

## Thermal expansion of scapolite

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### ABSTRACT

Thermal expansion coefficients were measured for four natural and one synthetic scapolite spanning the solid solution range from marialite to meionite (22–100% Me). Measurements of lattice parameters and unit-cell volumes were carried out at 20 °C before and after heating and at intervals of 100 °C over the temperature range 100–800 °C. The measurements were carried out on finely powdered samples using a heating stage designed for examining phase transitions in minerals (Salje et al., 1993). For all scapolite compositions, the unit-cell volume and the *a* lattice parameter were observed to increase linearly during heating, whereas the *c* lattice parameter remained essentially unchanged. These effects are reversible, as unit-cell volumes and lattice parameters revert to their initial values after the samples are cooled from 800 °C.

The thermal expansion of the unit-cell constants measured in this study, *V* and *a*, does not vary linearly with composition. The new data are consistent with the earlier measurements of Graziani and Lucchesi (1982) only for scapolites of relatively sodic composition; for more calcic scapolites, the new data predict a much greater thermal expansion, with  $\alpha V_{\text{meionite}}$  being almost four times that originally obtained in the earlier study.

### INTRODUCTION

Scapolite is the general name given to minerals described by the general formula  $(\text{Ca}, \text{Na}, \text{K})_4(\text{Al}, \text{Si})_6\text{Si}_6\text{O}_{24}(\text{Cl}, \text{CO}_3, \text{SO}_4)$ . These minerals have an Al-Si framework structure, with large cavities containing the cations and smaller cages containing the anions (Fig. 1). The presence of primary scapolite in lower crustal rocks (Shaw, 1960a; Evans et al., 1969; Coolen, 1982; Bradshaw, 1989; Moecher and Essene, 1991) and in granulite inclusions found within alkalic basaltic and kimberlitic pipes (Bobrievich and Sobolev, 1957; Lovering and White, 1969; Dawson, 1971) suggests that this mineral may be an important storage site for volatiles in the lower crust, and Moecher and Essene (1991) have used scapolites to measure the activity of  $\text{CO}_2$  in rocks from lower crustal settings. To exploit scapolite as a tool for determining volatile content in petrological studies of the lower crust, it is, however, critical that we have well-constrained thermodynamic properties for this mineral.

The scapolite solid solution series is subdivided into two binary solid solutions involving the exchange of  $\text{Na}_4\text{ClSi}_2$  for  $\text{NaCa}_3\text{CO}_3\text{Al}_2$  for compositions between the sodium chloride end-member marialite ( $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ ) and an intermediate carbonate end-member mizzonite ( $\text{NaCa}_3\text{Al}_3\text{Si}_7\text{O}_{24}\text{CO}_3$ ) and involving the exchange of  $\text{NaCa}_3\text{CO}_3\text{Si}$  for  $\text{Ca}_4\text{CO}_3\text{Al}$ , operating over a smaller compositional range spanning from mizzonite to the calcium carbonate end-member meionite ( $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ ) (Evans et al., 1969). Several crystallographic and thermal parameters vary along the solid solution series. Marialite and Cl-free scapolites with compositions between miz-

zonite and meionite belong to space group *I4/m*, whereas Cl-bearing scapolites with compositions between marialite and mizzonite belong to space group *P4/m* (e.g., Hassan and Buseck, 1988). Ordering of  $(\text{Na}_4\text{Cl})^{3+}$  and  $(\text{NaCa}_3\text{CO}_3)^{5+}$  clusters occurs for compositions between marialite and mizzonite (Hassan and Buseck, 1988). Despite the break in solid solution at mizzonite and the differences in ordering behavior of the two binary solid solutions marialite-mizzonite and mizzonite-meionite, there is no sharp structural break at mizzonite, and Lin and Burley (1973a) suggested that the *a* lattice parameter, and thus the unit-cell volume, *V*, increased approximately linearly with increasing meionite content from marialite to meionite (Fig. 2).

Levien and Papike (1976) studied the effects of heating on the structure of a marialitic scapolite  $(\text{Na}_{2.47}\text{Ca}_{1.33}\text{K}_{0.20})\text{Si}_{2.05}\text{Al}_{3.95}\text{Si}_6\text{O}_{24}\text{Cl}_{0.59}(\text{CO}_3)_{0.37}(\text{SO}_4)_{0.04}$ , and demonstrated that *a* and *V* increased with increasing temperature, whereas the *c* lattice parameter remained essentially unchanged. They proposed that heating resulted in the rotation of the Si-Al tetrahedron in a plane perpendicular to *c*, operating to increase the width of the cation channels (Fig. 3). Increasing the meionitic component of the scapolite (i.e.,  $\text{Al}^{3+}$  content of the Al-Si framework) also resulted in the rotation of the Al-Si framework, but the sense of rotation operated to decrease the width of the cation channels. A more detailed study of the thermal expansion of samples spanning the marialite-mizzonite-meionite solid solution range (from 17.6 to 87.3% Me) by Graziani and Lucchesi (1982) confirmed the occurrence of these effects and demonstrated that the thermal expansion was also a function of the composition of scap-

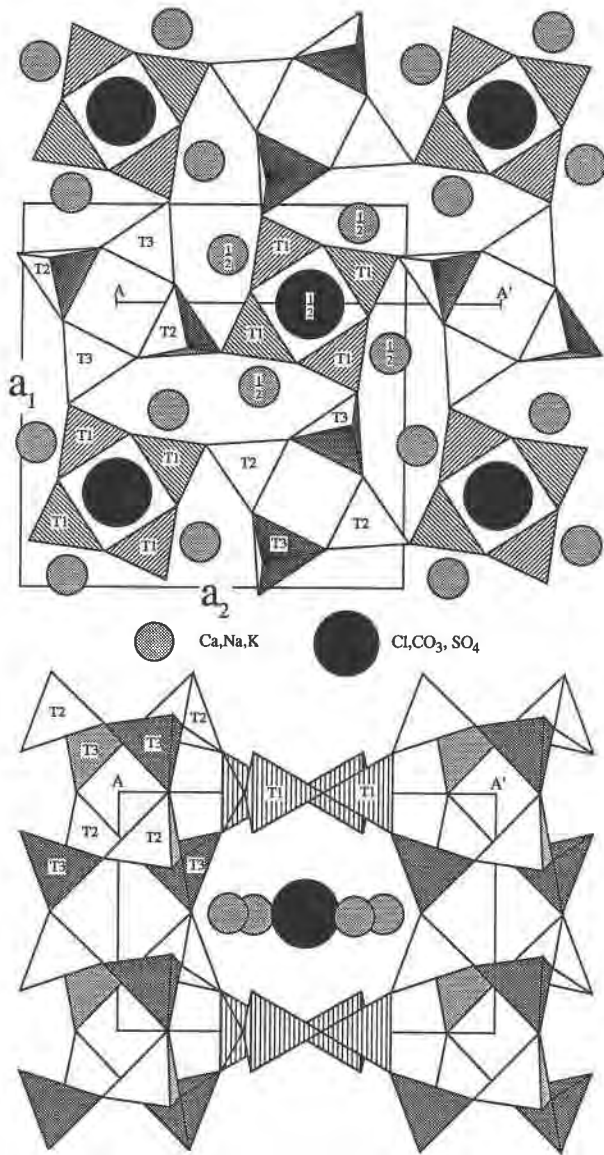


Fig. 1. The structure of scapolite projected on (001) (top) and (100) (bottom) after Papike and Stephenson (1966). Tetrahedra in both views are labeled T1, T2, and T3 to distinguish framework sites identified by previous studies (Lin and Burley, 1973b, 1973c, 1975; Levien and Papike, 1976). The unit cell of a marialitic scapolite is shown for reference.

Fig. 2. Variations in room-temperature measurements of (a) the  $a$  lattice parameter, (b) the  $c$  lattice parameter, and (c) the unit-cell volume,  $V$ , with meionite content,  $X_{Al}$ . The solid circles show data from this study; the open circles and squares and the crosses show data for natural and synthetic samples, respectively, taken from the studies of Papike and Zoltai (1965), Papike and Stephenson (1966), Ulbrich (1973a, 1973b), Lin and Burley (1973a, 1973b, 1973c, 1975), Orville (1975), Levien and Papike (1976), Goldsmith and Newton (1977), Graziani and Lucchesi (1982), Oterdoom and Wenk (1983), and Aitken et al. (1984). The samples used in this study lie within the spread of available data.

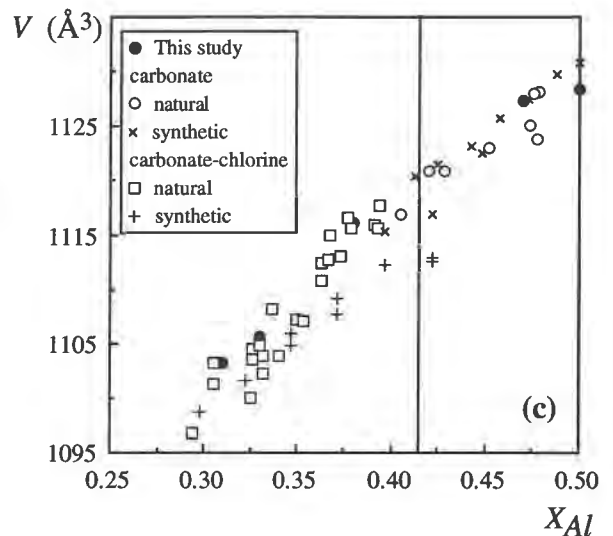
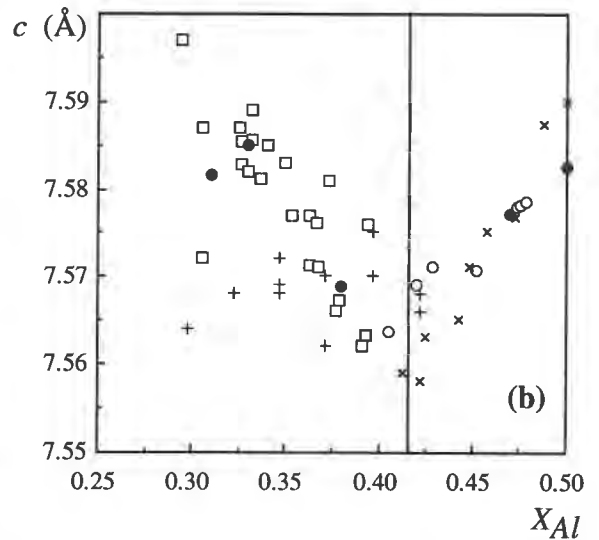
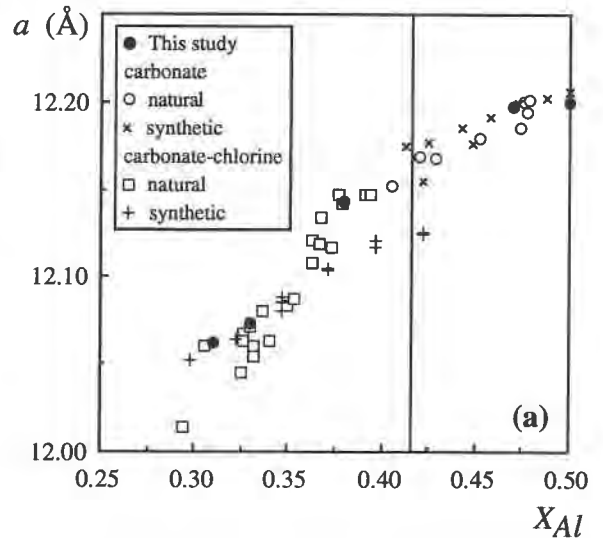
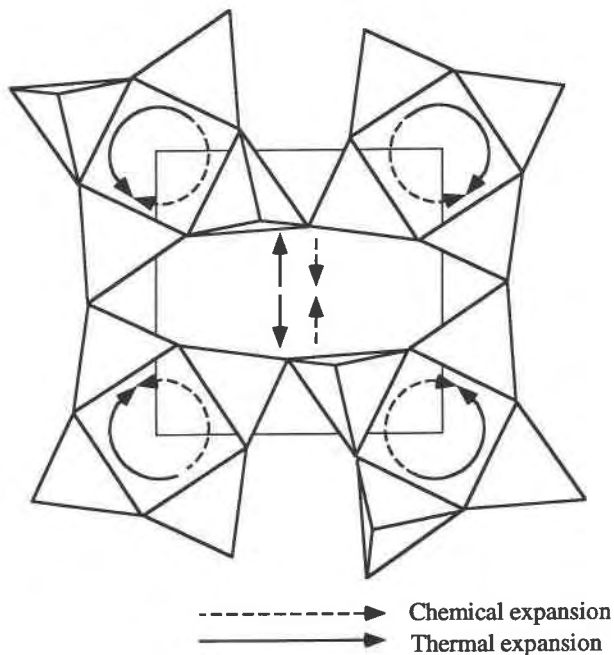


TABLE 1. Microprobe analyses of scapolites used in this study

	LoT	1960246	ON-27A	ON-6A	ON-8
SiO <sub>2</sub>	39.0	40.6	49.0	54.5	56.7
Al <sub>2</sub> O <sub>3</sub>	32.6	30.7	25.6	23.1	21.6
CaO	24.2	21.6	14.6	8.8	5.5
Na <sub>2</sub> O	0.0	1.3	4.9	8.7	10.8
K <sub>2</sub> O	0.0	0.4	1.0	1.1	1.2
Cl <sup>-</sup>	0.0	0.3	1.4	3.3	4.1
SO <sub>3</sub> <sup>2-</sup>	0.0	0.2	0.1	0.6	0.1
	95.8	95.1	96.6	100.1	100.0
O ≡ Cl <sub>2</sub> SO <sub>3</sub>	0.0	0.1	0.2	0.8	0.9
Total	95.8	95.0	96.4	99.3	99.1
Cations					
Si	6.0	6.3	7.4	8.0	8.2
Al	6.0	5.6	4.6	4.0	3.7
Ca	4.0	3.6	2.4	1.4	0.9
Na	0.0	0.4	1.5	2.5	2.9
K	0.0	0.1	0.1	0.1	0.2
Anions					
Cl <sup>-</sup>	0.0	0.1	0.2	0.4	0.5
S	0.0	0.0	0.0	0.1	0.0

Note: scapolite compositions were recalculated to 16 cations. SO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup> are calculated with the assumption of 25O<sup>2-</sup> equivalents pfu.



olite. Again, despite the break in the solid solution at mizzonite, these thermal expansion relationships appeared to be linear with composition, and Graziani and Lucchesi (1982) derived a series of linear relationships among  $da/dT$ ,  $dV/dT$ , and scapolite composition (%Me). However, a recent study of the thermodynamic properties of meionite (Baker and Newton, 1994) presented a measurement of the thermal expansion of synthetic meionite. This value is very different from that derived by extrapolating the linear relationship of Graziani and Lucchesi (1982) to the 100% Me composition. The purpose of this study is to redetermine and compare the thermal expansion of scapolites spanning the marialite-mizzonite and mizzonite-meionite solid solutions.

Fig. 3. The effects of chemical and thermal expansion on the scapolite structure (after Levien and Papike, 1976). The arrows show the direction of rotation of tetrahedra: in as the meionite content increases and out as the temperature increases. These rotations all take place within the (001) plane, and both result in an expansion of  $a$ .

## EXPERIMENTAL DETAILS

### Sample descriptions

Five scapolite samples ranging from Me<sub>22</sub> to Me<sub>100</sub> were obtained. The composition of each sample was determined using the Cameca SX-50 electron microprobe in

TABLE 2. Lattice parameter and unit-cell volume data for each of the samples with changing temperature

Sample	Cell parameter	20 °C	99 °C	197 °C	295 °C	393 °C	492 °C
LoT	$a$ (Å)	12.1996(9)	12.2084(10)	12.2165(10)	12.2287(9)	12.2383(10)	12.2456(9)
	$c$ (Å)	7.5825(8)	7.5856(9)	7.5836(10)	7.5885(9)	7.5902(9)	7.5881(15)
	$V$ (Å <sup>3</sup> )	1128.49(15)	1130.6(17)	1131.81(18)	1134.8(17)	1136.84(17)	1137.87(28)
1960246	$a$ (Å)	12.1970(7)	12.2042(6)	12.2141(7)	12.2239(8)	12.2328(8)	12.2432(8)
	$c$ (Å)	7.5771(7)	7.5779(7)	7.5793(8)	7.5808(9)	7.5826(7)	7.5842(9)
	$V$ (Å <sup>3</sup> )	1127.21(12)	1128.67(12)	1130.71(14)	1132.75(15)	1134.67(14)	1136.84(15)
1960246**	$a$ (Å)	12.1996(11)	12.2065(11)	12.2163(8)	12.2257(9)	12.2356(8)	12.2447(10)
	$c$ (Å)	7.5768(10)	7.5739(10)	7.5796(7)	7.5809(8)	7.5816(7)	7.5807(8)
	$V$ (Å <sup>3</sup> )	1127.66(19)	1128.50(19)	1131.16(13)	1133.10(15)	1135.04(14)	1136.89(17)
ON-27A	$a$ (Å)	12.1430(10)	12.152(10)	12.1624(8)	12.1732(9)	12.1848(10)	12.1967(9)
	$c$ (Å)	7.5688(7)	7.5689(7)	7.5674(7)	7.5674(7)	7.5684(7)	7.5694(7)
	$V$ (Å <sup>3</sup> )	1116.03(16)	1117.73(16)	1119.39(14)	1121.40(15)	1123.68(16)	1126.02(15)
ON-6A	$a$ (Å)	12.0733(9)	12.0849(11)	12.0979(10)	12.1125(11)	12.1254(11)	12.1421(9)
	$c$ (Å)	7.5849(7)	7.5833(8)	7.584(7)	7.5842(8)	7.5853(8)	7.5861(6)
	$V$ (Å <sup>3</sup> )	1105.61(16)	1107.51(91)	1109.97(17)	1112.69(18)	1115.24(18)	1118.44(14)
ON-8	$a$ (Å)	12.0626(10)	12.0752(11)	12.0910(11)	12.1055(11)	12.1230(10)	12.1382(8)
	$c$ (Å)	7.5815(7)	7.5799(7)	7.5788(7)	7.5797(9)	7.5779(8)	7.5785(6)
	$V$ (Å <sup>3</sup> )	1103.14(16)	1105.24(18)	1107.95(18)	1110.75(19)	1113.71(18)	1116.58(13)

Note: figures in brackets refer to the uncertainty ( $\pm 1\sigma$ ) in the last digit or digits. Measurements were made under vacuum unless otherwise indicated.

\* After heating.

\*\* Measurement made in a N atmosphere.

the Department of Earth Sciences in Cambridge. Si, Al, Ca, and K were recorded using an ED Si(Li) detector system, and Na, SO<sub>3</sub>, and Cl were analyzed using a WD detector and halite and barite standards. An accelerating voltage of 15 kV and a beam current of 10 nA were used, with acquisition times of 50 s for ED and 100 s for WD. The compositions of the scapolites are given in Table 1.

Sample LoT was synthesized from a mix of synthetic anorthite and calcite seeded with synthetic meionite (crystallized at 1350 °C and 15 kbar from a homogeneous 3:1 molar mix of synthetic anorthite and calcite) at 900–950 °C and 3.5 kbar with an anhydrous oxalic acid flux for 48 h. The result was a nearly complete yield of large crystals of meionite (up to 100 μm).

Sample 1960246 (Harker collection number) was made available by the Sedgwick Museum of the University of Cambridge. The sample comes from Monte Somma, Vesuvius, Italy, and the scapolites occur as idiomorphic, colorless crystals within a geode.

Samples ON-27A, ON-6A, and ON-8 were kindly made available by D. M. Shaw. Sample ON-6A is a yellow to colorless, transparent crystal taken from a pegmatitic skarn from Monmouth, Ontario. Sample ON-8 is an opaque, blue-gray crystal taken from a syenitic pegmatite from Gooderham, Ontario. Sample ON-27 comprised a finely ground scapolite separated from a pegmatitic skarn. The sample was collected at Olmsteadville, New York. Further details of these samples can be found in Shaw (1960a, 1960b).

### High-temperature X-ray diffraction measurements

The unit-cell constants for each sample were determined using a heating stage designed in the Department of Earth Sciences, Cambridge, for examining phase transitions in minerals. Details of the design are given in Salje et al. (1993). A small amount of sample was crushed, mixed with an internal standard (Si), and spread over a

Pt heating strip. A strictly monochromatic (CuKα<sub>1</sub>), focused X-ray beam diffracted from the sample was collected by a 4K-PSD detector. The temperature of the heating strip was monitored with ultrathin Pt-Rd thermocouples welded onto the Pt heating strip. The temperatures were calibrated by measuring the temperature of the α-β quartz transition for a pure SiO<sub>2</sub> sample. The measured temperature for the transition was 10 °C above the accepted value, and a linear temperature correction passing through this data point and the assumption of a correction of 0 °C at room temperature (20 °C), i.e.,  $T_{\text{actual}} = 20 + 0.0177T_{\text{obs}}$ , were applied to the temperatures at which lattice parameters were measured in the subsequent experiments.

Unit-cell constants of each of the scapolites were determined in vacuum (<10<sup>-1</sup> mbar) at a series of temperatures between 20 and 800 °C by least-squares refinement of at least 45 peak positions. For each successive temperature measurement, the sample was heated for half an hour to allow for thermal equilibration before an X-ray spectrum was collected. The sample was then cooled to room temperature (20 °C), and the unit-cell constants were measured to ensure that there had been no permanent change in the lattice constants as a result of heating.

## RESULTS AND DISCUSSION

The results of the measurements are shown in Table 2 and Figure 4. The values obtained for *V* and *a* for each of the five samples lie within the range of values determined in previous studies of scapolites (Fig. 2), and *a* and *V* are seen to increase with increasing temperature, whereas *c* remains approximately constant, as originally observed by Levien and Papike (1976). The relative changes in *a* and *V*,  $\Delta a/a_0$  and  $\Delta V/V_0$ , with temperature measured in this study were fitted to a linear relationship using a least-squares refinement. These slopes,  $d(\Delta a/a_0)/dT$  and  $d(\Delta V/V_0)/dT$ , vary with scapolite composition (Fig. 5), but the present data do not show a linear variation in thermal expansion with composition as was found in the study of Graziani and Lucchesi (1982). Given that there are differences in the exchange vectors operating in the marialite-mizzonite and mizzonite-meionite compositional ranges and that the ordering behavior in these two portions of the solid solution are different, such a nonlinear relationship might be expected, and the thermal expansion data might best be fitted by dividing the solid solution into two separate segments contiguous at the mizzonite composition. However, the data in the present study do not uniquely define the relationship between thermal expansion and composition in the marialite-mizzonite and mizzonite-meionite solid solutions, and these relationships can be equally well modeled by two straight line segments contiguous at mizzonite (Fig. 5b, curve i), e.g.,

meionite-mizzonite

$$d(\Delta V/V_0)/dT = 1.04 \cdot 10^{-5} + 1.62 \cdot 10^{-5} X_{\text{Al}}$$

TABLE 2.—Continued

590 °C	688 °C	786 °C	20 °C*
12.254(16)	12.2666(9)	12.2752(8)	12.1994(8)
7.5901(8)	7.5909(7)	7.5915(8)	7.5827(7)
1139.74(16)	1142.19(15)	1143.89(15)	1128.50(15)
12.2551(8)	12.2659(8)	12.2769(8)	12.1973(8)
7.5843(9)	7.5854(9)	7.5849(9)	7.5777(9)
1139.07(15)	1141.23(15)	1143.22(16)	1127.36(16)
12.2542(11)	12.2683(12)	12.2782(13)	12.1977(10)
7.5811(10)	7.5792(7)	7.5855(10)	7.5765(9)
1138.36(18)	1141.03(20)	1143.53(22)	1127.25(17)
12.2093(10)	12.2248(10)	12.2367(9)	12.1428(13)
7.5707(8)	7.5732(7)	7.5750(7)	7.5700(15)
1128.53(17)	1131.77(16)	1134.26(15)	1116.18(22)
12.1586(10)	12.1704(12)	12.1837(10)	12.0733(9)
7.5845(8)	7.5847(9)	7.5849(7)	7.5859(7)
1121.22(17)	1123.44(20)	1125.89(18)	1105.76(15)
12.1595(8)	12.1741(7)	12.1877(11)	12.0605(8)
7.5791(7)	7.5792(7)	7.5781(10)	7.5799(6)
1120.61(15)	1123.30(13)	1125.66(20)	1102.53(13)

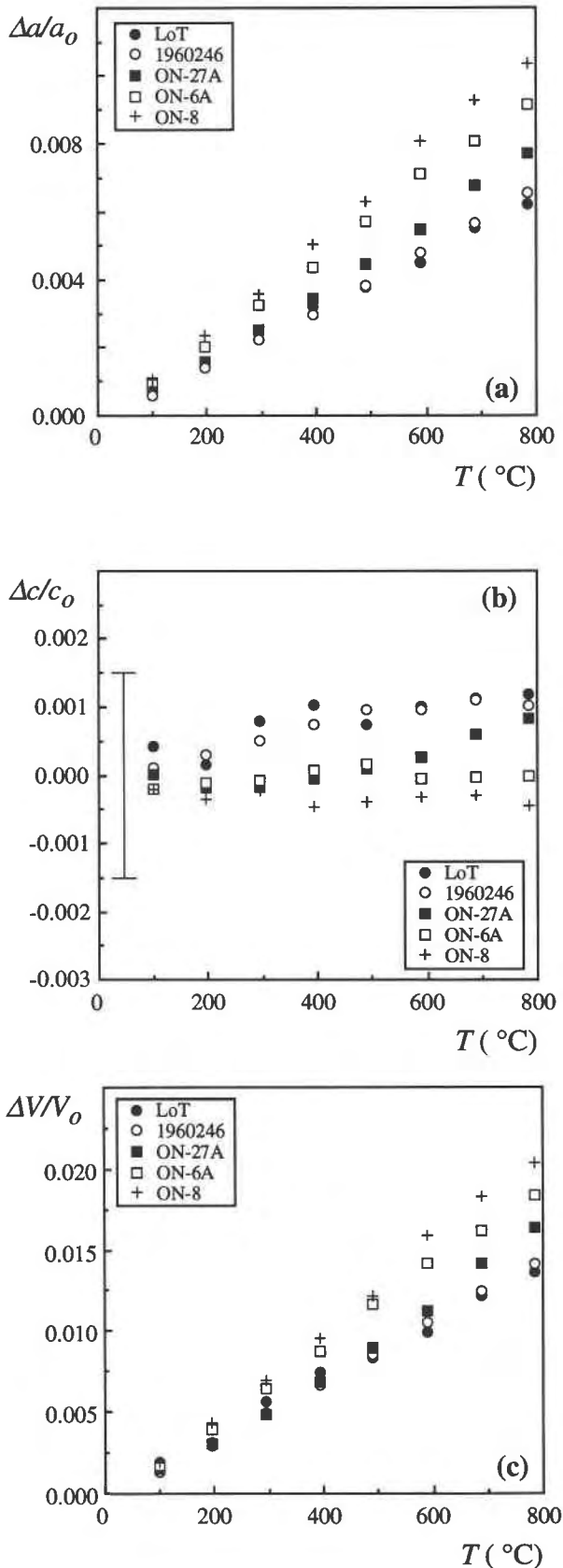


Fig. 4. The effect of temperature on the unit-cell parameters of the samples: (a)  $\Delta a/a_0$  vs.  $T$ , (b)  $\Delta c/c_0$  vs.  $T$ , and (c)  $\Delta V/V_0$  vs.  $T$ . The  $1\sigma$  error bar on  $\Delta c/c_0$  is as shown;  $1\sigma$  error bars on all other points are smaller than the symbols. All samples show a linear change in  $\Delta a/a_0$  and  $\Delta V/V_0$  with  $T$ :

$$\text{LoT: } \Delta a/a_0 = 8.175 \cdot 10^{-6} \Delta T, \quad \Delta V/V_0 = 1.816 \cdot 10^{-5} \Delta T$$

$$1960246: \Delta a/a_0 = 8.342 \cdot 10^{-6} \Delta T, \quad \Delta V/V_0 = 1.838 \cdot 10^{-5} \Delta T$$

$$\text{ON-27A: } \Delta a/a_0 = 9.774 \cdot 10^{-6} \Delta T, \quad \Delta V/V_0 = 2.024 \cdot 10^{-5} \Delta T$$

$$\text{ON-6A: } \Delta a/a_0 = 1.203 \cdot 10^{-6} \Delta T, \quad \Delta V/V_0 = 2.414 \cdot 10^{-5} \Delta T$$

$$\text{ON-8: } \Delta a/a_0 = 1.367 \cdot 10^{-6} \Delta T, \quad \Delta V/V_0 = 2.679 \cdot 10^{-5} \Delta T.$$

The magnitude of the slope of these lines is inversely proportional to the meionite content of the samples. The  $c$  lattice parameter remains essentially unchanged as temperature rises.

mizzonite-marialite

$$d(\Delta V/V_0)/dT = 5.18 \cdot 10^{-5} - 8.32 \cdot 10^{-5} X_{\text{Al}}$$

or by two smooth curves with identical slopes at the mizzonite composition (e.g., Fig. 5b, curve ii). These two models predict very different values for the thermal expansion of scapolites of composition close to mizzonite and marialite, and further work on the thermal expansion of scapolites from these compositional ranges should allow the derivation of a more exact form of the variation in thermal expansion with composition for the scapolite solution series.

Although the measurements made in this study are similar to those of Graziani and Lucchesi (1982) and Levien and Papike (1976) for sodic scapolites, they are clearly different from those made by Graziani and Lucchesi (1982) for calcic scapolites. The use of a N atmosphere is the only apparent difference between the method used in the study of Graziani and Lucchesi (1982) and that used in the present work. A measurement of the thermal expansion of sample 1960246 (equivalent in composition to sample 8 of Graziani and Lucchesi, 1982) was thus made in a N atmosphere ( $P = 1$  bar) (Table 2). This measurement was not significantly different from that made in vacuum (Fig. 5b), and the reason for the difference between the two sets of measurements for calcic scapolites thus remains unclear.

The most significant difference between the two sets of measurements is the implied value for  $\alpha V (=d\Delta V/dT)$  for meionite. The value of  $\alpha V$  for end-member meionite of  $62 \cdot 10^{-5}$  J/(bar·K) derived from the results of this study is significantly greater than the value of  $\alpha V$  of  $\sim 15 \cdot 10^{-5}$  J/(bar·K) calculated using the original calibration of Graziani and Lucchesi (1982). Attempts to use a value for  $\alpha V_{\text{meionite}}$  of  $15 \cdot 10^{-5}$  J/(bar·K) combined with measured values of  $\beta V_{\text{meionite}}$  of Hazen and Sharp (1988) to produce a reasonable fit to the experimental data on meionite stability presented by Baker and Newton (1994) have all failed because the calculated slopes of the reactions are

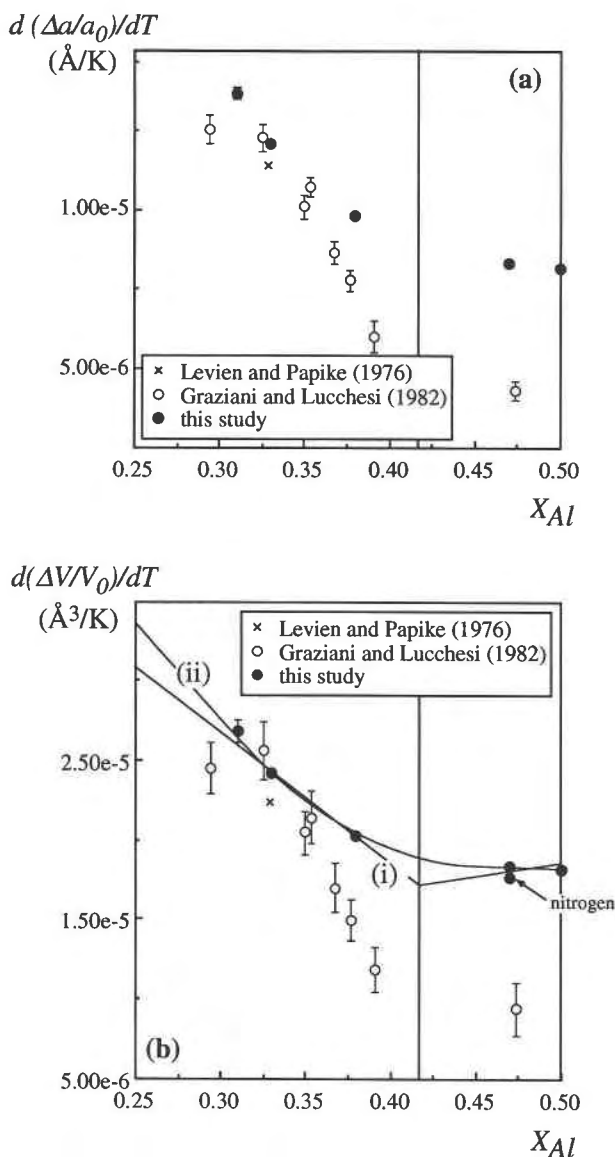


Fig. 5. Variation in (a)  $d(\Delta a/a_0)/dT$  and (b)  $d(\Delta V/V_0)/dT$ , plotted as a function of the  $X_{Al}$  content of the sample (solid circles). The measurement of  $d(\Delta V/V_0)/dT$  for sample 1960246 in a N atmosphere is indicated. The results of previous studies (Graziani and Lucchesi, 1982; open circles; Levien and Papike, 1976;  $\times$ ) have been regressed in an identical way to the samples in the present study and are also shown in the figure. The  $2\sigma$  error bars on the measurements (calculated purely from the errors in refined unit-cell parameters) are smaller than the symbols used unless otherwise indicated. Curves i and ii show possible model relationships between the thermal expansion and the composition for the scapolite solid solution series. The position of mizsonite is shown by the vertical line for reference.

far steeper than would be justified by the experimental brackets. This suggests that  $\alpha V_{\text{meionite}}$  must indeed be higher than estimated from the original measurements of Graziani and Lucchesi (1982).

## ACKNOWLEDGMENTS

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