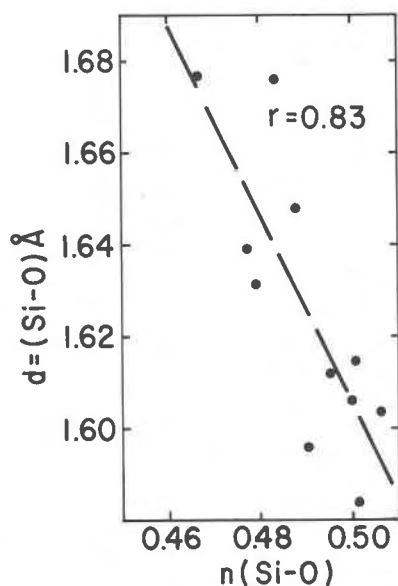


Fig. 7. Scatter diagram of the observed Si-O bond lengths, $d(\text{Si-O})$, plotted against $n(\text{Si-O})$, the Mulliken bond overlap population. The $n(\text{Si-O})$ values were calculated for a $\text{Si}_3\text{O}_8^{8-}$ ion with all bond lengths clamped at 1.63 Å, and the valence angles set at those observed for rosenhahnite.

the Si-OH bonds be longer than the Si-O(br) bonds. In rosenhahnite, the mean Si-OH bond length (1.662 Å) is slightly longer than the mean Si-O(br) bond length (1.656 Å).

Summary and conclusions

(1) The crystal structure of rosenhahnite consists of three crystallographically-independent Ca-polyhedra and a hydroxylated trisilicate group.

(2) The trisilicate group, $[\text{Si}_3\text{O}_8(\text{OH})_2]$ with point symmetry 1, consists of a central SiO_4 tetrahedron sharing corners with two terminal $\text{SiO}_3(\text{OH})$ tetrahedra. The Si-OH(nbr) bonds (av. 1.662 Å) are significantly longer than the Si-O(nbr) bonds (av. 1.603 Å); the Si-O(br) bonds average 1.656 Å. The two Si-O-Si angles are 146.1 and 128.0°.

(3) Lack of symmetry in the trisilicate group and differences in the dimensions of the three silicate tetrahedra are the result of bonding of the terminal oxygen atoms with asymmetrically distributed calcium atoms around the trisilicate group.

(4) The Si-O bond length variations within the $[\text{Si}_3\text{O}_8(\text{OH})_2]$ group may be rationalized in terms of a Mulliken population analysis calculated for a $[\text{Si}_3\text{O}_{10}]^{8-}$ ion with all the Si-O bond lengths clamped at 1.63 Å and the angles set at those observed for the group in rosenhahnite.

Acknowledgments

We are greatly indebted to Professor A. Pabst, University of California, Berkeley, and Mr. Leo Rosenhahn, San Anselmo, California, for the donation of the rosenhahnite crystals which made this research possible.

References

- Baur, W. H. (1961) Distorted coordination polyhedra in heteropolar crystal structures and the electrostatic valence rule of Pauling. *Naturwiss.*, 48, 549.
- (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Am. Crystallogr. Assoc.*, 6, 125-155.
- (1971) The prediction of bond length variations in silicon-oxygen bonds. *Am. Mineral.*, 56, 1573-1599.
- Cromer, D. T. and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave function. *Acta Crystallogr.*, A24, 321-324.
- and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for x-rays. *J. Chem. Phys.*, 53, 1891-1898.
- Donnay, G. and R. Allmann (1968) Si_3O_{10} groups in the crystal structure of ardenite. *Acta Crystallogr.*, B24, 845-855.
- Dunn, P. J. (1975) Rosenhahnite, a second occurrence with the zeolites of the Durham quarry, Durham, Wake County, North Carolina. *Mineral. Rec.*, 6, 300-301.
- Finger, L. W. (1969) Determination of cation distributions by least-squares refinement of x-ray data. *Carnegie Inst. Wash. Year Book*, 67, 216-217.
- Gibbs, G. V., M. M. Hamil, S. J. Louisnathan, L. S. Bartell and H. Yow (1972) Correlations between Si-O bond length, Si-O-Si angle and bond overlap populations calculated using extended Hückel molecular orbital theory. *Am. Mineral.*, 57, 1578-1613.
- , S. J. Louisnathan, P. H. Ribbe and M. W. Phillips (1974) Semiempirical molecular orbital calculations for the atoms of the tetrahedral framework in anorthite, low albite, maximum microcline and reedmergnerite. In W. S. MacKenzie and J. Zussman, Eds., *The Feldspars*, p. 49-67. Manchester University Press, Manchester.
- Jeffrey, J. W. and P. F. Lindley (1973) Remarkable new silicate structure. *Nature*, 241, 42-43.
- Karle, J. and I. L. Karle (1966) The symbolic addition procedure for phase determination for centrosymmetric and non-centrosymmetric crystals. *Acta Crystallogr.*, 21, 849-859.
- Kornev, A. N., N. G. Batalieva, B. A. Maksimov, V. V. Ilyukhin and N. V. Belov (1972) Crystal structure of the talenite $\text{Y}_3[\text{Si}_3\text{O}_{10}](\text{OH})$. *Sov. Phys. Doklady*, 17, 88-90.
- Laughon, R. B. (1971) The crystal structure of kinoite. *Am. Mineral.*, 56, 193-200.
- Louisnathan, S. J. and G. V. Gibbs (1972) The effect of tetrahedral angles on Si-O bond overlap populations for isolated tetrahedra. *Am. Mineral.*, 57, 1614-1642.
- Maksimov, B. A., V. V. Ilyukhin and N. V. Belov (1968) Crystal structure of K,Y-triorthosilicate $\text{K}_3\text{Y}[\text{Si}_3\text{O}_8(\text{OH})_2]$ (in Russian). *Dokl. Akad. Nauk SSSR*, 181, 591-594.
- Moore, P. B. and J. M. Bennett (1968) Kornerupine: its crystal structure. *Science*, 159, 524-526.
- Pabst, A., E. B. Gross and J. T. Alfors (1967) Rosenhahnite, a new hydrous calcium silicate, from Mendocino County, California. *Am. Mineral.*, 52, 336-351.
- Simonov, M. A., Yu. K. Egorov-Tismenko and N. V. Belov (1968)

- The new $[\text{Si}_3\text{O}_{10}]$ radical in the structure of $\text{Na}_4\text{Cd}_2[\text{Si}_3\text{O}_{10}]$. *Sov. Phys. Doklady*, 13, 293-295.
- Smith, J. V. (1953) Reexamination of the crystal structure of melilite. *Am. Mineral.*, 38, 643-661.
- Treushnikov, E. N., V. V. Ilyukhin and N. V. Belov (1971) Crystal structure of Na,Ca triorthosilicate, $\text{Na}_2\text{Ca}_3(\text{Si}_3\text{O}_{10})$. *Sov. Phys. Crystallogr.*, 16, 56-58.
- Wan, C. and S. Ghose (1975) Stereochemical configuration of the trisilicate group in rosenhahnite, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$ (abstr). *Trans. Am. Geophys. Union*, 56, 1076.

Manuscript received, February 2, 1976; accepted for publication, July 21, 1976.