Scapolite crystal chemistry: aluminum–silicon distributions, carbonate group disorder, and thermal expansion

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Abstract

Crystal structure parameters have been determined for a compositionally intermediate scapolite $(Na_{2.47}Ca_{1.33}K_{0.20})$ $(Si_{8.05}Al_{3.95})O_{24}Cl_{0.59}(CO_3)_{0.37}(SO_4)_{0.04}$ in space group $P4_2/n$ before and after a heating cycle. In addition, unit-cell parameters have been determined with room-temperature data collected before and after heating, and with data collected at 400°, 600°, 700°, 800°, 900° and 1000°C. Both a and volume increase with temperature while c remains constant. Thermal expansion of a results from rotation of four-membered rings of tetrahedra in the (001) plane. Tetrahedral bond distances suggest that this sample has a highly ordered Si–Al distribution with $T1$ and $T3$ occupied by Si^{4+} and $T2$ occupied by Al^{3+}. The irreversible change in tetrahedral bond distances after the sample was heated to 1000°C suggests a slight amount of disordering has taken place. This change also affected the unit-cell parameters. The carbonate group was refined as a rigid body with realistic bond distances and angles using the least-squares computer program RFINE4. The refinement confirms the model of Papike and Stephenson (1966) and suggests that the group tilts only slightly out of the (001) plane. Normalized primitive reflections which violate $I4/m$ symmetry decrease in intensity with temperature up to 1000°C but do not dissappear.

Introduction

Scapolites, a group of rock-forming silicates that exhibit many structural complexities, can, as a first approximation, be considered as solid solutions between marialite, $Na_4Al_3Si_9O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}CO_3$. These formulae are written in the form most consistent with the scapolite structure, but can also be written as marialite, $3NaAlSi_3O_8 \cdot NaCl$ and meionite, $3CaAl_2Si_2O_8 \cdot CaCO_3$ to show an analogy with plagioclase feldspar chemistry. Three coupled substitutions are evident in this solid solution series: $Na^{1+} \rightleftharpoons Ca^{2+}$; $Si^{4+} \rightleftharpoons Al^{3+}$; $Cl^{1-} \rightleftharpoons CO_3^{2-}$. All three substitutions are active in the more sodic part of the series [Ca/(Ca + Na) < 0.75] while in the less sodic part [Ca/(Ca + Na) > 0.75], the substitution is NaSi $\rightleftharpoons$ CaAl, the same as in the plagioclase feldspars (Evans *et al.*, 1969). At Ca/(Ca + Na) > 0.75 the anion site is filled with CO_3^{2-} (Papike, 1964; Evans *et al.*, 1969).

The first reasonably complete structure models of scapolite were reported by Pauling (1930) and Schiebold and Seumel (1932). The structure of a Na-rich scapolite was first refined by Papike and Zoltai (1965)

and that of a Ca-rich scapolite by Papike and Stephenson (1966). Lin and Burley (1973a, 1973c, 1975) reported three additional structural refinements. The space group of scapolite is a function of composition. The theoretical end-members, marialite and meionite, display diffraction symmetry consistent with space group $I4/m$, but intermediate compositions have reflections that violate this symmetry and reduce the space group to a primitive type. Papike and Stephenson (1966) reported diffuse reflections violating the body-centered symmetry but did not treat them in the structural refinement. Lin and Burley (1973a, 1973b, 1973c, 1975) state that the true space group is $P4_2/n$, and their three refinements are reported in this space group, even though they did not observe reflections violating $I4/m$ symmetry in their meionite-rich scapolite. Ulbrich (1973) also states that the space group for intermediate compositions is $P4_2/n$. Phakey and Ghose (1972) and Buseck and Iijima (1974), however, conclude from electron diffraction studies that the space group for intermediate compositions is $P4$ or $P4/m$.

Infrared spectra (Papike, 1964; Schwarcz and Speelman, 1965) suggest that the carbonate group is,

in fact, a trigonal group similar to those in other substances. The role of a trigonal carbonate group in a tetragonal mineral was first addressed by Papike and Stephenson (1966), who suggested that the carbonate group in each unit cell is displaced off the four-fold axis ($I4/m$) and disordered over four different positions in the (001) plane. Because scapolites are volatile-containing silicates, there has recently been renewed petrologic interest in them as possible storage sites for volatiles in the lower crust or upper mantle. Lovering and White (1964) described sulfur-rich scapolite as a primary constituent in granulite inclusions occurring with eclogite and ultrabasic rocks in the breccia- and basalt-filled pipes of eastern Australia. Newton and Goldsmith (1975) report that meionite, $Ca_4Al_6Si_6O_{24}CO_3$, has an unusually high thermal stability, exceeding 1500°C at 20 kbar. Meionite thus may play a role as a primary mineral in deep-seated magmatic processes, and may be a major storage site for CO_2 in the lower crust.

In this study we have investigated: (1) the Al–Si distribution in a scapolite derived from a slowly cooled metamorphic rock; (2) the precise location of the carbonate group within the scapolite structure; and (3) the thermal expansion of this mineral.

Experimental

Data were collected on a single crystal from sample ON-6 ($Na_{2.47}Ca_{1.33}K_{0.20}$) ($Si_{8.05}Al_{3.95}$)$O_{24}Cl_{0.59}(CO_3)_{0.37}$ $(SO_4)_{0.04}$ (Shaw, 1960) (0.25 mm × 0.15 mm × 0.10 mm). This sample is from a scapolite-pyroxene granulite outcrop in Monmouth Township, Ontario (Lin and Burley, 1973b).

The crystal used was found to be of suitable quality by examining Weissenberg photographs, which displayed sharp spots with no split reflections. Next it was mounted parallel to its a axis on a quartz fiber with specially prepared high-temperature cement (Brown et al., 1973). The crystal and fiber were then placed in a silica-glass capillary (0.5 mm in diameter) which was evacuated and sealed.

Because of the scapolite space-group controversy, the first data set was collected assuming no extinctions. All $h + k$ = odd for l = 0 reflections were found to be indistinguishable from background, and were assumed to be of zero intensity. This suggests $P4_2/n$ as the most likely choice for the scapolite space group. The primitive reflections which violate $I4/m$ symmetry ($h + k + l$ = odd) were found to be present and were treated in the refinement. Integrated intensities were measured using a PDP-15 computer-controlled Picker four-circle diffractometer with MoK_α radiation (0.7107Å) monochromatized by a graphite crystal. A total of 1778 independent reflections were measured in the before-heating experiment and 1657 in the after-heating experiment. Intensities were collected using an ω-2θ scan (2°/min) with five-second background counts on each side of the peak, and then converted to structure factors by applying Lorentz and polarization corrections, but no absorption corrections (μ_l = 12.2cm^{-1}). A standard reflection, (040), which was repeated every 20 reflections during data collection, showed less than one standard deviation variation in its structure factor.

Initial positional parameters and temperature factors for all atoms except the CO_3^{2-} group were taken from Lin and Burley (1973a). Original carbonate positions were estimated from Fourier and difference Fourier maps.

Both isotropic and anisotropic refinements were executed using scattering factors from Doyle and Turner (1968). The structure was initially refined in the space group $P4_2/n$ using the least-squares program, RFINE2, written by L. W. Finger. Final refinements used RFINE4, (Finger and Prince, 1975) a program which permitted refinement of the CO_3^{2-} group as a rigid body. The carbonate group was constrained to be planar with a fixed C–O distance of 1.3Å. The refined parameters for the group included the position of the center, the rotation and tilt of the triangle of oxygens, and thermal parameters corresponding to the motion associated with uniaxial translation of the entire group.

Errors on isotropic temperature factors were calculated using the program BCONV, and errors on bond distances were calculated using the program BONDX. Both programs were written by B. A. Wechsler and use diagonal matrix elements only.

In the anisotropic refinement of the before-heating data, all 1660 reflections of the $P4_2/n$ data set were accepted and resulted in a final unweighted R of 0.072 and a final weighted R of 0.052. In the anisotropic refinement of the after-heating data, again all reflections were accepted resulting in a final unweighted R of 0.080 and a final weighted R of 0.054. The weighting scheme was $W = 1/\sigma_F^2$ where σ_F is the standard deviation of the structure factor based on counting statistics (Prewitt and Sleight, 1968).

Cell-parameter determinations at each temperature were made using 2θ values of 13 to 17 independent reflections. 2θ values were collected at each successive temperature as temperature was increased, and then at room temperature after the heating cycle. The cell

TABLE 2. Final positional parameters and equivalent isotropic temperature factors (Å) for scapolite before and after heating. These parameters are (¼, ¼, ¼) greater than those reported for the $I4/m$ space group by Papike and Zoltai (1965)

Atom		Before Heating	After Heating
Na,Ca	x	0.6136(1)	0.6127(1)
	y	0.5361(1)	0.5358(1)
	z	0.7641(2)	0.7634(2)
	B	1.99(2)	2.14(3)
Cl	x	0.7500	0.7500
	y	0.7500	0.7500
	z	0.7500	0.7500
	B	3.87(9)	5.02(9)
T1	x	0.5892(1)	0.5891(1)
	y	0.6592(1)	0.6595(1)
	z	0.2469(1)	0.2472(2)
	B	0.57(1)	0.65(1)
T2	x	0.9097(1)	0.9097(1)
	y	0.1659(1)	0.1662(1)
	z	0.0492(1)	0.0487(1)
	B	0.65(2)	0.69(2)
T3	x	0.6626(1)	0.6629(1)
	y	0.0857(1)	0.0857(1)
	z	0.9619(1)	0.9613(1)
	B	0.60(2)	0.68(2)
O1	x	0.7084(2)	0.7080(2)
	y	0.6016(2)	0.6011(2)
	z	0.2523(3)	0.2525(4)
	B	1.17(4)	1.27(5)
O2	x	0.9430(2)	0.9424(2)
	y	0.1268(2)	0.1277(2)
	z	0.2626(3)	0.2617(4)
	B	1.14(4)	1.29(5)
O3	x	0.6000(2)	0.6005(2)
	y	0.1906(2)	0.1915(2)
	z	0.0447(3)	0.0439(4)
	B	1.32(5)	1.43(6)
O4	x	0.7949(2)	0.7953(2)
	y	0.0964(2)	0.0974(2)
	z	0.9681(3)	0.9685(4)
	B	1.28(5)	1.44(6)
O5	x	0.5202(2)	0.5198(2)
	y	0.6179(2)	0.6184(2)
	z	0.0774(3)	0.0767(4)
	B	1.42(6)	1.56(7)
O6	x	0.6216(2)	0.6216(2)
	y	0.9783(2)	0.9788(2)
	z	0.0775(3)	0.0766(4)
	B	1.20(5)	1.43(7)
C	x	0.26(2)	0.26(2)
	y	0.23(2)	0.23(2)
	z	0.24(2)	0.24(2)
	B	4.3(4)	4.3(4)
O7	x	0.27(7)	0.27(7)
	y	0.12(7)	0.12(7)
	z	0.25(7)	0.25(7)
	B	4.3(4)	4.3(4)

TABLE 2, continued

Atom		Before Heating	After Heating
O8	x	0.36(7)	0.36(7)
	y	0.28(7)	0.28(7)
	z	0.24(7)	0.24(7)
	B	4.3(4)	4.3(4)
O9	x	0.17(7)	0.17(7)
	y	0.28(7)	0.28(7)
	z	0.24(7)	0.24(7)
	B	4.3(4)	4.3(4)

parameters were refined using the program CELRF, C. T. Prewitt's modified version of PODEX.

Observed and calculated structure factors are listed in Table 1,[1] positional parameters and equivalent isotropic temperature factors in Table 2, interatomic distances within tetrahedra in Table 3, interatomic angles of linking tetrahedra in Table 4, interatomic distances between the Na,Ca site and its coordinating oxygens and Cl in Table 5, betas for each of the positional parameters in Table 6, and cell parameters for the crystal at room temperature both before and after heating and at 400°, 600°, 700°, 800°, 900°, and 1000°C in Table 7.

Scapolite structure

The scapolites are framework aluminosilicates with a unique arrangement of 4-membered tetrahedral rings which form two distinct types of channels, the first of which contains either Na^{1+} or Ca^{2+}. These oval-shaped channels run parallel to the c axis and are best shown in Figures 1 and 2, projections down the c axis of marialite and meionite respectively. The second channel type contains the volatile constituent, CO_3^{2-} shown in Figure 2 or Cl^{1-} shown in Figures 1 and 3. Figure 3, which is a projection down the a_2 axis perpendicular to section AA' in Figure 1, shows the five-membered tetrahedral rings where the aluminum avoidance rule is broken as meionite content is increased. Meionite contains half aluminum and half silicon tetrahedra, so half of the five-membered tetrahedral rings must contain 3 Al^{3+} and 2 Si^{4+} tetrahedra. One oxygen must link two aluminums, thus breaking the aluminum avoidance rule. The solid-solution limit (for ordered scapolite structures) be-

[1] To obtain observed and calculated structure factors from the final cycle of each anisotropic refinement, order document AM-76-021 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street, N. W., Washington, D. C., 20006. Please remit $1.00 for the microfiche.

TABLE 3. Interatomic distances within tetrahedra

Atom	Before Heating	After Heating
	T–O distances (Å)	
T1–01	1.598(2)	1.601(3)
T1–01'	1.605(3)	1.607(3)
T1–05	1.610(2)	1.617(3)
T1–06	1.625(2)	1.632(3)
mean	1.610	1.615
T2–02	1.732(2)	1.725(3)
T2–03	1.736(3)	1.724(3)
T2–04	1.732(3)	1.723(3)
T2–05	1.742(3)	1.734(3)
mean	1.736	1.727
T3–02	1.608(2)	1.607(3)
T3–03	1.605(3)	1.611(3)
T3–04	1.603(3)	1.607(3)
T3–06	1.638(2)	1.637(3)
mean	1.614	1.615
	O–O distances (Å)	
T1 Tetrahedron		
01–01'	2.631(3)	2.644(3)
01–05	2.637(3)	2.643(4)
01–06	2.608(3)	2.614(4)
01'–05	2.651(3)	2.653(4)
01'–06	2.626(3)	2.636(4)
05–06	2.617(3)	2.627(4)
mean	2.628	2.636
T2 Tetrahedron		
02–03	2.803(3)	2.786(4)
02–04	2.883(3)	2.868(4)
02–05	2.743(3)	2.731(4)
03–04	2.925(3)	2.901(3)
03–05	2.881(3)	2.867(4)
04–05	2.753(3)	2.746(3)
mean	2.831	2.816
T3 Tetrahedron		
02–03	2.698(2)	2.701(4)
02–04	2.602(3)	2.605(4)
02–06	2.570(3)	2.570(4)
03–04	2.676(3)	2.675(3)
03–06	2.587(3)	2.594(3)
04–06	2.663(3)	2.670(4)
mean	2.633	2.636

TABLE 4. Interatomic angles of linking tetrahedra

Atoms	Before Heating	After Heating
01–T1–01'	110.4(1)	111.0(1)
01–T1–05	110.6(1)	110.4(2)
01–T1–06	108.0(1)	107.9(2)
05–T1–01'	111.1(1)	110.7(2)
06–T1–01'	108.8(1)	108.9(2)
05–T1–06	107.9(1)	107.9(1)
mean	109.5	109.5
02–T2–03	107.8(1)	107.8(1)
02–T2–04	112.6(1)	112.5(1)
02–T2–05	104.3(1)	104.3(1)
03–T2–05	115.0(1)	114.6(1)
03–T2–05	111.9(1)	112.1(1)
04–T2–05	104.8(1)	105.2(1)
mean	109.4	109.4
02–T3–03	114.2(1)	114.2(1)
02–T3–04	108.2(1)	108.3(1)
02–T3–06	104.7(1)	104.8(1)
03–T3–04	113.1(1)	112.5(1)
03–T3–06	105.8(1)	106.0(1)
04–T3–06	110.5(1)	110.8(1)
mean	109.4	109.4
T1–01–T1'	159.5(2)	159.0(2)
T2–02–T3	139.0(2)	139.5(2)
T2–03–T3	145.9(2)	146.4(2)
T2–04–T3	147.9(2)	148.5(2)
T1–05–T2	137.1(2)	137.1(2)
T1–06–T3	138.5(2)	138.4(2)

1000°C, where it undergoes permanent shortening. Figure 4c shows the change in volume with temperature, which is linear until 1000°C, and again is anomalously large at 1000°C and after heating. We believe these permanent changes in cell parameters are caused by a small amount of disordering of Al^{3+} and Si^{4+} in the three tetrahedral sites.

Table 3 lists the tetrahedral bond distances for both the before-heating and after-heating data. The bond distances in the before-heating data are consist-

yond which the aluminum avoidance rule must be violated occurs when Al/Si = ½, very close to the ratio which occurs in sample ON-6.

Aluminum–silicon distributions

Figure 4 shows changes in cell parameters with temperature. Figure 4a shows the expansion of the *a* cell dimension with temperature. The anomalous lengthening of *a* at 1000°C is a permanent change and is reflected in the *a* cell dimension after the heating cycle. Figure 4b shows the variation in the *c* cell dimension as a function of temperature. Cell constant *c* is constant with increasing temperature until

TABLE 5. Interatomic distances of the Na,Ca coordination polyhedron

Atom	Distance (Å) Before Heating	After Heating
Na,Ca – 02	2.341(3)	2.346(3)
Na,Ca – 03	2.516(3)	2.527(3)
Na,Ca – 04	2.484(3)	2.498(3)
Na,Ca – 05	2.808(3)	2.809(3)
Na,Ca – 05'	2.740(3)	2.739(3)
Na,Ca – 06	2.879(3)	2.870(3)
Na,Ca – 06'	3.000(3)	2.989(3)
Na,Ca – C1	3.064(1)	3.076(1)

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TABLE 6. Betas for positional parameters

Atom	Beta	Before Heating	After Heating	Atom	Beta	Before Heating	After Heating
Na,Ca	11	0.00328(7)	0.00321(8)	O4	11	0.0010(1)	0.0013(2)
	22	0.00283(7)	0.00303(7)		22	0.0029(2)	0.0033(2)
	33	0.0105(2)	0.0121(3)		33	0.0069(4)	0.0070(5)
	12	0.00167(5)	0.00164(6)		12	-0.0004(1)	-0.0007(2)
	13	-0.0002(1)	-0.0003(2)		13	-0.0005(2)	-0.0004(2)
	23	-0.0000(1)	0.0001(1)		23	0.0000(2)	0.0002(3)
C1	11	0.0066(2)	0.0095(2)	O5	11	0.0024(2)	0.0027(2)
	22	0.0066(2)	0.0095(2)		22	0.0018(2)	0.0020(2)
	33	0.0170(9)	0.0170(9)		33	0.0079(4)	0.0085(5)
	12	0.0	0.0		12	0.0002(1)	0.0001(2)
	13	0.0	0.0		13	-0.0028(2)	-0.0019(3)
	23	0.0	0.0		23	-0.0009(2)	-0.0014(3)
T1	11	0.00077(4)	0.00087(5)	O6	11	0.0015(2)	0.0020(2)
	22	0.00079(4)	0.00091(5)		22	0.0018(2)	0.0021(2)
	33	0.0035(1)	0.0040(1)		33	0.0071(4)	0.0084(5)
	12	-0.00005(3)	-0.00005(4)		12	-0.0001(1)	-0.0004(2)
	13	-0.00012(8)	-0.0002(1)		13	-0.0007(2)	-0.0002(3)
	23	-0.00012(8)	0.0001(1)		23	0.0013(2)	0.0024(3)
T2	11	0.00095(6)	0.00101(7)	C	11	0.008(1)	0.008(1)
	22	0.00119(6)	0.00119(7)		22	0.008(1)	0.008(1)
	33	0.0030(1)	0.0034(2)		33	0.016(3)	0.016(3)
	12	0.00008(5)	-0.00002(6)		12	0.0000(0)	0.0000(0)
	13	0.00024(7)	0.00034(9)		13	0.0000(0)	0.0000(0)
	23	0.00011(8)	0.00021(9)		23	-0.0001(1)	-0.0001(1)
T3	11	0.00091(5)	0.00101(7)	O7	11	0.008(1)	0.008(1)
	22	0.00112(6)	0.00131(7)		22	0.008(1)	0.008(1)
	33	0.0027(1)	0.0030(2)		33	0.016(3)	0.016(3)
	12	0.00001(4)	-0.00005(6)		12	0.0000(0)	0.0000(0)
	13	-0.00013(7)	-0.00013(8)		13	0.0000(0)	0.0000(0)
	23	0.00003(7)	-0.00018(9)		23	-0.0001(1)	-0.0001(1)
O1	11	0.0010(1)	0.0013(1)	O8	11	0.008(1)	0.008(1)
	22	0.0023(1)	0.0020(1)		22	0.008(1)	0.008(1)
	33	0.0071(4)	0.0083(4)		33	0.016(3)	0.016(3)
	12	0.0002(1)	0.0004(1)		12	0.0000(0)	0.0000(0)
	13	0.0002(2)	-0.0008(3)		13	0.0000(0)	0.0000(0)
	23	0.0001(3)	-0.0002(3)		23	-0.0001(1)	-0.0001(1)
O2	11	0.0027(1)	0.0030(2)	O9	11	0.008(1)	0.008(1)
	22	0.0019(1)	0.0021(1)		22	0.008(1)	0.008(1)
	33	0.0032(3)	0.0038(4)		33	0.016(3)	0.016(3)
	12	0.0009(1)	0.0010(1)		12	0.0000(0)	0.0000(0)
	13	0.0005(2)	0.0005(3)		13	0.0000(0)	0.0000(0)
	23	-0.0003(2)	-0.0003(3)		23	-0.0001(1)	-0.0001(1)
O3	11	0.0025(2)	0.0027(2)				
	22	0.0016(2)	0.0018(2)				
	33	0.0069(4)	0.0072(5)				
	12	0.0007(1)	0.0006(2)				
	13	0.0002(2)	-0.0001(3)				
	23	-0.0007(2)	-0.0007(2)				

ent with essentially complete order, with $T1$ and $T3$ containing only Si^{4+} and $T2$ containing only Al^{3+} (Levien *et al.*, 1975). Lin and Burley (1975) predicted what we actually find, namely that a scapolite of this composition, because of the intensity of its primitive reflections, will have a totally ordered Al–Si distribution. Our sample's composition is just past the critical Al/Si ratio of ½, this ratio being the point

TABLE 7. Unit cell parameters of scapolite ON-6 at several temperatures

T	24°C Before	24°C After	400°C	600°C	700°C	800°C	900°C	1000°C
$a(\text{Å})$	12.0686(4)	12.0817(3)	12.1206(4)	12.1480(3)	12.1606(4)	12.1745(3)	12.1867(3)	12.2102(4)
$c(\text{Å})$	7.5812(3)	7.5758(3)	7.5790(3)	7.5798(3)	7.5792(4)	7.5798(3)	7.5797(3)	7.5750(4)
$V(\text{Å}^3)$	1104.21(4)	1105.82(4)	1113.42(4)	1118.59(4)	1120.81(5)	1123.45(4)	1125.70(4)	1129.35(5)
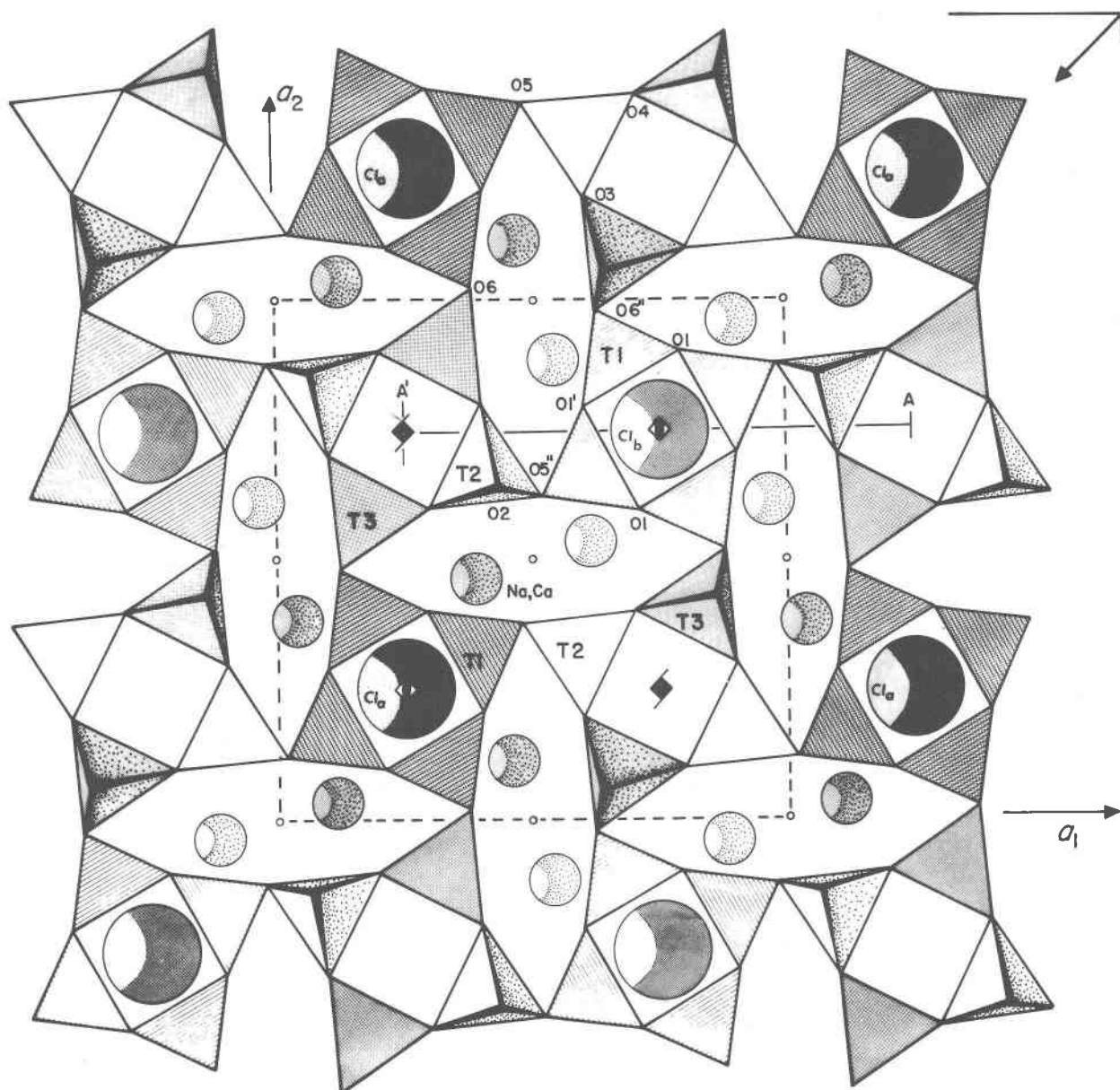
FIG. 1. The structure of marialite scapolite projected down the c axis. $T1$ tetrahedra are striped; $T2$, white; and $T3$, dotted. Shaded $T1$ tetrahedra are at approximately $z = \frac{3}{4}$, unshaded at $z = \frac{1}{4}$ while shaded chlorines (Cl_a) and Na,Ca's are at approximately $z = \frac{1}{4}$ and unshaded at $z = \frac{3}{4}$. The primitive cell and all symmetry elements are delineated. Symmetrically equivalent atoms (*e.g.*, Ol and Ol') are distinguished only for the purpose of identifying distinct bond distances and angles. A projection perpendicular to AA' is shown in Fig. 3.
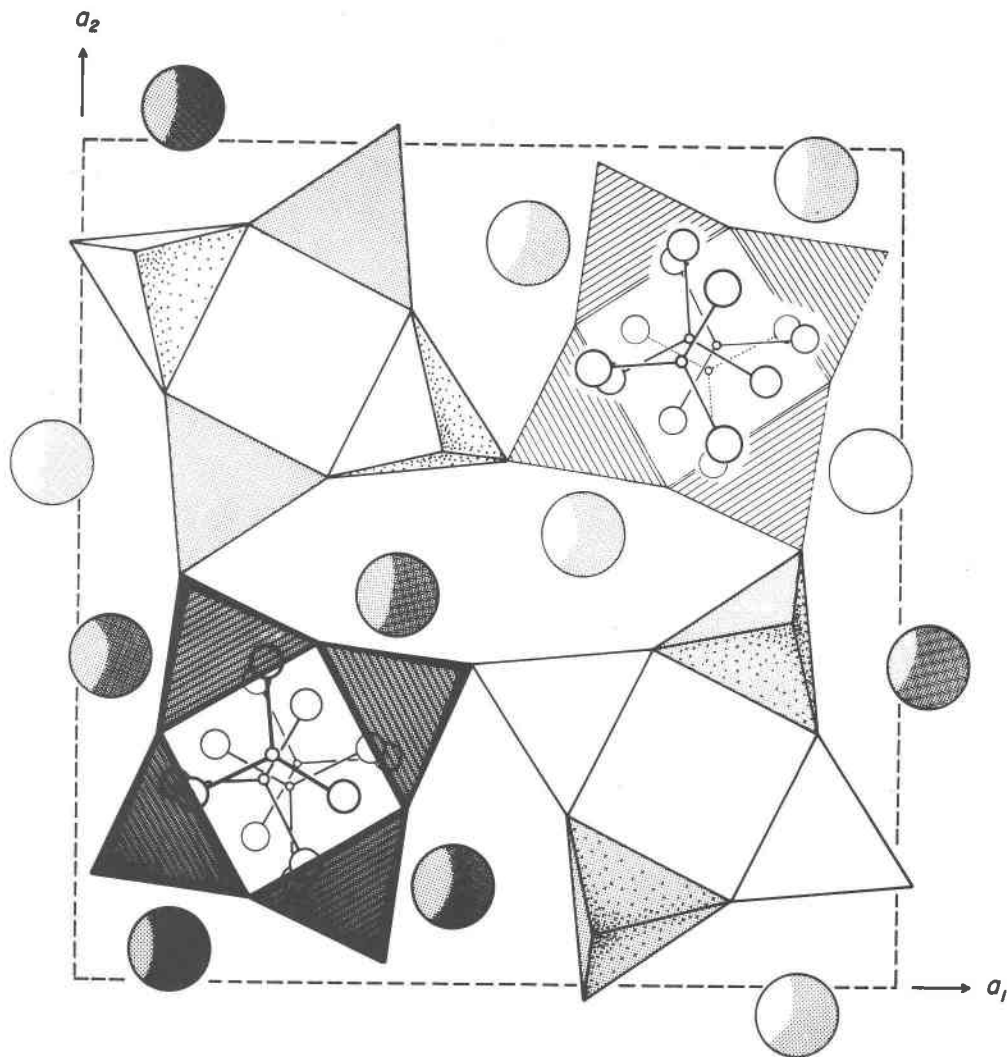
FIG. 2. The structure of meionite scapolite projected down the c axis showing the positions of the disordered carbonate group.

after which an ordered scapolite must violate the aluminum avoidance rule. If $T2$ is totally filled with Al^{3+}, then any additional Al^{3+} must enter $T1$ or $T3$. All $T1$ and $T3$ tetrahedra are linked to $T2$ tetrahedra (Fig. 3); therefore an Al^{3+}–O–Al^{3+} bond would be made, and the aluminum avoidance rule would be broken.

The tetrahedral bond distances indicate that, after heating, $T1$ increases and $T2$ decreases in size, while $T3$ remains the same. These changes, although small, may reflect a slight amount of disordering that has taken place with Al^{3+} exchanging for Si^{4+} in $T1$, and Si^{4+} replacing Al^{3+} in $T2$. The way this disordering would affect the cell dimensions can be seen in Figure 3. As Si^{4+} is added to $T2$, a path parallel to c through

the tetrahedral network would contain fewer large Al^{3+} tetrahedra, creating a net shortening of c. As Al^{3+} substitutes into $T1$, a path parallel to a would contain more Al^{3+} tetrahedra, and a would undergo a net lengthening.

In an independent study, 2θ values were collected on a crystal of sample ON-8 (Shaw, 1960). Several crystals were then heated for one week at 990°C in a sealed platinum capsule. A good-quality crystal was selected from those heated, and 2θ values were collected on it as well. The changes in cell parameters after heating are in the same direction and of the same magnitude as ON-6 with a increasing and c decreasing.

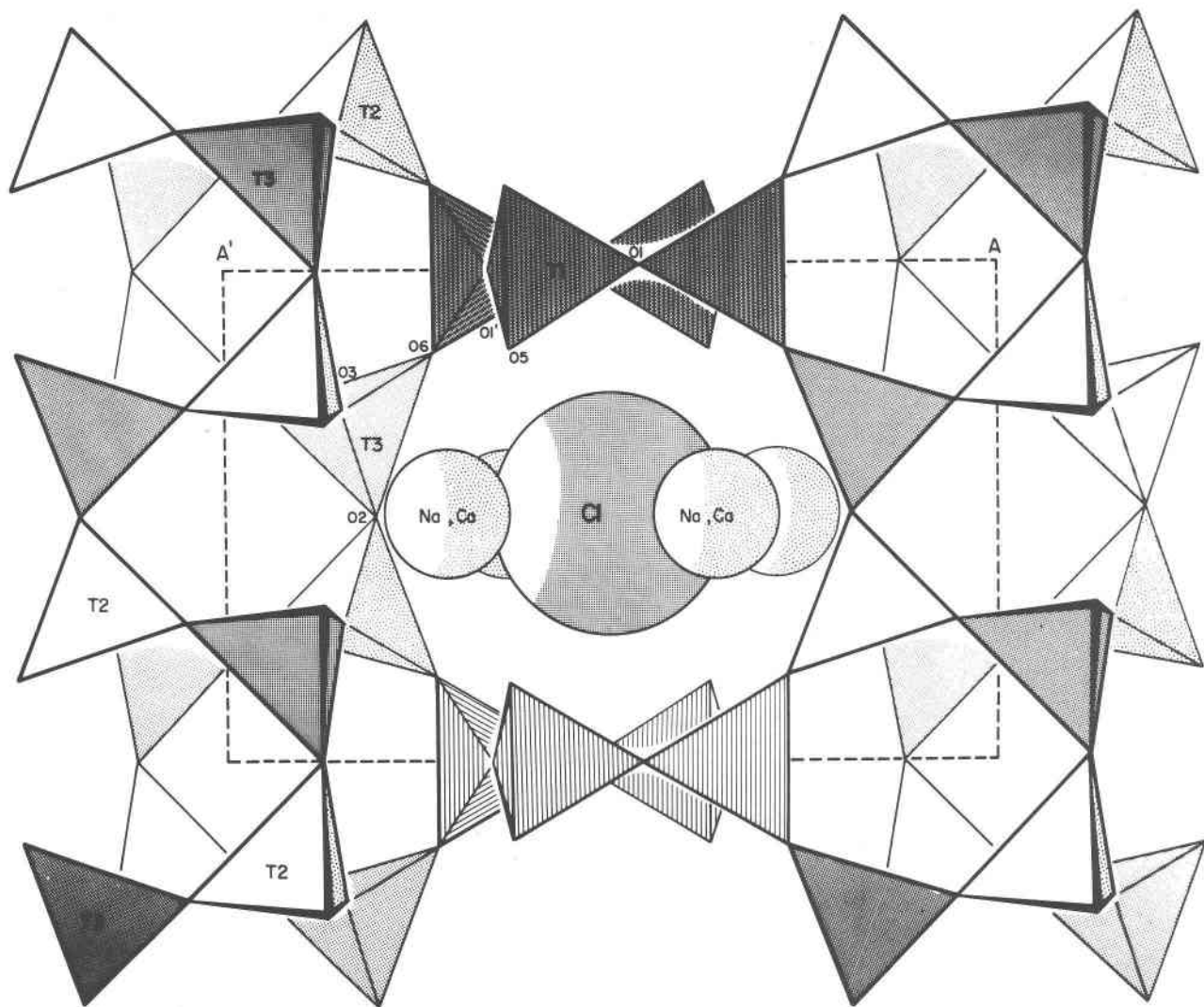We do not believe that this change in cell dimen-

FIG. 3. The structure of marialite scapolite projected down the a_2 axis, perpendicular to section AA' in Fig. 1. Tetrahedra are shaded to be consistent with Fig. 1.

sions reflects significant loss of the volatile components for two reasons. First, the crystal was heated in a sealed, evacuated silica-glass capillary with an inner diameter of 0.5 mm and a length of 14 mm. Very little volume of gas would be needed to crack this capillary; yet it did not break during or after heating. Fourier maps also support carbonate retention. The carbonate–oxygen peaks are the same height on both the before-heating and after-heating maps. A loss of 10 percent or more of the carbonate should be detectable on the Fourier maps. In the before-heating Fourier map the four carbon positions superimpose with the chlorine to form one large central peak (Fig. 5). The lack of change in this peak implies no chlorine loss. The after-heating Fourier

map puts the disordered CO_3^{2-} group further from the center of the cavity, which has been enlarged during heat treatment. If CO_2 were lost and O^{2-} left in its place, it would probably take the same position as the chlorine anion. When the Cl^{1-} electron density is subtracted using a Fourier difference map, there is no electron density left that could be construed as being O^{2-}, again indicating carbonate retention.

Refinement of carbonate

In past refinements of scapolite, carbonate has either not been refined (Papike and Stephenson, 1966) or has been refined in a manner inconsistent with the constraints of a carbonate group (Lin and Burley, 1973a, 1973c, 1975). Using the computer program
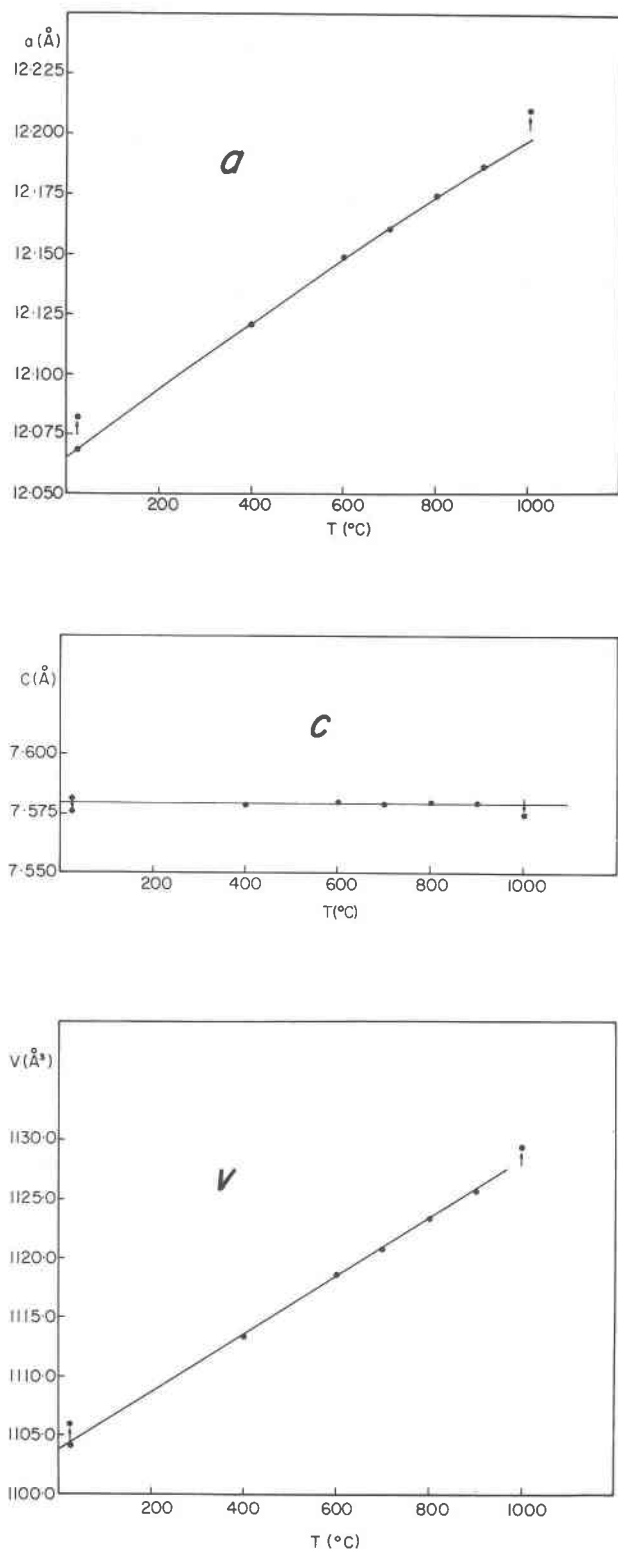
FIG. 4. Variation in unit-cell parameters with increasing temperature. Arrows point to anomalous cell dimensions discussed in the text.

RFINE4, (Finger and Prince, 1975) we were able to refine the carbonate group as a rigid body, with realistic bond distances and angles. Figure 5 shows the contours of the Fourier map overlain by the four refined, disordered carbonate-group positions. Over half the volatile-containing cavities in this sample contain chlorine. The others would have only one of the carbonate positions filled at any one time (Fig. 6). Therefore, each unit cell containing carbonate must actually be *triclinic*, but the average symmetry of the entire crystal is consistent with the tetragonal space group $P4_2/n$. This refinement indicates that tilting of the CO_3^{2-} group out of the (001) plane is minimal, probably less than three degrees, which is contrary to earlier published results (Lin and Burley, 1973a, 1973b, 1973c, 1975).

We think that this is a good model for several reasons. First, the refinement converged with the positions of the carbonate oxygens and the carbon falling within the areas of highest electron density. In Figure 5 oxygens O7 and O8 fall within one electron density peak, and O9 falls into a second peak of equal intensity. The peak containing O9 is partially caused by a Fourier termination error, so it does not actually represent equal electron density to the peak containing O7 and O8. An essentially flat difference map results from this model.

This model is also the only model which gave realistic calcium to carbonate-oxygen bond distances; all other models gave at least one distance that was much shorter than would be predicted by ionic radii. The high uncertainties on the CO_3^{2-} positional parameters, causing the large errors in these bond distances (0.8Å), are due to the low atomic weight of the atoms involved (carbon and oxygen), to the large amount of thermal motion in this group, and to the small amount of CO_3^{2-} in the crystal. Each of the disordered CO_3^{2-} positions contains less than 10 percent CO_3^{2-}. The Na,Ca site has a large and fairly anisotropic temperature factor, probably caused by a slight splitting of the positions of the Na^{1+} and Ca^{2+} cations. The positional parameters for this site are the average of the position for Na^{1+} and Ca^{2+}. The Na^{1+} cation is probably located closer to the 4_2 axis on which the Cl^{1-} position is fixed. Therefore, the Na^{1+} to Cl^{1-} distance listed in Table 5 is anomalously long. By the same argument the actual position of the Ca^{2+} cation is located further from the 4_2 axis, making the distances computed for Ca^{2+} to carbonate–oxygen bonds anomalously short. Refinement attempts using a different site for Na^{1+} than for Ca^{2+}, instead of a single Na,Ca site, were unsuccessful.
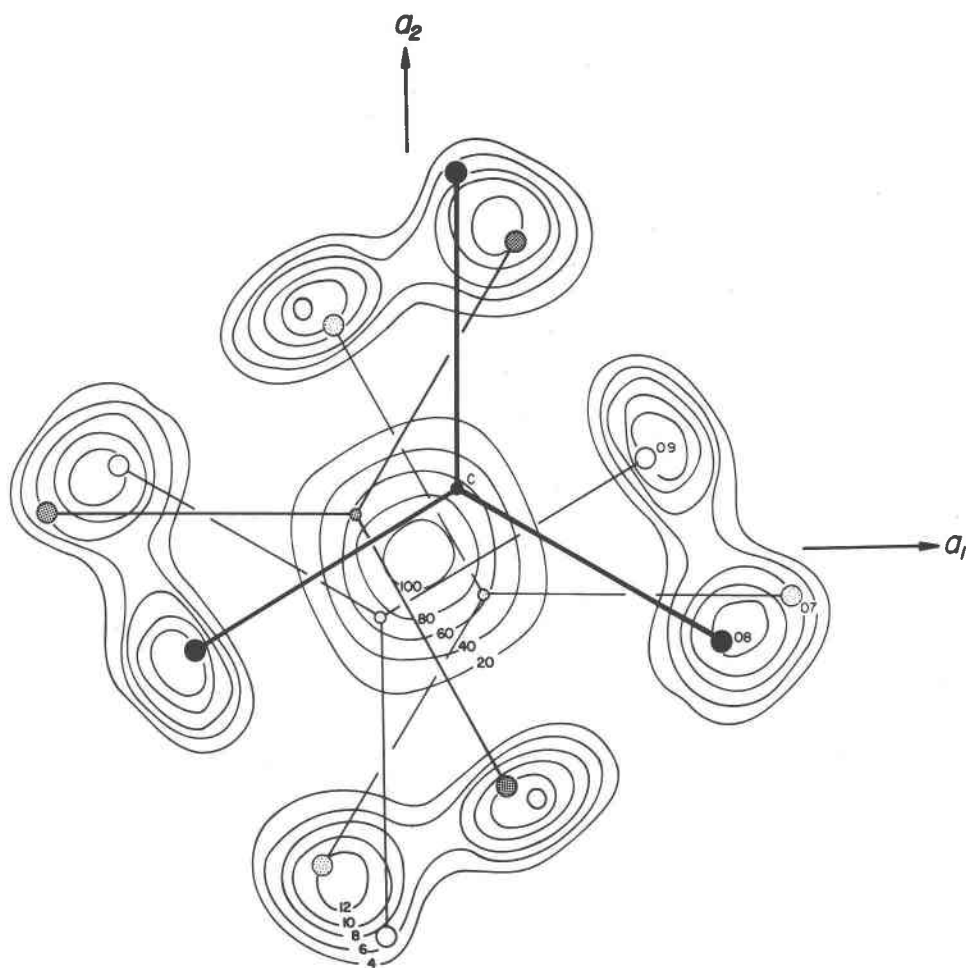
FIG. 5. Fourier (F_{obs}) map of Cl^{1-} and CO_3^{2-} in section at $z = \frac{1}{4}$ overlain by the four refined positions for the CO_3^{2-} group.

Ca^{2+} has an unusual coordination polyhedron in scapolite. In Figure 6 Ca' and Ca''' are coordinated by two carbonate oxygens while Ca'' and Ca'''' are coordinated by only one. Ca^{2+} is also coordinated by seven noncarbonate oxygens (Table 5). These seven oxygens plus either one or two carbonate oxygens give calcium a coordination number of either 8 or 9 depending on the position of the CO_3^{2-} group in the unit cell. This refinement of the carbonate group confirms the disordered CO_3^{2-} model of Papike and Stephenson (1966).

Changes caused by temperature and chemistry

Eugster *et al.* (1962) and Papike (1964) describe a linear variation of the cell parameters with *composition*. In Figure 4 we show an almost linear relationship of the cell parameters with *temperature*. Figure 7

shows a as a function of both meionite content (dotted line) and temperature (solid line) to compare chemical and thermal effects. Sample ON-6 was used for the thermal study, so it is plotted on the figure both at 33.5 percent meionite (Papike, 1964) and at room temperature. The two lines are drawn with the same slope, so a change in a reflects parallel changes in chemistry and temperature. An increase in meionite content from zero to 67 percent causes the same amount of expansion of the a cell dimension as raising the temperature from room temperature to 1000°C.

Although increasing the meionite component and increasing the temperature have similar effects on the a cell dimension, the change in a is caused by two different mechanisms. Papike and Stephenson (1966) reported that increased meionite content causes rota-
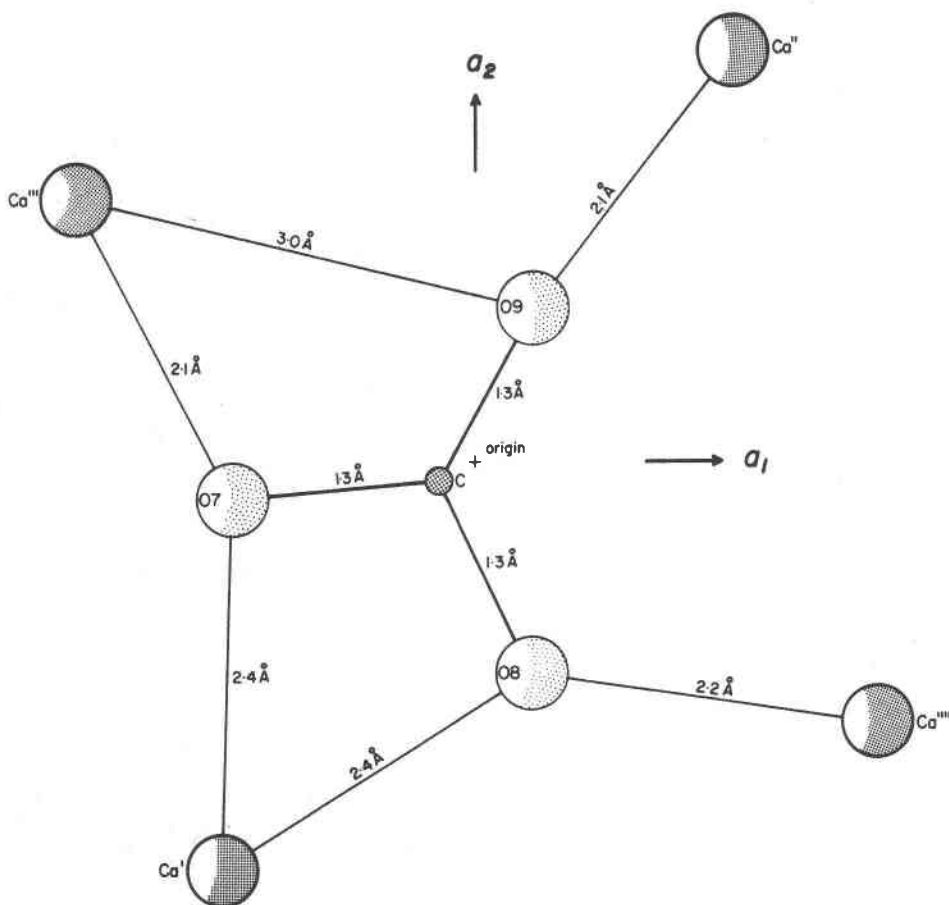
FIG. 6. Position of single carbonate group in its Ca^{2+} environment. Ca' and Ca''' are coordinated by two CO_3^{2-} oxygens while Ca'' and Ca'''' are coordinated by only one. Errors on calcium to oxygen bond distances are 0.8Å.

tion of the tetrahedral rings "in" (Fig. 8) causing the short axis of the cation channel (measured from O6 to O6'' in Fig. 1) to decrease in length. Increased temperature has the opposite effect on these channels. The short axis increases in length while the long axis between O5 and O5'' stays relatively constant. The channel width divided by the channel length is plotted as a function of temperature in Figure 9. Thermal expansion causes the tetrahedra to rotate in the opposite direction from increased meionite content (Fig. 8), resulting in a more open structure. The change in channel width can account for most of the expansion of a with increasing temperature. The c cell dimension remains constant with both compositional and thermal variation. As meionite content is increased, Al^{3+} cations enter tetrahedra that affect the a cell dimension but not the c cell dimension ($T1$). The dimension c remains constant with temperature be-

cause it is difficult to displace or rotate tetrahedra that link in that direction.

Scapolite subsolidus

Scapolite was originally refined in the space group $I4/m$ by Papike and Zoltai (1965) and Papike and Stephenson (1966) because $h + k + l =$ odd reflections are weak and diffuse even in long precession photographs and absent in near end-member compositions (Lin and Burley, 1973b, 1973c). More recent refinements including those in this paper have used the primitive space group $P4_2/n$ (Lin and Burley, 1973a, 1973c, 1975). To see if the structure becomes body-centered at a higher temperature, we plotted normalized structure factors of primitive reflections which violate $I4/m$ as a function of temperature. To avoid seeing an artifact of data collection at different temperatures, all reflections were normalized by di-
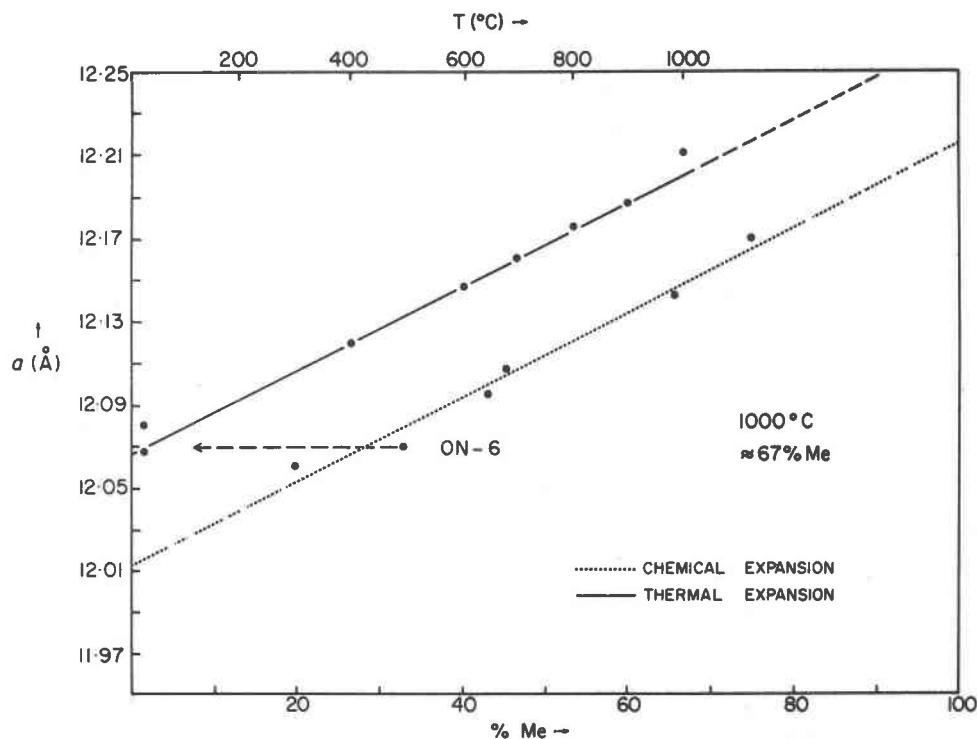
FIG. 7. Variation in *a* with increasing temperature and increasing meionite composition. The thermal study was performed on sample ON-6 so it is plotted both at 33.5 percent meionite composition and at room temperature. The same amount of expansion is caused in *a* by increasing the meionite content from 0 to 67 percent as by increasing the temperature from room temperature to 1000°C. Unit-cell data for scapolites other than ON-6 are from Papike (1964).

viding them by the average standard reflection at each temperature. If at any temperature these normalized reflections were all of zero intensity, the structure would be body-centered and have $I4/m$ symmetry. These reflections do not go to zero intensity at 1000°C but do decrease significantly. Because these data were collected on an intermediate composition, the primitive reflections are rather strong. Near end-member compositions, which have weak or no primitive reflections and are considered to approach the body-centered structure at low temperatures, may display body-centered symmetry at temperatures lower than 1000°C.

Conclusions

(1) With increased temperature the volume increases in a linear fashion, the *a* cell dimension increases in a nearly linear fashion, while the *c* cell dimension remains constant.

(2) Sample ON-6 has essentially totally ordered Si^{4+} and Al^{3+} distribution with Si^{4+} filling $T1$ and $T3$ and Al^{3+} filling $T2$ as predicted by Lin and Burley (1975).
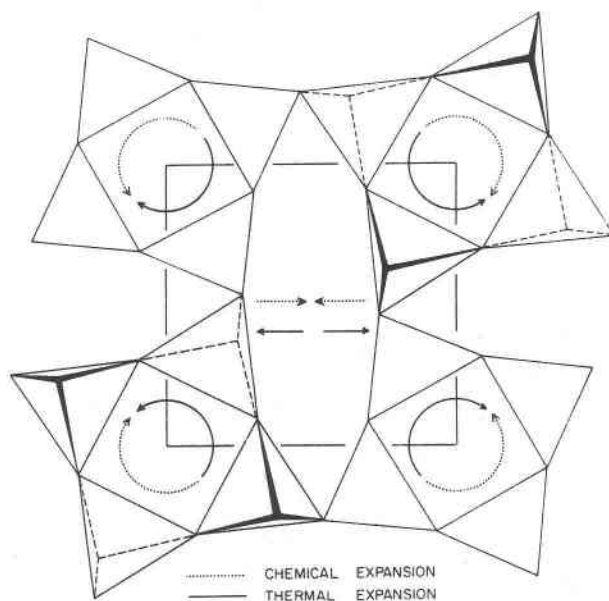

FIG. 8. Dotted arrows show rotation of tetrahedra "in" as meionite content increases, closing the channel. Solid arrows show rotation of tetrahedra "out" as temperature increases, opening the channel. This rotation takes place in the (001) plane. Both effects result in the expansion of the *a* cell dimension.
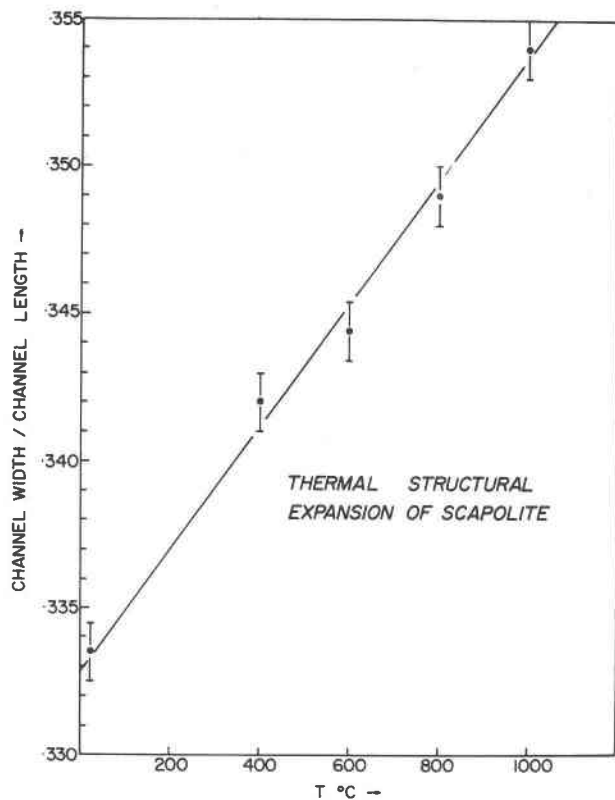
FIG. 9. Variation in channel width (06–06″) divided by channel length (05–05″) with increasing temperature. Oxygens 06, 06″, 05, and 05″ are shown in Fig. 1.

but do not disappear in the intermediate composition studied. Thus this sample approaches body-centered symmetry at higher temperatures, but has not yet reached it at 1000°C.

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(3) All three cell parameters undergo an irreversible change at 1000°C. Both a and volume increase while c decreases. This change, coupled with the direction of the changes in the tetrahedral bond distances, suggests a small amount of Al^{3+} and Si^{4+} disordering has taken place.

(4) The refinement indicates that the trigonal carbonate group can be disordered in a manner consistent with the $P4_2/n$ space group and that the group is very close to being in the (001) plane, tilting less than three degrees.

(5) Both increased meionite content and temperature lengthen the a cell dimension, but by different mechanisms. Increased meionite substitutes larger Al^{3+} for smaller Si^{4+} causing a to lengthen and at the same time causing tetrahedra to rotate "in" decreasing the width of the Na^{1+} and Ca^{2+} containing channel. Increased temperature allows the tetrahedra to rotate "out" widening the cation containing channels and creating a more open structure.

(6) At high temperature, the primitive reflections which violate $I4/m$ symmetry decrease in intensity

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