American Mineralogist, Volume 67, pages 1229–1241, 1982

The thermal behavior of scapolites

GIORGIO GRAZIANI AND SERGIO LUCCHESI

Istituto di Mineralogia e Petrografia, Università degli Studi
Piazzale Aldo Moro 5, 00186 Rome, Italy

Abstract

Eight scapolite samples from different geologic settings were selected so as to fully represent the marialite–meionite series.

Thermal analyses (TG and DTA), as well as mass spectrometer analysis with a heating device, were used to define the release of the volatile components during heating. In the temperature range up to 800° C, the emission of H_2O, SO_2, CO_2, NaCl, and KCl was observed to occur continuously, but with five evident steps. The presence of SO_2 in the gaseous phase may be due to decomposition reactions.

X-ray powder diffractograms recorded every 100° C during heating up to 800° C indicated an increase in a and V, which occurred linearly in the whole marialite–meionite series, with a trend inversely proportional to the percentage of meionite present in each sample.

The relationships between increases in lattice parameters, with rising temperature, and percentage of meionite may be expressed by the equations:

$$da/dT = -1.59 \times 10^{-6}\ \text{Me\%} + 1.85 \times 10^{-4} \qquad (r^2 = 0.996)$$
$$dV/dT = -0.3 \times 10^{-3}\text{Me\%} + 0.034 \qquad (r^2 = 0.998)$$

The trends in a and V are reversible since samples treated to 800° C revert to initial cell parameters upon cooling. Temperature increases did not clearly affect the value of c, which remained constant. Beyond 800° C the unit cell parameter a increased anomalously, in an irreversible way, while the breakdown of the mineral started producing various compounds: plagioclase, which invariably has a lower calcium content than the scapolite from which it derives, halite and calcium aluminum silicates.

Refractive index measurements carried out during heating and on the cooled sample, confirmed such behavior, at least to a first approximation, showing for both ϵ and ω a linear increase during heating and a reversal of this trend to the initial values upon cooling.

Introduction

The composition of natural scapolite is related to solid solution between two theoretical end-members: marialite, $Na_4(Al_3Si_9O_{24})Cl$ and meionite, $Ca_4(Al_6Si_6O_{24})CO_3$ (Strunz, 1978, p. 484). Such minerals show a rather complicated substitution scheme with three coupled replacements in which Na^+, Si^{4+} and Cl^- are replaced by Ca^{2+}, Al^{3+} and CO_3^{2-}, respectively (Papike, 1964). This anionic substitution occurs only for percentages of meionite below 75, since at higher values the anion site is filled with CO_3^{2-} (Papike, 1964; Evans *et al.*, 1969). Scapolites are characterized by a substantial amount of volatiles, which, besides Cl^-, CO_3^{2-} and F^-, include H_2O, whose structural role is not well defined (Evans *et al.*, 1969), and sulphur, coordinated as SO_4^{2-}, as demonstrated by X-ray spectroscopy (Chappel and White, 1968) and electron microprobe determinations (Lovering and Widdowson, 1968). The sulphur content can reach the highest percentage among the volatile components (Knorring and Kennedy, 1958), being favored by high pressure (Lovering and White, 1969).

Infrared absorption spectroscopic studies have made it possible to determine the relation between the percentage content of CO_2 and SO_3 (Schwarcz and Speelman, 1965):

$$SO_3\ (\text{wt.\%}) = 0.704\ CO_2\ (\text{wt.\%}) - 0.800$$

The scapolite framework is characterized by two types of four-membered silicate tetrahedral rings, both lying parallel to the (001) plane (Papike, 1964;

0003–004X/82/1112–1229$02.00

Papike and Zoltai, 1965; Papike and Stephenson, 1966; Lin and Burley, 1973a, 1973b, and 1975). As the meionite content increases, rings of the first type rotate in a counter-clockwise direction, and those of the second in a clockwise direction. The array of rings delimits cavities of smaller and larger size, the former occupied by cations and the latter by anions. An increase in meionite content also affects the values of the lattice parameters, resulting in a linear increase in a and a change in c (Ulbrich, 1973).

The correlation between crystallographic data and meionite content was also investigated by Burley *et al.* (1961), who recognized a sharp decrease in the angular distance (Δ) between the reflections of the (400) and (112) planes as scapolite calcium content increased.

Levien and Papike (1976) investigated the problem of the effects of temperature increase on a 33.5 percent meionite sample. They identified a rotation of the four-membered rings of tetrahedra in the (001) plane, during heating, in an opposite direction to that due to increasing meionite content. Such behavior resulted in a "more open structure", leading to an increase in a and V values while c remained constant.

The correlation between chemical composition and physical properties was also investigated by Shaw (1960), who found linear relationships between meionite content, volatile components, density and the mean refractive indices.

The presence of scapolite as a primary constituent of granulite inclusions found within eclogite and ultrabasic rocks (Lovering and White, 1964), and its characteristic high temperature and pressure stability (Newton and Goldsmith, 1976), suggested that this mineral could be a storage site for volatiles, especially CO_2, in the lower crust (Goldsmith, 1976). The petrologic and mineralogic interest in scapolites suggested that it would be useful to investigate the thermal behavior of the marialite–meionite series in more detail defining the effects of temperature increases and the order in which the volatile components are released.

Material and methods

Various scapolite samples from different geologic settings and representing most of the marialite–meionite series were selected from numerous examined specimens of crystals free from macroscopic inclusions. With the intent of preliminary checking of the meionite content of each idiomorphous sample, the mean refractive indices were evaluated using oriented laminae parallel to the {100} prism (Shaw, 1960). The immersion method was adopted. A water cell connected with the central plate of the microscope controlled the temperature of the circulating liquid, within a range of about 50° C. An Abbé refractometer, connected in parallel to the water system, allowed the refractive index of the mounting liquid (Cargille Laboratory) to be determined at any time, for the sodium doublet. The meionite content of the massive samples was evaluated by means of X-ray powder diffraction, adopting the angular shift (Δ) method, as suggested by Burley *et al.* (1961).

Samples 1 and 2, from the Umba deposit, NE Tanzania, consist of idiomorphous, gem-quality crystals of considerable size (*ca.* 5 mm × 10 mm × 20 mm). They are both without inclusions, and respectively violet and yellow in color. Their setting is characterized by pegmatitic intrusions related to dunites and other ultrabasic rocks, as well as by metamorphic rocks of various type, mainly pre-Cambrian gneisses and marbles (Solesbury, 1967). Scapolite crystals have been found both in contact zones and in secondary deposits (Zwaan, 1971).

Samples 3 and 5 are scapolite crystals originally mined at Ankazobé and Gabenja respectively, in Madagascar. The crystal from the first locality, which belonged to the Eppler Collection, Munich, West Germany, is idiomorphous, large in size (*ca.* 30 mm × 30 mm × 60 mm), and of a lighter grey color; it is crossed by numerous growth channels and two-phase fluid inclusions, most of them anhedral. The samples from Gabenja, is an idiomorphous, yellowish crystal (*ca.* 2 mm × 2.5 mm × 10 mm), without inclusions, kindly supplied by the National Museum of Natural History, Smithsonian Institution, sample 141364. In the former locality scapolite is usually found in heterogeneous beryl-bearing pegmatite enriched in euxenite and monazite (Lacroix, 1919).

Two massive Canadian scapolites, from Gooderham, near Haliburton, Ontario, sample 4, and Grenville, Quebec, sample 7, were kindly made available by the National Museum of Natural History, Smithsonian Institution, samples 126018 and R 13120. The former was found among altered gabbros, marbles, skarns, and nepheline and corundum syenites (Adams and Barlow, 1911). The setting of the Grenville sample, on the other hand, comprises a variety of pre-Cambrian rocks including metagabbros, amphibolites, gneisses and marbles in which

scapolite presumably crystallized through the introduction of chlorine from granite magma (Buddington, 1939).

Sample 6 came from Manchester, New Hampshire, U.S.A.; it is a transparent crystalline fragment (*ca.* 5 mm × 7 mm × 8 mm) with an idiomorphous habit. Such scapolite occurs in irregular columnar masses, in a biotite schist with narrow calcareous bands interbedded with granite and pegmatite lenses (Stewart, 1941).

Sample 8, which was kindly made available by the Museo di Mineralogia, Istituto di Mineralogia e Petrografia of the University of Rome, Italy, sample 7536/20, was found at Pianura, in the Mount Somma–Vesuvius area, Italy. The idiomorphous, colorless, transparent crystal of fairly small size (*ca.* 4 mm × 5 mm × 10 mm) includes green pyroxenes; it was found in a geode from volcanic ejecta mainly composed of limestone associated with pyroxene and leucite (Scherillo, 1935).

Electron probe microanalyses were then performed on a JEOL JSM-50A using natural and synthetic standards. Matrix corrections were made according to the EMPADR VII program described by Rucklidge and Gasparrini (1969). All iron was calculated as FeO. The CO_2 content of the total gaseous phase emitted by the substance after heating at 1000° C was determined by means of the high sensitivity analyzer of Scarano and Calcagno (1975), using an air current with constant CO_2 content as carrier. The H_2O content was estimated by assessing the difference between the thermogravimetric results and the chemical data for the other volatile components. The density of all the samples was measured with a Berman balance.

Differential thermal analyses (DTA) were carried out on a BDL micro-differential thermal analyzer equipped with a semi-microprobe (capacity: 25 μl). The thermocouples were made with Platinel II and the experiments were performed in flowing air (5 ml/min), with a thermal gradient of 10° C/min in the 25–1400° C temperature range. Under the same experimental conditions used for DTA, thermal gravimetric analyses were carried out with a TGS-2 Perkin Elmer thermogravimetric system using about 10 mg of material for each analysis.

Serious obstacles were faced in performing the thermal analyses, since striking variations in the quantitative ratios between each weight loss became apparent when the experiments were carried out under differing experimental conditions. Even when the chemical homogeneity of a sample had been checked by electron microprobe analyses, it was found that the thermal studies may be strongly influenced by experimental conditions. A current of air gave better resolution than nitrogen or even a static atmosphere. The way the samples were prepared turned out to be very important, especially regarding grinding and loading techniques. Thus, such factors may cause great difficulties in obtaining and assessing data on the amounts of H_2O, CO_2 and SO_3 present in a sample.

Mass spectrometric experiments were performed in an attempt to identify the gaseous components released in the same temperature range, 25–1400° C, under high vacuum conditions. The equipment used was a Nuclide magnetic sector mass spectrometer, equipped with a Knudsen cell source: an alumina-lined tantalum crucible was placed in the cell and the temperatures were measured with a chromel–alumel thermocouple inserted on the bottom of the cell. The background pressure was maintained at about 10^{-6}–10^{-8} torr throughout the evaporation experiments. Full identification of carbon dioxide and water vapor, among the volatiles released during heating, was hindered by the fact that they are non-condensable gases, in the experimental conditions chosen, and by the unavoidable presence of small amounts of them in the apparatus.

The samples were also analyzed in a dry nitrogen current of 5 ml/min in the temperature range of 25–1000° C every 100°±5° C, with an X-ray powder diffractometer equipped with an AF 3000 heating camera. Ni-filtered Cu$K\alpha$ radiation, scanning from 10° to 70° at 1/2° 2Θ per minute, was used to detect any structural variations within the sample being heated. Scapolite was kept at the chosen temperature for 30 minutes before each diffractogram was recorded, to ensure the stabilization of every specimen at the experimental temperature, since this isothermal stage proved to be the most suitable for this purpose. After heating, the same experiments were performed on each sample at room temperature, using the same procedures.

Unit cell parameters were estimated from X-ray powder diffraction data indexed by Gibbs and Bloss (1961) using a least-squares refinement (Farinato and Loreto, 1975) with semiconductor-grade silicon metal (Jarrel Ash J. M., spectroscopy impurity less than 300 ppm) as an internal standard.

To investigate any changes in the refractive indices occurring during heating, the minimum deviation method was adopted; a polarizing Stoe goni-

meter was used, and measurements were carried out with a sodium light at 589.0 nm. The heating device consisted of a single crystal heater similar to that described by Brown *et al.* (1973). Two prisms were prepared for each sample. They were oriented parallel to the optic axis of the sample, and their orientation was checked by means of a universal stage. The maximum angle between the reflecting faces was 68° and the minimum was 60°. This value was calculated by assuming the hypothetical variation in the refractive indices that might have occurred during heating, and its effect on the variation of the minimum deviation angle (Franziani, 1965).

The measurements taken during heating were performed with a heating rate of 10° C/min, every 50°±5° C, in the temperature range of 25–450° C,

Table 1. Electron microprobe analyses and physical data of scapolites

	1	2	3	4	5	6	7	8
SiO_2	58.67	55.77	52.78	52.01	50.98	49.10	47.22	41.28
TiO_2	0.01	-	0.02	-	0.01	-	0.04	-
Al_2O_3	20.74	22.75	24.16	24.13	25.13	25.25	25.76	31.53
FeO ●	0.09	0.17	0.48	0.30	0.25	0.24	0.08	0.05
MnO	0.01	-	0.01	-	tr.	-	-	-
MgO	0.11	0.09	0.27	0.26	0.04	0.01	0.09	0.28
CaO	4.17	6.93	8.97	10.11	12.94	14.20	16.16	20.77
Na_2O	10.59	9.31	7.85	7.25	5.24	4.90	4.05	1.40
K_2O	1.22	0.79	1.06	0.86	0.86	0.89	0.52	0.46
H_2O^+, H_2O^- ▲	0.54	0.35	0.42	0.58	0.38	0.21	1.53	0.29
CO_2 ■	1.08	0.91	1.63	1.61	2.87	2.71	2.79	4.30
SO_3	0.03	0.06	0.20	0.81	0.11	1.29	1.26	0.34
F	tr.	-	-	-	-	0.04	-	-
Cl	3.01	2.96	2.42	2.07	1.36	1.26	0.45	0.20
	100.27	100.09	100.27	99.99	100.17	100.10	99.95	100.90
O ≡ Cl, F	0.68	0.66	0.55	0.47	0.31	0.30	0.10	0.05
Total	99.59	99.42	99.72	99.52	99.86	99.80	99.85	100.85
	Numbers of ions on the basis of 12 (Si, Al)							
Si	8.471	8.104	7.795	7.758	7.590	7.471	7.304	6.315
Al	3.529	3.896	4.205	4.242	4.410	4.529	4.696	5.685
	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Ti	0.001	-	0.002	-	0.001	-	0.005	-
Fe	0.011	0.021	0.059	0.037	0.031	0.031	0.010	0.006
Mn	0.001	-	0.001	-	-	-	-	-
Mg	0.024	0.019	0.059	0.058	0.009	0.002	0.020	0.064
Ca	0.645	1.079	1.419	1.616	2.064	2.315	2.679	3.404
Na	2.965	2.623	2.248	2.097	1.513	1.446	1.214	0.415
K	0.225	0.146	0.200	0.164	0.163	0.173	0.102	0.090
	3.87	3.89	3.99	3.97	3.78	3.97	4.03	3.98
H	0.520	0.339	0.414	0.577	0.377	0.213	1.578	0.296
C	0.213	0.181	0.329	0.328	0.583	0.563	0.589	0.898
S	0.003	0.007	0.022	0.091	0.012	0.147	0.146	0.039
F	-	-	-	-	-	0.019	-	-
Cl	0.736	0.729	0.606	0.523	0.343	0.325	0.118	0.052
	0.95	0.92	0.96	0.94	0.94	1.05	0.85	0.99
Me %	17.6	28.8	38.6	43.1	55.7	59.2	67.3	87.3
ε	1.53810(8)	1.54001(8)	1.54762(6)	-	1.54933(9)	1.55543(7)	-	1.56602(5)
ω	1.5491(1)	1.55867(6)	1.5618(1)	-	1.5743(1)	1.57687(6)	-	1.5924(1)
D (g/cm^3)	2.586(4)	2.594(4)	2.607(5)	2.621(4)	2.688(3)	2.683(5)	2.706(3)	2.741(4)
a (Å)	12.014(3)	12.045(4)	12.083(3)	12.087(5)	12.134(4)	12.147(3)	12.147(3)	12.185(5)
c (Å)	7.597(3)	7.587(3)	7.583(3)	7.577(3)	7.571(4)	7.566(3)	7.562(3)	7.578(4)

● Total iron as FeO.

▲ Determined with a thermogravimetric analyser.

■ Measured with a CO_2 analyser.

while those taken at room temperature after heating were carried out on samples heated to a maximum of 800° C.

Results

Chemical composition

The presence of minute inclusions in scapolite necessitated the use of an electron microprobe for chemical analyses (Ingamells and Gittings, 1967). Each analysis shown in Table 1 gives the mean of the data collected from at least five different positions.

The percentage of meionite in each sample was evaluated by the relationship between the components: Me% = [(Ca + Mg + Fe + Mn + Ti)/(Na + K + Ca + Mg + Fe + Mn + Ti)] × 100, suggested by Shaw (1960). These data were in good agreement with those obtained during the preliminary examinations, using optical and structural methods (Shaw, 1960; Burley *et al.*, 1961; Ulbrich, 1973).

Thermal study

The thermogravimetric curves (TG) for the eight samples show similar trends, with steady losses interrupted by five steps of more conspicuous weight loss. The continuity of the steady weight loss makes it hard to exactly identify the initial and final emission temperatures of each of the five steps (Fig. 1). The first of these stages is not well defined. It begins at about 80° C and ends at about 130° C. The second starts at 230–240° C and continues to 350° C, varying considerably in intensity from sample to sample and showing no clear correlation with meionite content. The next weight-loss step is similar beginning at about 420° C and ending at about 520° C.

In all the eight samples the fourth and fifth weight-loss steps appear to be the most significant. The fourth starts at about 660° C and ends at about 800° C, with weight loss increasing with the percentage meionite in the sample. Conversely, the weight-loss corresponding to the fifth step is inversely correlated with meionite content; this step begins at 940° C and ends between 1250° and 1300° C. This behavior is made conspicuous by the derivative thermogravimetric curve (DTG), which, in all samples, has an almost identical pattern.

The differential thermal curve (DTA) shows three clear endothermic peaks, with peak temperatures of about 100°, 710° and 1030° C, corresponding to the first, fourth and fifth weight losses. A wide-ranging

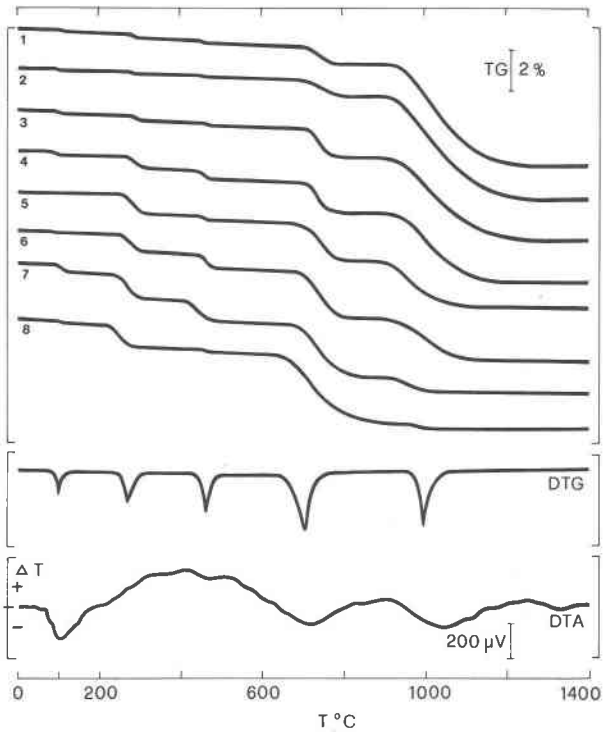

Fig. 1. Thermogravimetric curves of scapolites showing a common trend, with steady overall weight loss interrupted by five steps of sudden weight loss. Such behavior is confirmed by the DTG and DTA experiments; a representative curve is shown for each.

broad exothermic effect is recognizable between 150° and 650° C. The peak temperature of the second endothermic effect corresponds to that reported by Kauffman and Dilling (1950), although they did not note the other two.

To understand the order in which the volatile components were released the samples were analyzed by a mass spectrometer designed for vaporization studies on solids at high temperatures, and the gaseous phase evolved was checked for: H_2O, HF, Na, HCl, F_2, K, CO_2, CaO, NaCl, KCl, Cl_2, SO_2, SO_3, Na_2O, K_2O, Na_2Cl_2, and K_2Cl_2.

First, the whole spectrum was scanned; then the single compounds were examined repeatedly at constant temperature, so as to define any variations in their partial pressure and clarify the release modalities (Fig. 2).

These experiments provided evidence that the H_2O loss, which starts at 70–100° C, because of the high vacuum operating conditions, reaches a maximum between 150° and 250° C, gradually exhausting and stopping at about 400° C. The emission of CO_2 begins at about 100° C, increases slowly,

reaches its maximum partial pressure value at about 600° C, then decreases gradually and ends at 850° C. The release of sulphur as SO_2 begins at a temperature between 300° and 350° C, reaches a maximum at about 450° C end then gradually decreases, persisting at trace levels until almost 1200° C.

The emission of NaCl begins at a temperature between 750° and 850° C, becomes quite conspicuous between 900° and 1000° C, then diminishes fairly rapidly, and stops at about 1250° C. The presence of KCl was recognized in the same temperature range. At the same time, small amounts of Na, Cl and K were detected; their presence was attributed to the dissociation of such halogen compounds.

In addition to these volatiles, particularly in the mass spectra recorded beyond 600–800° C, small amounts of other compounds have been identified. Their intensities were roughly 0.1–0.01 percent of CO_2 and NaCl, the most abundant species in such experimental conditions. Also intermediate reaction products and perhaps hydrocarbon molecules were noted.

In the gaseous phase, no sulphur, SO_3 or HCl was noted, even though the latter has been reported in scapolites (Donnay *et al.*, 1978).

X-ray diffraction

X-ray powder diffraction patterns were run for each sample, at different temperatures and at room temperature after heating, to assess the relationships between temperature, percentage meionite content and any changes in unit cell parameters.

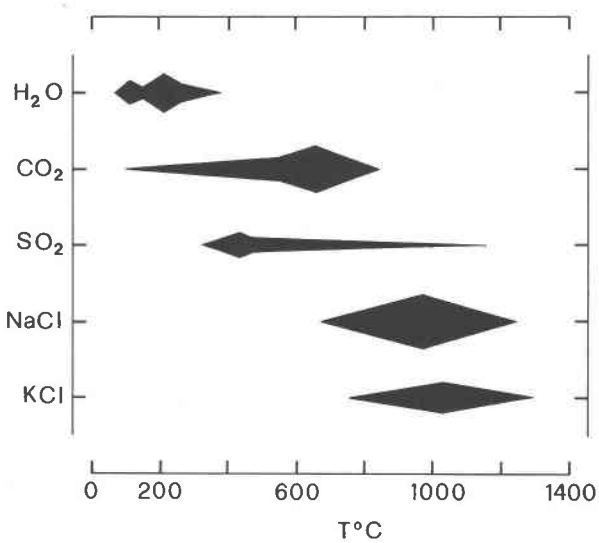

Fig. 2. The release range of volatile components during heating. Continuous weight loss is shown by the length of each silhouette, while the main emission temperature is marked by the maximum.

It was noted that each lattice parameter shows a peculiar trend during temperature increase, independent of the meionite content of the various samples (Table 2). During heating the a values showed a steady, almost linear increase that was inversely proportional to the percentage meionite content of the sample (Fig. 3).

The slope values of these straight lines were then plotted *vs.* each chemical composition, by means of a linear regression, yielding the following relation ($r^2 = 0.996$):

$$da/dT = -1.59 \times 10^{-6}\text{Me\%} + 1.85 \times 10^{-4}$$

where da/dT represents the slope of the straight line relative to the increase in a during heating and Me% is the meionite percentage of the heated sample (Fig. 4). The value of c remained almost constant as noted by Levien and Papike (1976).

The unit cell volume increases linearly in inverse proportion to the meionite content of the scapolite sample (Fig. 4). The correlation between its increase and the chemical composition may be expressed by the relation ($r^2 = 0.998$):

$$dV/dT = -0.3 \times 10^{-3}\text{Me\%} + 0.034$$

where dV/dT represents the slope of the straight line relative to the increase in the volume of the unit cell versus temperature and Me% is the meionite content.

When the experiments were carried out at room temperature, after heating the a, c, and V values were identical to the initial values, within the limits of experimental error, independent of the temperature reached by the sample. At the same time, the values of the angular shift (Δ) between the (400) and (112) reflections, whose variations were correlated with meionite content by Burley *et al.* (1961), were measured for both experimental cycles. A decrease during heating and an unchanged value after each cycle, were evidenced.

In investigating the relationships between the a value of each sample, measured at preselected temperatures and its chemical composition, it was found that the differences between the values of the a parameter recorded for different samples decreased steadily with rising temperatures, up to 700° C. Thus the difference between the a values of the two end-members, marialite and meionite, fell by 44 percent, from 0.171 to 0.095, when the

temperature was raised from 100° to 700° C. At higher temperatures this uniformity broke down, because of incipient breakdown phenomena, displayed by the release of NaCl and KCl, especially in the samples with the lowest percentage of meionite.

X-ray powder diffractograms recorded at temperatures over 700° C, at 100° C intervals, revealed the presence of various compounds, among which plagioclase and halite have been recognized. The former displayed a sodium content higher than that of the scapolite from which it was derived (Fig. 5). The albite content of this plagioclase has been evaluated from the X-ray powder patterns using the Δ(131), Δ(241) methods proposed by Bambauer *et al.* (1967).

Optical results

The refractive indices of the six transparent samples were first measured at high temperatures, and then at room temperature, after cooling. The former measurements continued up to a maximum of 450° C, since beyond this temperature the radiating energy of the heated scapolite prisms made it impossible to clearly distinguish the emission doublet of sodium. The measurements at room temperature were performed after the sample had been heated to

Table 2. Crystal data for scapolites at different temperatures

Sample number	Unit cell parameters (Å)	T (°C) 25°	100°	200°	300°	400°	500°	600°	700°	800°
1	a●	12.014(3)■	12.019(5)	12.041(3)	12.057(4)	12.068(4)	12.087(4)	12.098(3)	12.119(3)	12.129(4)
	a▲	12.014(3)	12.018(3)	12.017(4)	12.011(3)	12.009(3)	12.011(3)	12.018(4)	12.015(2)	12.021(3)
	c	7.597(3)	7.588(3)	7.596(3)	7.601(3)	7.598(4)	7.589(3)	7.591(3)	7.598(4)	7.597(2)
	c	7.597(3)	7.598(2)	7.594(3)	7.590(4)	7.597(3)	7.599(3)	7.592(3)	7.603(4)	7.599(3)
	V	1096.7(8)	1096(1)	1101.3(7)	1105.1(9)	1106.5(9)	1108(1)	1111.2(9)	1116.1(8)	1117.7(9)
	V	1096.7(8)	1097.4(7)	1096.7(9)	1095.0(9)	1095.7(7)	1096.4(7)	1096.7(9)	1097.7(8)	1098.2(7)
2	a	12.045(4)	12.063(5)	12.077(4)	12.089(4)	12.097(3)	12.116(3)	12.130(4)	12.142(3)	12.161(4)
	a	12.045(4)	12.041(3)	12.049(4)	12.046(3)	12.044(3)	12.039(2)	12.052(3)	12.046(4)	12.041(3)
	c	7.587(3)	7.582(3)	7.588(2)	7.578(3)	7.592(3)	7.586(4)	7.582(4)	7.585(3)	7.590(3)
	c	7.587(3)	7.584(3)	7.589(3)	7.579(2)	7.585(3)	7.586(2)	7.589(4)	7.588(4)	7.587(3)
	V	1100(1)	1103(1)	1106.8(9)	1107(1)	1111.1(8)	1113.8(9)	1115.7(9)	1118.3(9)	1122(1)
	V	1100(1)	1099.7(8)	1101.9(9)	1099.9(7)	1100.5(8)	1099.7(6)	1102.3(8)	1101.1(9)	1100.1(8)
3	a	12.083(3)	12.088(4)	12.102(4)	12.117(3)	12.128(4)	12.140(3)	12.150(4)	12.166(4)	12.178(2)
	a	12.083(3)	12.081(3)	12.088(2)	12.083(3)	12.079(4)	12.084(3)	12.080(3)	12.084(3)	12.085(3)
	c	7.583(3)	7.578(4)	7.582(3)	7.589(4)	7.581(3)	7.583(3)	7.584(3)	7.585(3)	7.588(3)
	c	7.583(3)	7.581(3)	7.583(3)	7.588(4)	7.578(4)	7.586(2)	7.588(3)	7.583(3)	7.582(4)
	V	1107.2(7)	1107.4(9)	1110.6(7)	1114.3(9)	1115.2(9)	1117.7(8)	1119.7(8)	1122(1)	1125.5(6)
	V	1107.2(7)	1106.6(8)	1108.2(6)	1108.1(8)	1105.7(9)	1108.0(8)	1107.3(8)	1107.4(7)	1107.5(9)
4	a	12.087(5)	12.109(4)	12.113(2)	12.127(3)	12.140(3)	12.153(5)	12.160(3)	12.173(2)	12.185(2)
	a	12.087(5)	12.093(3)	12.090(4)	12.087(3)	12.089(3)	12.089(4)	12.097(2)	12.085(3)	12.091(2)
	c	7.577(3)	7.571(4)	7.576(3)	7.579(4)	7.569(4)	7.581(5)	7.578(3)	7.577(4)	7.572(3)
	c	7.577(3)	7.568(4)	7.574(3)	7.576(3)	7.577(3)	7.575(4)	7.579(2)	7.571(3)	7.575(4)
	V	1107(1)	1110(1)	1111.7(7)	1114.8(9)	1115.6(9)	1119(1)	1120.6(7)	1123.0(8)	1124.4(7)
	V	1107(1)	1106.8(8)	1107.3(9)	1106.9(8)	1107.5(7)	1107.0(9)	1109.2(6)	1105.8(7)	1107.5(8)
5	a	12.134(4)	12.149(3)	12.155(3)	12.163(3)	12.172(3)	12.187(3)	12.198(3)	12.203(2)	12.210(4)
	a	12.134(4)	12.130(3)	12.135(3)	12.137(3)	12.129(2)	12.132(3)	12.138(3)	12.133(4)	12.140(3)
	c	7.571(4)	7.578(4)	7.570(3)	7.569(2)	7.574(3)	7.566(3)	7.572(3)	7.576(4)	7.569(4)
	c	7.571(4)	7.568(3)	7.574(3)	7.570(4)	7.567(3)	7.569(2)	7.572(3)	7.575(2)	7.571(3)
	V	1114.9(9)	1118.6(8)	1118.6(8)	1119.7(7)	1122.3(8)	1123.8(8)	1126.7(8)	1128.3(8)	1128(1)
	V	1114.9(9)	1113.7(8)	1115.5(7)	1115.1(9)	1113.2(7)	1114.1(7)	1115.7(7)	1115.3(8)	1115.9(8)
6	a	12.147(3)	12.153(3)	12.164(4)	12.175(3)	12.184(2)	12.192(2)	12.201(2)	12.209(3)	12.218(4)
	a	12.147(3)	12.141(4)	12.145(3)	12.142(2)	12.152(3)	12.148(4)	12.144(3)	12.145(5)	12.141(4)
	c	7.566(3)	7.568(4)	7.561(4)	7.567(3)	7.564(2)	7.571(3)	7.567(3)	7.562(4)	7.565(3)
	c	7.566(3)	7.566(3)	7.561(4)	7.567(3)	7.565(3)	7.572(3)	7.567(4)	7.568(2)	7.558(3)
	V	1116.5(7)	1117.8(8)	1118(1)	1121.8(7)	1123.0(5)	1124.0(7)	1126.6(6)	1127.3(8)	1129.4(9)
	V	1116.5(7)	1115.3(9)	1115.4(8)	1115.7(7)	1117.3(8)	1117.5(9)	1116.0(9)	1116(1)	1114.1(9)
7	a	12.147(3)	12.153(3)	12.158(4)	12.167(3)	12.174(4)	12.182(2)	12.192(4)	12.196(3)	12.203(2)
	a	12.147(3)	12.149(3)	12.143(4)	12.145(3)	12.147(3)	12.148(3)	12.152(2)	12.148(3)	12.155(4)
	c	7.562(3)	7.556(3)	7.561(4)	7.563(3)	7.559(2)	7.563(3)	7.567(3)	7.560(4)	7.562(3)
	c	7.562(3)	7.561(3)	7.576(3)	7.560(4)	7.558(3)	7.563(3)	7.560(3)	7.559(3)	7.564(4)
	V	1115.9(7)	1116.1(7)	1117.8(9)	1119.7(8)	1120.3(7)	1122.5(6)	1124(1)	1124.6(9)	1126.2(7)
	V	1115.9(7)	1116.2(8)	1115.9(9)	1115.3(8)	1115.3(8)	1116.2(8)	1116.6(6)	1115.7(8)	1117(1)
8	a	12.185(5)	12.196(3)	12.196(3)	12.200(4)	12.209(3)	12.209(2)	12.216(2)	12.220(4)	12.224(2)
	a	12.185(5)	12.181(3)	12.187(3)	12.188(3)	12.185(4)	12.183(4)	12.187(3)	12.126(3)	12.182(2)
	c	7.578(4)	7.579(4)	7.584(3)	7.577(3)	7.581(3)	7.576(4)	7.579(3)	7.575(3)	7.582(4)
	c	7.578(4)	7.573(2)	7.577(4)	7.578(3)	7.581(4)	7.575(3)	7.576(4)	7.579(3)	7.574(3)
	V	1125(1)	1127.5(9)	1128.2(7)	1127.8(9)	1130.1(7)	1129.5(8)	1131.1(7)	1131.2(9)	1133.2(7)
	V	1125(1)	1123.8(8)	1125.4(9)	1125.9(8)	1125(1)	1124.5(9)	1125.3(8)	1125.6(8)	1124.1(7)

● Data collected during heating.

▲ Data collected after heating.

■ Standard deviations are indicated in parentheses in terms of the last significant figures.

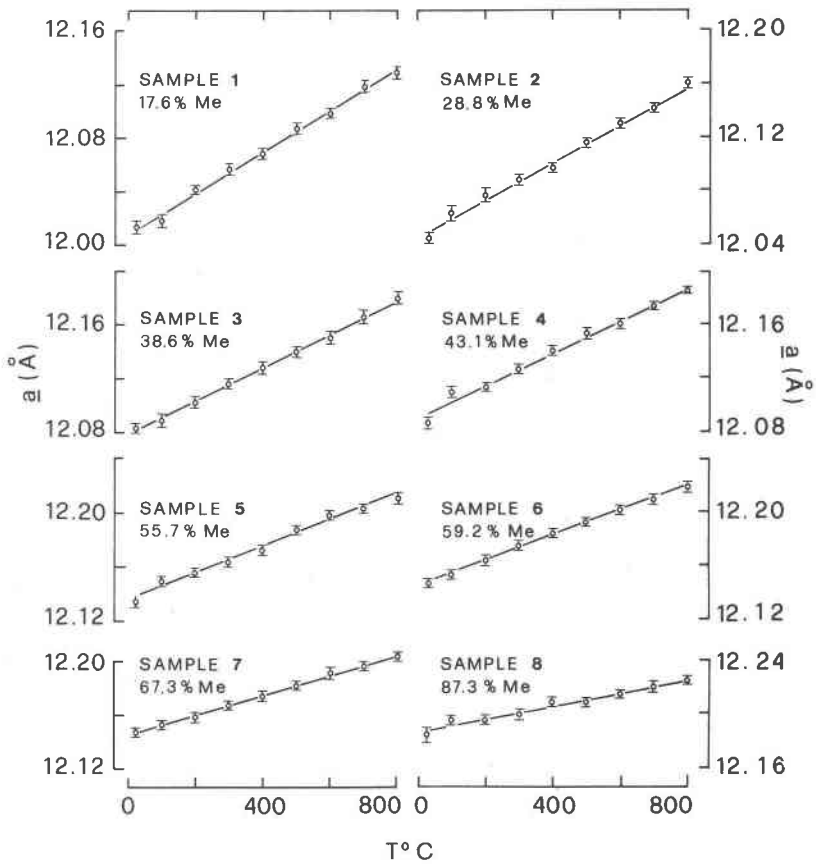

Fig. 3. Variations in a during heating. All the samples show a linear trend with a slope inversely proportional to the meionite content of the specimen.

a maximum of 800° C, a limit slightly below the temperature at which plagioclase and sodium and potassium chloride form.

The heating experiments indicated that rising temperatures lead to a linear increase in the values of the refractive indices, up to 350–375° C, at a slightly higher rate in the case of ε than in that of ω. As a first approximation, this increase was proportional to the meionite content of the sample.

The slope values relative to linear increase of both ε and $(\varepsilon + \omega)/2$ during heating, have been plotted *vs.* chemical composition, by means of a linear regression yielding the following relation:

$$d\varepsilon/dT = 1.30 \times 10^{-7}\text{Me\%} + 15.23 \times 10^{-7}$$

$$d[(\varepsilon + \omega)/2]/dT = 1.13 \times 10^{-7}\text{Me\%} + 5.22 \times 10^{-7}$$

where $d\varepsilon/dT$ and $d[(\varepsilon + \omega)/2]/dT$ refer to the increase of ε and the mean refractive index during heating, while Me% is the meionite percentage of the heated sample. However, a wide data dispersion was noted, since the correlation coefficients are respectively of $r^2 = 0.907$ and $r^2 = 0.850$, which does not allow a clear linear correlation. At higher temperatures, a sudden increase was recognized for both the refractive indices, inversely proportional to the meionite content (Fig. 6).

The refractive indices measured after cooling to room temperature were almost unchanged for each sample over the whole temperature range investigated. Slight variations from the linear trend were noted, however, when measurements were performed after heating to temperatures above 600° C, especially on sulphur rich samples and on those containing a low percentage of meionite. The variations were at the estimated error limits of about ±0.001. A decrease in birefringence values was also found in all the samples, following a linear trend inversely proportional to meionite content.

Color, too, was affected by heating. There was a progressive fall in color intensity, until the samples became completely colorless at temperature between 350° and 400° C.

Discussion

The thermal analyses showed a similar trend for all the examined samples, independent of the amounts of the various gaseous compounds released.

Up to the temperature of 850° C, the release of H_2O, CO_2, and SO_2 can be roughly correlated with the meionite content of the sample examined. It should be stressed, however, that CO_2 and SO_3 content can be related to the percentage of meionite on a stoichiometric basis (Shaw, 1960), while this is not true for H_2O, whose structural role has not yet been clearly defined (Evans *et al.*, 1969). An excessive uncertainity, nearly 30–40 percent, may, thus, occur in assessing the meionite content of the scapolite samples. Thus better results were obtained by investigating the relationship between meionite content and the weight loss occurring between 390° and 850° C; in this way only the amounts of CO_2 and SO_2 released were involved (Fig. 7).

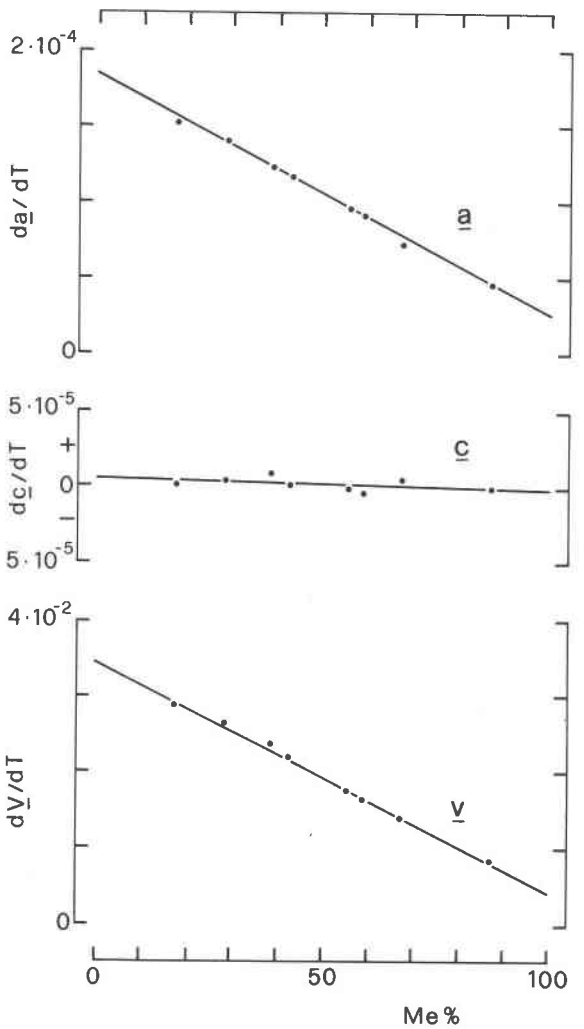

Fig. 4. Increasing rate of lattice parameter variation during heating, *vs.* the meionite content of the sample.

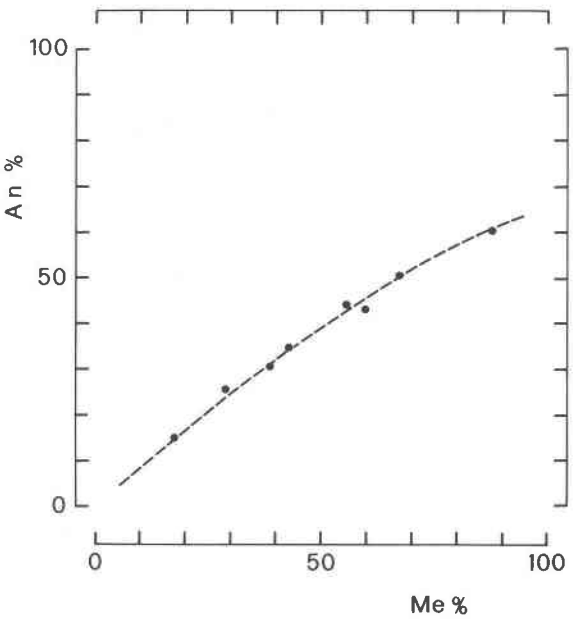

Fig. 5. Variation in the anorthite content of the plagioclase formed *vs.* meionite content of the scapolite.

The release of NaCl and KCl, which takes place between 800° C and 1250° C, displays a linear trend when plotted against the meionite content of the specimen; the highest values being found in the sodium-rich samples (Fig. 7), similar to the results of Evans *et al.* (1969).

The thermogravimetric data, supported by stoichiometric considerations, suggest that all the chlorine present is released as halogen compounds in this temperature range. The appreciable degree of scattering seen in the upper graph in Figure 7 may be due to the presence of potassium chloride, which is always found, even if in small amounts, in scapolites. The presence of potassium, which is considered to be structurally equivalent to sodium in such minerals, increases the total weight loss to be expected from a sample with a given meionite content.

A number of chemical data reported by Shaw (1960), Ingamells and Gittings (1967), and Evans *et al.* (1969) were plotted using the least squares method against meionite content, yielding a linear relation. This was done by calculating the total weight of NaCl and KCl which could be released by

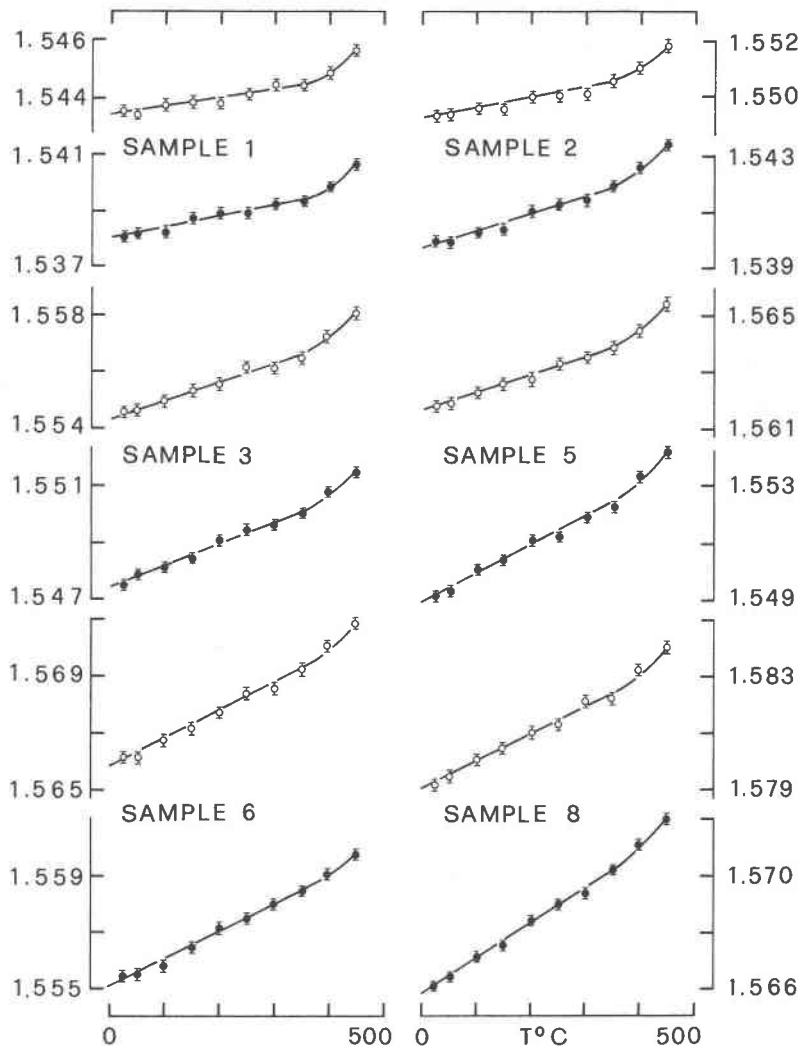

Fig. 6. Increase in ε (filled circles) and mean refractive index (open circles) during heating. All the samples show a linear trend up to 350–375° C proportional to the meionite content, followed by a sudden increase.

the sample, assuming a complete loss of chlorine, and a Na/K ratio the same in the solid and gaseous phases. The fact that the straight line in the upper graph in Figure 7 cuts the abscissa at about 80 percent Me can be explained by the fact that at higher meionite content the anion sites contain only CO_3^{2-}.

The H_2O release occurs until *ca.* 400° C with two main weight losses respectively starting at 70–100° C and 150–250° C, thus suggesting the existence of two types of H_2O in the scapolites. However, the absence of a wide emission gap between the two weight losses, and the continuous H_2O release, do not support such a hypothesis. Continuous emission is also characteristic of CO_2 and SO_2.

Chappel and White (1968) recognized the presence of SO_4^{2-} using X-ray fluorescence, while infrared studies by Schwarcz and Speelman (1965) revealed low amounts of SO_3^{2-}, while SiO_4^{4-} did not allow the recognition of SO_4^{2-}. The emission of SO_2, revealed by mass spectrometry, could suggest that it derives from SO_3^{2-}, according to the equilibrium: $2SO_3 \rightleftarrows 2SO_2 + O_2$. It should, however, be noted that it has been reported that the light alkaline metal sulphates vaporize by decomposition to the metal element, plus SO_2 and O_2 (Ficalora *et al.*, 1968). This reaction would account for the absence of SO_3 in the released gaseous phase. In this last case sulphur should be coordinated as SO_4^{2-} in scapolites.

Papike and Stevenson (1966) investigated the effect of the chemical composition of scapolite on

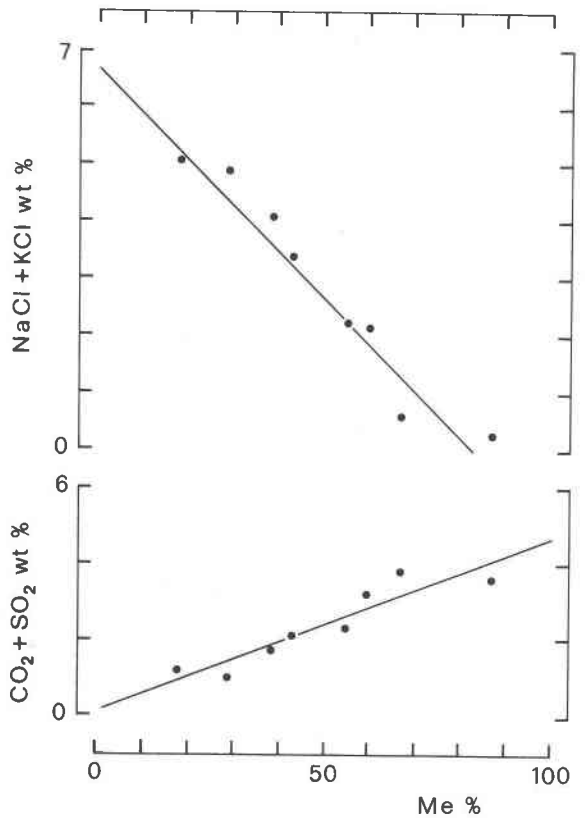

Fig. 7. Relationship between the release of volatiles and meionite content. The total CO_2 + SO_2 weight loss rises as the percentage of meionite falls, while the total NaCl + KCl weight loss fails, reaching zero at about 80% Me.

its structure, suggesting that with rising meionite content, Al^{3+} cations enter Si^{4+} tetrahedra, making them rotate and thus increasing the value of *a*.

The thermal expansion of scapolites which leads to an increase in *a* and constant *c* during heating, has already been investigated in a 33.5 percent meionite scapolite by Levien and Papike (1976) and could be attributed to the rotation of Si and Al tetrahedra in a direction opposite to that caused by chemical composition; this would lead to an opening of the cation channels and thus to an increase in the values of *a*.

The *c* parameter, on the other hand, remains constant with both compositional and thermal variation because it is difficult to rotate tetrahedra that link in that direction.

It is, however, striking that the present study, carried out on specimens representative of the whole marialite–meionite series, indicates that during heating the increases in *a* and *V* are inversely proportional to the meionite content. The relationship could be attributed to the effect of the reverse rotation of a ring of tetrahedra due to simultaneous changes in chemical composition and temperature. This hypothesis would account for the reversibility of the thermal expansion of this mineral, since in samples cooled from temperatures no higher than 800° C, *a* returns to its initial value at room temperature (Table 2). It should be noted that slight discrepancies from this behavior may be caused by cooling rate.

When heating exceeds 1000° C, an irreversible increase in *a* to anomalously high values occurs in all the examined samples. This may be due to a small degree of disordering of Al^{3+} and Si^{4+} in the tetrahedral sites (Levien and Papike, 1976), and to the breakdown of scapolite. Such breakdown produces various materials: halite, plagioclase and calcium compounds. The former easily sublimes even during short isothermal stages above 1000° C.

The plagioclase produced displays an anorthite percentage which is lower than that of the scapolite from which it derives. In addition, the emission of NaCl and KCl raises the calcium content of scapolite during the formation of plagioclase. It is remarkable that, under equilibrium conditions, the anorthite content of plagioclase, when crystallized with scapolite, is normally 20–25 percent lower than the coexisting meionite content of scapolite (Heitanen, 1967), though such behavior does not always occur, especially in calcium-rich scapolites (Haughton, 1971). Calcium compounds have not been clearly recognized in the X-ray diffraction patterns but their existence has been inferred by stoichiometric considerations bearing in mind that the unmixing of more sodic plagioclase from scapolite implies a calcium remnant which should give way to the formation of calcium aluminum silicates with lower silicon content than the contemporaneously formed plagioclase.

As a first approximation, the refractive indices, too, follow the general trend increasing their values during heating, that is, consistent with more meionitic values. However, the considerable disagreement noted in the linear regression between such increase and meionite percentage may be ascribed to the close dependence of the refractive indices of scapolite on the content of components such as S, K, H and excess carbon (Shaw, 1960). Thus the sudden and conspicuous increase in the refractive indices of all the samples examined at temperatures above 375° C could be attributed to the second release of H_2O. Conversely, the decrease in birefringence

values followed a linear trend during heating in all the samples, and did not seem to be influenced by the sudden increase in the corresponding refractive indices.

Conclusions

(1) For all the scapolites examined, the thermal analyses indicate a common trend, in which the release of volatiles occurred uninterruptedly over the whole temperature range, but with five evident specific steps corresponding to the loss of H_2O, SO_2, CO_2, NaCl, and KCl. The weight loss of the last four was correlated with meionite content.

(2) Heating resulted in linear increases in a and V that were inversely proportional to the meionitic percentage of the examined sample. The relationships between the increases in the lattice parameters, with rising temperature, and the percentage of meionite, can be expressed by the equations:

$$da/dT = -1.59 \times 10^{-6}\text{Me\%} + 1.85 \times 10^{-4} \qquad (r^2 = 0.996)$$

$$dV/dT = -0.3 \times 10^{-3}\text{Me\%} + 0.034 \qquad (r^2 = 0.998)$$

The lattice parameters in samples cooled to room temperature after heating to a maximum of 800° C returned to their initial values. In both cases c remained constant.

(3) An irreversible increase in a beyond *ca.* 1000° C was followed by the formation halite, plagioclase and possibly calcium aluminum silicates. The unmixed plagioclase was less calcic than the scapolite from which it was derived.

(4) The optical data confirmed these findings, showing an increase of the refractive indices during heating and a sharp increase corresponding to the second release of H_2O.

Acknowledgments

We wish to thank Prof. W. F. Eppler, Munich, West Germany, and Dr. P. E. Desautels, Dept. of Mineral Sciences, Smithsonian Institution, Washington, U.S.A., for their collaboration in providing some scapolite samples. We are grateful to Proff. F. Baroncelli, CNEN Laboratory of Analytical Chemistry, Casaccia, and A. D. Magri, Institute of Analytical Chemistry, University of Rome, Italy, for their kind assistance in carrying out thermal analyses. Thanks are also extended to Prof. G. Balducci and G. Gigli, Institute of Physical Chemistry, University of Rome, Italy, for performing and interpreting the mass spectrometer experiments on heating. The constructive suggestions of Prof. M. Fornaseri, Institute of Geochemistry, University of Rome, Italy, are gratefully acknowledged.

This work was supported both by the grant from the University of Rome for inclusions studies and from the Italian National Research Council (CNR), CT 80.02608.05.

References

Adams, F. D. and Barlow, A. E. (1911) Géologie des régions d'Haliburton et Bancroft, Provincie d'Ontario. Geological Survey of Canada Mémoire, 6.

Bambauer, H. U., Corlett, M., and Eberhard, E. (1967) Diagrams for the Determination of Plagioclase using X-ray Powder Methods (Part III of Laboratory Investigations on Plagioclase). Schweizerische Mineralogische und Petrographische Mitteilungen, 47, 333–349.

Brown, G. E., Sueno, S., and Prewitt, C. T. (1973) A new single crystal heater for the precession camera and four-circle diffractometer. American Mineralogist, 58, 698–704.

Buddington, A. F. (1939) Adirondack igneous rocks and their metamorphism. Geological Society of America Memoirs, 7.

Burley, B. J., Freeman, E. B., and Shaw, D. M. (1961) Studies on scapolite. Canadian Mineralogist, 6, 670–679.

Chappel, B. W. and White, A. J. R. (1968) The X-ray spectrographic determination of sulphur coordination in scapolite. American Mineralogist, 53, 1735–1738.

Donnay, G., Shaw III, C. F., Butler, I. S. and O'Neil, J. R. (1978) The presence of HCl in scapolites. Canadian Mineralogist, 16, 341–345.

Evans, B. W., Shaw, D. M., and Haughton, D. R. (1969) Scapolite stoichiometry. Contributions to Mineralogy and Petrology, 24, 293–305.

Farinato, R. and Loreto, L. (1975) A least-squares refinement of the crystal lattice constants and evaluation of their errors, using the direct unit-cell. Rendiconti della Società Italiana di Mineralogia e Petrologia, 31, 487–500.

Ficalora, P. J., Uy, O. M., Muenow, D. W., and Margrave, J. L. (1968) Mass spectrometric studies at high temperatures. XXIX, Thermal decomposition and sublimation of alkali metal sulphates. Journal of the American Ceramic Society, 51, 574–577.

Franzini, M. (1965) L'errore nella misura dell'indice di rifrazione, il metodo della deviazione minima nei prismi. Atti della Socità Toscana di Scienze Naturali, Serie A, 72, 589–593.

Gibbs, G. V. and Bloss, F. D. (1961) Indexed powder diffraction data for scapolite. American Mineralogist, 46, 1493–1497.

Goldsmith, J. R. (1976) Scapolites, granulites and volatiles in the lower crust. Geological Society of America Bulletin, 87, 161–168.

Haughton, D. R. (1971) Plagioclase–scapolite equilibrium. Canadian Mineralogist, 10, 854–870.

Hietanen, A. (1967) Scapolite in the Belt Series in the St. Joe-Clearwater Region, Idaho. Geological Society of America, Special Paper 86.

Kauffman, A. J. and Dilling, E. D. (1950) Differential thermal curves of certain hydrous and anhydrous minerals, with a description of the apparatus used. Economic Geology, 45, 222–244.

Knorring, O von and Kennedy, W. Q. (1958) The mineral paragenesis and metamorphic status of garnet–horneblende–pyroxene–scapolite gneiss from Ghana (Gold Coast), Mineralogical Magazine, 31, 846–859.

Ingamells, C. O. and Gittins, J. (1967) The stoichiometry of scapolite. Canadian Mineralogist, 9, 214–236.

Lacroix, A. (1919) Sur une scapolite des pegmatites de Madagascar constituant une gemme. Comptes Rendus de l'Accademie des Sciences, Paris, 169, 261–264.

Levien, L. and Papike, J. J. (1976) Scapolite crystal chemistry: aluminum–silicon distributions, carbonate group disorder, and thermal expansion. American Mineralogist, 61, 864–877.

Lin, S. B. and Burley, B. J. (1973a) Crystal structure of a sodium and chlorine-rich scapolite. Acta Crystallographica, B29, 1272–1278.

Lin, S. B. and Burley, B. J. (1973b) The crystal structure of meionite. Acta Crystallographica, B29, 2024–2026.

Lin, S. B. and Burley, B. J. (1975) The crystal structure of an intermediate scapolite–wernerite. Acta Crystallographica, B31, 1806–1814.

Lovering, J. F. and White, A. J. R. (1964) The significance of primary scapolite in granulitic inclusions from deep-seated pipes. Journal of Petrology, 5, 195–218.

Lovering, J. F. and White, A. J. R. (1969) Granulitic and eclogitic inclusions from basic pipes at Elegate, Australia. Contributions to Mineralogy and Petrology, 21, 9–52.

Lovering, J. F. and Widdowson, J. R. (1968) Electron microprobe determination of sulphur coordination in minerals. Lithos, 1, 264–267.

Newton, R. C. and Goldsmith, J. R. (1976) Stability of the end-member scapolites: $3NaAlSi_3O_8 + NaCl$, $3CaAl_2Si_2O_8 + CaCO_3$, $3CaAl_2Si_2O_8 + CaSo_4$. Zeitschrift für Kristallographie, 143, 333–353.

Papike, J. J. (1964) The crystal structure and crystal chemistry of scapolite. Ph.D. Thesis, University of Minnesota.

Papike, J. J. and Zoltai, T. (1965) The crystal structure of a marialite scapolite. American Mineralogist, 50, 641–655.

Papike, J. J. and Stephenson, N. C. (1966) The crystal structure of mizzonite, calcium- and carbonate-rich scapolite. American Mineralogist, 51, 1014–1027.

Rucklidge, J. and Gasperrini, E. L. (1969) Electron microprobe analytical data reduction. EMPADR VII. Manual reissue, Department of Geology, University of Toronto, Toronto, Canada.

Scarano, E. and Calcagno, C. (1975) High sensitivity carbon dioxide analyser. Analytical Chemistry, 47, 1055–1065.

Scherillo, A. (1935) La meionite del Somma-Vesuvio. Periodico di Mineralogia, 6, 227–239.

Schwarcz, H. P. and Speelman, E. L. (1965) Determination of sulphur and carbon coordination in scapolite by infrared absorption spectrophotometry. American Mineralogist, 50, 656–666.

Shaw, D. M. (1960) The geochemistry of scapolite. Part I. Previous work and general mineralogy. Journal of Petrology, 1, 218–260.

Solesbury, F. W. (1967) Gem corundum pegmatites in NE Tanganyka. Economic Geology, 62, 983–991.

Stewart, G. W. (1941) Idocrase and scapolite from Manchester, New Hampshire. American Mineralogist, 26, 509–511.

Strunz, H. (1978) Mineralogische Tabellen. Geest and Porting, Leipzig.

Ulbrich, H. H. (1973) Cristallographic data and refractive indices of scapolites. American Mineralogist, 58, 81–92.

Zwaan, P. C. (1971) Yellow scapolite, another gem–mineral from Umba, Tanzania. Journal of Gemmology, 12, 304–309.

Manuscript received, August 5, 1981;
accepted for publication, April 28, 1982.