

THERMAL BEHAVIOR OF SCAPOLITE $Me_{79.6}$ AND $Me_{33.3}$

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ABSTRACT

Scapolite-group minerals have the general formula $(Na,Ca,K)_4[(Al,Si)_{12}O_{24}](Cl,CO_3,SO_4)$. Thermal analyses (DTA, DSC, and TG) were carried out on two samples ($Me_{79.6}$ and $Me_{33.3}$) using a Netzsch STA 409 EP/3/D simultaneous TG–DTA apparatus and a Netzsch STA 449C simultaneous TG–DSC instrument. The DTA–TG results indicate that $Me_{79.6}$ loses 5.7 wt.% in two steps at different rates: at 1171°C, $CO_2(g)$ and minor NaCl are lost together, followed by a small amount of $SO_3(g)$ at about 1232°C, and the residue melts at 1407°C. High-temperature X-ray-diffraction (XRD) data also indicate that the $Me_{79.6}$ residue melts between 1300 and 1400°C. $Me_{33.3}$ loses 5.2 wt.% of NaCl, $CO_2(g)$, and minor $SO_3(g)$ in a single step at 1199°C, and the residue melts at 1319°C. The residue of $Me_{79.6}$ melts at a higher temperature than $Me_{33.3}$ because its framework composition is closer to that of anorthite, whereas that of $Me_{33.3}$ is closer to that of albite. The cage clusters $[Na_4 \bullet Cl]^{3+}$ and $[NaCa_3 \bullet CO_3]^{5+}$ in $Me_{33.3}$ are ordered, whereas the clusters $[NaCa_3 \bullet CO_3]^{5+}$ and $[Ca_4 \bullet CO_3]^{6+}$ in $Me_{79.6}$ are disordered. The DSC curve for scapolite $Me_{33.3}$ shows a transition at about 299°C arising from disordering of $[Na_4 \bullet Cl]^{3+}$ and $[NaCa_3 \bullet CO_3]^{5+}$ clusters on heating.

Keywords: scapolite-group minerals, solid solution, differential thermal analysis, thermogravimetry, differential scanning calorimetry, X-ray diffraction.

SOMMAIRE

Les minéraux du groupe de la scapolite répondent à la formule générale $(Na,Ca,K)_4[(Al,Si)_{12}O_{24}](Cl,CO_3,SO_4)$. Nous avons effectué des analyses thermiques [analyse thermique différentielle (DTA), calorimétrie différentielle à balayage (DSC), et thermogravimétrie (TG)] sur deux échantillons, $Me_{79.6}$ et $Me_{33.3}$, avec des appareils Netzsch STA 409 EP/3/D (spectres TG–DTA simultanés) et Netzsch STA 449C (spectres TG–DSC simultanés). Les résultats DTA–TG montrent que $Me_{79.6}$ perd 5.7% de sa masse en deux étapes à des taux différents: à 1171°C, $CO_2(g)$ et la proportion mineure de NaCl partent ensemble, et ensuite, la faible quantité de $SO_3(g)$ à environ 1232°C, et le résidu fond à 1407°C. Une analyse par diffraction X (XRD) à température élevée révèle que le résidu de $Me_{79.6}$ fond entre 1300 et 1400°C. Par contre, $Me_{33.3}$ perd 5.2% de sa masse sous forme de NaCl, $CO_2(g)$, et la faible fraction de $SO_3(g)$ dans une seule étape, à 1199°C, et le résidu fond à 1319°C. Le résidu de $Me_{79.6}$ fond à une température plus élevée que le résidu de $Me_{33.3}$ parce que sa composition se rapproche davantage de l'anorthite, tandis que la composition de l'échantillon de $Me_{33.3}$ est plus semblable à l'albite. Les groupements des cages dans la structure de $Me_{33.3}$, $[Na_4 \bullet Cl]^{3+}$ et $[NaCa_3 \bullet CO_3]^{5+}$, sont ordonnés, tandis que les groupements $[NaCa_3 \bullet CO_3]^{5+}$ et $[Ca_4 \bullet CO_3]^{6+}$ des cages de $Me_{79.6}$ sont désordonnés. La courbe DSC pour la scapolite $Me_{33.3}$ montre une transition à environ 299°C à cause du désordre du contenu des cages, $[Na_4 \bullet Cl]^{3+}$ et $[NaCa_3 \bullet CO_3]^{5+}$, lors du réchauffement.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe de la scapolite, solution solide, analyse thermique différentielle, thermogravimétrie, calorimétrie différentielle à balayage, diffraction X.

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INTRODUCTION

Scapolites are a common group of rock-forming framework minerals that occur in a wide variety of metamorphic and altered igneous rocks (see Deer *et al.* 1992). Scapolites may also be storage sites for volatiles in the lower crust and upper mantle (Lovering & White 1969). The framework of scapolite consists of AlO_4 and SiO_4 tetrahedra, which form four-membered rings. These rings define continuous oval-shaped channels parallel to the z axis that contain Na^+ and Ca^{2+} cations, and larger cages that contain Cl^- and CO_3^{2-} anions. Each Cl^- and CO_3^{2-} anion is coordinated by four (Na, Ca) cations (Fig. 1). The resulting anion-cation cage clusters are centered at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ in space group $P4_2/n$ (origin choice 2; Levien & Papike 1976).

Scapolites form two solid solutions between the end-members marialite, $\text{Na}_4[\text{Al}_3\text{Si}_9\text{O}_{24}]\text{Cl} = \text{Me}_0$, and meionite, $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{CO}_3 = \text{Me}_{100}$ (*e.g.*, Hassan & Buseck 1988, Deer *et al.* 1992). By analogy with the

plagioclase series, the two end members may be expressed as $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$ (marialite) and $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$ (meionite). In some scapolites, there is a significant content of SO_4^{2-} anions that may result from a solid solution toward an ideal sulfatic end-member, silvialite, $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4$ (Teertstra *et al.* 1999, Deer *et al.* 1992). The meionite percentage [%Me = $100\text{Ca}/(\text{Na} + \text{Ca})$] may be used as a chemical index to indicate the composition of scapolite (Shaw 1960). Two continuous solid-solutions occur in scapolites: series (a) occurs between 0 and 75% meionite, *i.e.*, between Me_0 and $\text{NaCa}_3[\text{Al}_5\text{Si}_7\text{O}_{24}]\text{CO}_3 = \text{Me}_{75}$, and series (b) occurs between Me_{75} and Me_{100} (*e.g.*, Hassan & Buseck 1988, Deer *et al.* 1992). There is no sharp structural break at Me_{75} . Series (a) is governed by the replacement of $[\text{Na}_4 \cdot \text{Cl}]\text{Si}_2$ for $[\text{NaCa}_3 \cdot \text{CO}_3]\text{Al}_2$, whereas series (b) is governed by the replacement of $[\text{NaCa}_3 \cdot \text{CO}_3]\text{Si}$ for $[\text{Ca}_4 \cdot \text{CO}_3]\text{Al}$. The cage clusters $[\text{Na}_4 \cdot \text{Cl}]^{3+}$ and $[\text{NaCa}_3 \cdot \text{CO}_3]^{5+}$ in series (a) are ordered, whereas the clusters $[\text{NaCa}_3 \cdot \text{CO}_3]^{5+}$ and $[\text{Ca}_4 \cdot \text{CO}_3]^{6+}$ in series (b) are disor-

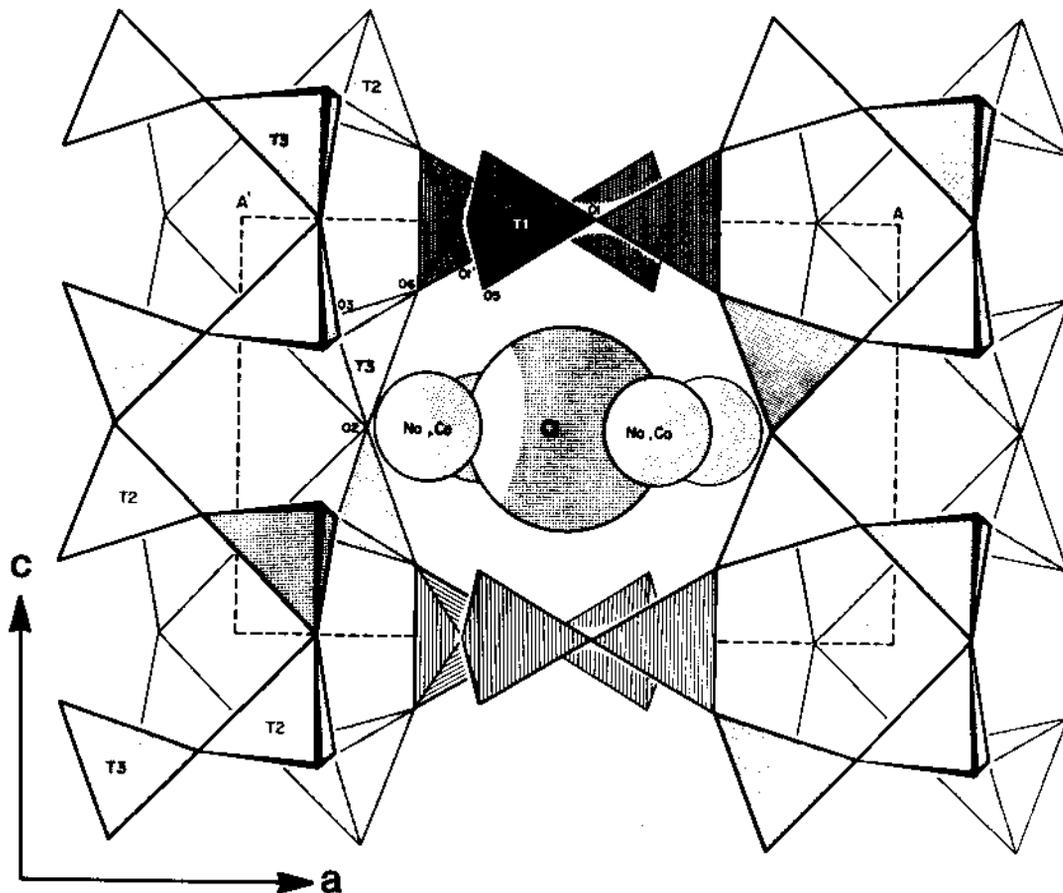


FIG. 1. Crystal structure of $P4_2/n$ scapolite $\text{Me}_{33.3}$ projected along b , showing the cage clusters (from Levien & Papike 1976).

dered (Hassan & Buseck 1988). One composition of scapolite from each of the two solid solutions (*i.e.*, Me_{79,6} and Me_{33,3}) were investigated in this study. One aim is to determine whether the [Na₄•Cl]³⁺ and [NaCa₃•CO₃]⁵⁺ clusters in series (a) change from the ordered to the disordered state on heating.

BACKGROUND INFORMATION

The *a* and *V* of scapolite increase linearly during heating, whereas *c* remains unchanged (Levien & Papike 1976, Graziani & Lucchesi 1982, Baker 1994). These unit-cell parameters are reversible on heating up to 800°C. The thermal expansion of scapolite is a function of composition. The *a* and *V* increase approximately linearly with increasing meionite content (Lin & Burley 1973), with a trend inversely proportional to the percentage of meionite present (Graziani & Lucchesi 1982). However, Baker (1994) showed that this variation is nonlinear, especially for the more calcic compositions. The cell parameters vary with framework composition and Al–Si order, but the influence of the interframework ions is only minor (Teertstra & Sherriff 1996).

Recently, a number of studies were carried out on the scapolite series (*e.g.*, Sokolova *et al.* 1996, 2000, Sherriff *et al.* 1998, 2000, Teertstra *et al.* 1999). Sherriff *et al.* (2000) examined trends in structural parameters and NMR spectra for the scapolite series and divided the series into three subseries. In this present study, we focus mainly on the ordering of clusters.

The results of chemical analyses of the scapolite samples used in this study indicate that Cl, CO₂ and SO₃ are the important volatiles that could be liberated on heating (Table 1). The temperatures where ordering or

disordering of clusters occurred, where volatiles were liberated, and where melting occurred were determined using differential thermal analysis (DTA), thermogravimetric (TG), and differential scanning calorimetry (DSC) techniques. The results for Me_{79,6} and Me_{33,3} are compared.

EXPERIMENTAL METHODS

One sample of scapolite, ON47, has a composition Me_{79,6}; it is from a skarn deposit, from Slyudyanka, Siberia, Russia. The crystals are white, bladed, and brittle. Sample ON7, with a composition Me_{33,3}, is from Monmouth Township, Ontario. Scapolite ON7 is a white, coarsely crystalline sample from a calcareous gneiss. Both of these samples have been well characterized (*e.g.*, Evans *et al.* 1969, Hassan & Buseck 1988, Teertstra & Sherriff 1996). Clean crystals of scapolite were handpicked and crushed to a powder using an agate mortar and pestle. Portions of the powder were used for simultaneous DTA–TG analyses, simultaneous DSC–TG analyses, and high-temperature X-ray diffraction (XRD).

A weighed amount of powdered sample (about 100 mg) was placed into an Al₂O₃ crucible for simultaneous DTA and TG analyses. The measurements were made in a static air environment with a fully computerized Netzsch STA 409 EP/3/D simultaneous TG–DTA instrument. The experimental technique was described by Hassan (1996). The TG curve was corrected for buoyancy effect, and the DTA curve was corrected for baseline effect. Corrections for buoyancy and baseline effects were obtained in a blank run using empty crucibles that were later used to run the sample in a second run, but the two experimental runs were made under identical conditions. The relationship between change in enthalpy and peak area in the DTA curve was determined by calibration using various standard materials.

The TG–DSC experiment was carried out using a fully computerized Netzsch STA 449C simultaneous TG–DSC instrument. About 6 mg of sample was heated at a rate of 10°C/min. from room temperature to 1200°C in a static air environment. The experimental details are similar to those described by Hassan (1996).

For sample Me_{79,6}, XRD data were also obtained using a fully computerized Siemens D5000 Diffractometer operating in the vertical position and in the θ – 2θ operating mode. CuK α radiation, obtained with a Ni filter, was used in conjunction with a position-sensitive detector. Data were collected for the 2θ range of 6 to 110°. A continuous scan was used with a step size of 0.014° and step time of 60.0 s. Data were collected at 25°C, 100°C, and thereafter at intervals of 100° to a maximum temperature of 1400°C.

TABLE 1. CHEMICAL COMPOSITION OF SCAPOLITE SAMPLES[†]

| Oxides | Me _{79,6} (ON47) | | Me _{33,3} (ON7) | | |
|--------------------------------|---------------------------|----------|--------------------------------|-------|----------|
| | wt.% | apfu | wt.% | apfu | |
| SiO ₂ | 44.00 | Si 6.836 | SiO ₂ | 55.20 | Si 8.082 |
| Al ₂ O ₃ | 28.20 | Al 5.164 | Al ₂ O ₃ | 22.70 | Al 3.918 |
| Na ₂ O | 2.55 | Na 0.768 | Na ₂ O | 8.30 | Na 2.356 |
| CaO | 18.90 | Ca 3.146 | CaO | 8.25 | Ca 1.294 |
| K ₂ O | 0.20 | K 0.640 | K ₂ O | 1.50 | K 0.280 |
| Cl | 0.03 | Cl 0.098 | Cl | 2.44 | Cl 0.606 |
| CO ₂ | 3.20 | C 0.668 | CO ₂ | 1.50 | C 0.300 |
| SO ₃ | 2.02 | S 0.235 | SO ₃ | 0.17 | S 0.019 |
| others ‡ | 0.29 | 0.029 | others ‡ | 0.39 | 0.037 |
| O–Cl | 0.01 | | 0.55 | | |
| Σ | 99.37 | | 99.91 | | |

[†] Analytical data, from Evans *et al.* (1969), are based on Al + Si = 12 atoms per formula unit (apfu).

[‡] Sum of TiO₂, Fe₂O₃, MnO, MgO, SrO, and P₂O₅; F < 0.05%.

Me_{79,6} is from Slyudyanka, Russia; Me_{33,3} is from Monmouth Township, Ontario, Canada.

RESULTS AND DISCUSSION

Scapolite $Me_{79.6}$

For the simultaneous DTA–TG analyses, 106.7 mg of finely powdered $Me_{79.6}$ was used. The TG and DTA curves and their corresponding derivative curves (DTG and DDTA, respectively) are shown (Fig. 2). Data obtained from these curves are summarized (Table 2).

Three peaks are observed in the DTA curve (Fig. 2); peaks 1 and 3 are well defined in both the DTA and DDTA curves, but the weak peak 2 is visible. Peaks 1 and 2 in the DTA curve are related to the loss of volatiles and correspond to the continuous weight-loss section in the TG curve (Fig. 2). Once volatiles are lost from the mineral, the resulting material is referred to as the residue. Peak 3 at 1407°C is related to the melting of $Me_{79.6}$ residue because there is no significant weight-loss in the TG curve. Melt (glass) was also visible in the crucible after the experiment. The high-temperature XRD traces indicate that $Me_{79.6}$ melts between 1300 and 1400°C because the XRD peaks at 1400°C are insignificant.

The DTG trace contains a well-defined peak 1 (Fig. 2). Peak 2 in the DTA trace does not show up clearly in the DTG trace (although it is related to a weight loss) probably because of the slow rate of loss in the TG curve over peak 2 compared to peak 1. From the

TABLE 2. CHARACTERISTIC DATA FOR SCAPOLITE $Me_{79.6}$ AND $Me_{33.1}$

| | $Me_{79.6}$ (ON47) | | | | $Me_{33.1}$ (ON7) | | | |
|----------------|--------------------|------|--------|------|-------------------|------|------|------|
| | TG | DTG | DTA | DDTA | TG | DTG | DTA | DDTA |
| | Peak 1 † | | | | | | | |
| Onset-T (°C) | 1156 | 1145 | 1152 | 1159 | 1108 | 1076 | 1077 | 1180 |
| Peak-T (°C) | | 1176 | 1171 | | | 1195 | 1199 | |
| End-T (°C) | 1199 | 1218 | 1222 | 1197 | 1222 | 1222 | 1225 | 1212 |
| % Wt. Loss | 4.4 | | | | 5.2 | | | |
| Enthalpy (J/g) | | | -2.34 | | | | 2.02 | |
| | Peak 2 ‡ | | | | | | | |
| Onset-T (°C) | 1199 | | 1222 | 1229 | | | | |
| Peak-T (°C) | | | 1232 | | | | | |
| End-T (°C) | | | 1250 | 1243 | | | | |
| % Wt. Loss | 1.3 | | | | | | | |
| Enthalpy (J/g) | | | -0.05 | | | | | |
| | Peak 3 ‡ | | | | | | | |
| Onset-T (°C) | | | 1355 | 1393 | | | 1225 | 1270 |
| Peak-T (°C) | | | 1407 | | | | 1319 | |
| End-T (°C) | | | --- | 1418 | | | 1371 | 1355 |
| Enthalpy (J/g) | | | -33.51 | | | | 3.05 | |

† Endothermic (peaks 1, 2, and 3 in $Me_{79.6}$), † exothermic (peaks 1 and 3 in $Me_{33.1}$). Peak 1 corresponds to loss of $CO_2(g)$ and NaCl in $Me_{79.6}$, and NaCl, $CO_2(g)$, and $SO_3(g)$ in $Me_{33.1}$.

‡ Peak 2 corresponds to loss of $SO_3(g)$ in $Me_{79.6}$. Peak 3 corresponds to melting in both samples.

For $Me_{79.6}$, total % wt. loss from start to finish is 6.4, including 0.7 at the beginning. For $Me_{33.1}$, total % wt. loss from start to finish is 6.0, including 0.8 at the beginning.

TG curve, a total weight-loss of 5.7 wt.% is obtained over peaks 1 and 2 (Table 2). This weight loss is attributed to the loss of $CO_2(g)$, $SO_3(g)$, and minor NaCl. From Table 1, the content of Cl in $Me_{79.6}$ is 0.008 *apfu*. This Cl is liberated in the form of NaCl, by analogy with sodalite-group minerals (Antao & Hassan 2002), and 0.008 *apfu* NaCl corresponds to 0.05 wt.% NaCl. The total wt.% of SO_3 , CO_2 , and 0.008 *apfu* NaCl is 5.5% (Table 1), which is comparable to 5.7 wt.% loss obtained from the TG curve (Table 2). Possibly both $CO_2(g)$ and the minor NaCl are liberated rapidly together at 1171°C, and are followed by $SO_3(g)$ at 1232°C (as indicated by the DTA curve). The total wt.% of CO_2 and 0.008 *apfu* NaCl is 3.25, compared to 4.4 wt.% obtained from the

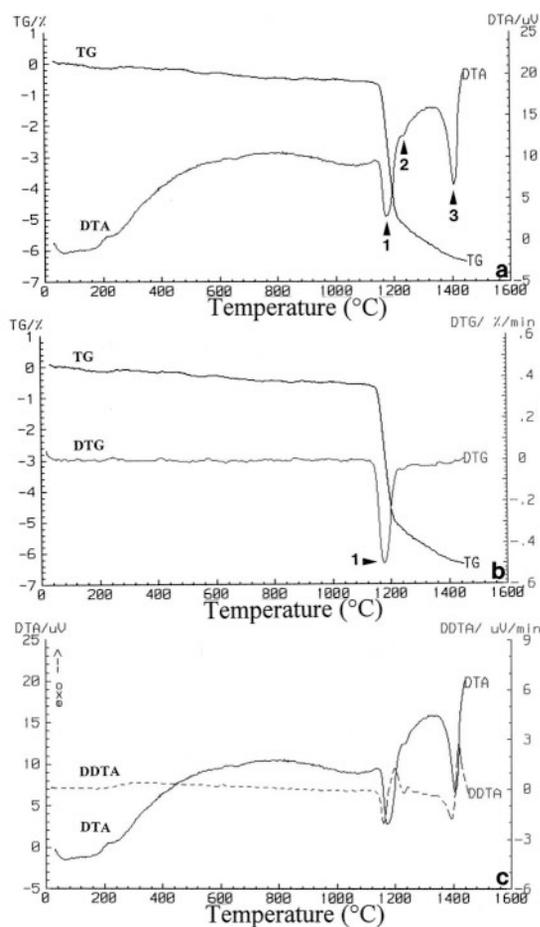


FIG. 2. Scapolite $Me_{79.6}$: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves. Corresponding peaks at a particular temperature are given the same number and are labeled on the DTA and DTG curves in this figure and in Figure 3. The exothermic direction is shown in c, along the vertical axis.

TG curve, and the wt.% of SO_3 is 2.02 compared to 1.3 wt.% obtained from the TG curve (Tables 1, 2).

The scapolite-group minerals are similar to the sodalite- and cancrinite-group minerals because they are all framework minerals that contain similar anions (e.g., Hassan 1997). In cancrinite, $CO_2(g)$ is liberated at 947°C (Hassan 1996), whereas in $Me_{79,6}$, $CO_2(g)$ together with NaCl are liberated at a higher temperature (1171°C). NaCl is also liberated in sodalite and tugtuptite (Antao & Hassan 2002). In sodalite, NaCl is liberated in two steps, at 1150 and 1284°C. In lazurite, $SO_3(g)$ is liberated in three steps, at 1320, 1370, and 1412°C (Hassan 2000), i.e., all at temperatures higher than 1232°C observed for the loss of SO_3 in $Me_{79,6}$ (Table 2).

Scapolite $Me_{33,3}$

For the DTA–TG analyses, 100.5 mg of finely powdered $Me_{33,3}$ was used. The thermal curves for $Me_{33,3}$ are shown in Figure 3; the data from these curves are summarized in Table 2. Two well-defined peaks are observed in the DTA curve (peaks 1 and 3, Fig. 3) and they are labeled according to those in $Me_{79,6}$. Peak 1 in the DTA curve is related to the loss of volatiles, and peak 3 at 1319°C is related to the melting of the residue of $Me_{33,3}$. The DTG trace contains a well-defined peak 1 at 1195°C, which corresponds to a weight loss of 5.2 wt.% (Table 2, Fig. 3). This weight loss is attributed to the loss of NaCl, $CO_2(g)$, and minor amounts of $SO_3(g)$. From results of the chemical analysis of $Me_{33,3}$, the content of Cl is 0.6 *apfu* (Table 1), and the theoretical wt.% corresponding to 0.6 NaCl is 4.06. The total wt.% of 0.6 NaCl, CO_2 , and SO_3 is 5.7 wt.% (Table 1), which is comparable to the weight-loss result (5.2 wt.%) obtained from the TG curve.

Previous thermal studies on scapolite indicate that in the temperature range up to 800°C, H_2O , SO_2 , CO_2 , NaCl and KCl are liberated in five discernable steps of weight loss (Graziani & Lucchesi 1982, Deer *et al.* 1992). At about 200–400°C, H_2O is lost, SO_2 at 300–600°C, and CO_2 at 400–800°C. Beyond about 800°C, NaCl and KCl are volatilized. However, in this study, the results obtained are quite different: the weight loss occurs in one continuous step and begins at temperatures beyond 1100°C. Moreover, our results are also supported by those of Baker (1994), who indicated that the unit-cell parameters for scapolite are reversible on heating up to 800°C.

The residue of $Me_{33,3}$ melts at a lower temperature than that of $Me_{79,6}$. This finding is related to the chemical composition of the two scapolite-group minerals. The framework composition of $Me_{79,6}$ is closer to anorthite, and anorthite melts at a higher temperature than albite. Therefore, $Me_{79,6}$ residue melts at a higher temperature than $Me_{33,3}$. Weight loss occurs at a higher temperature in $Me_{33,3}$ than in $Me_{79,6}$.

The DTA curve for $Me_{79,6}$ rises from the base line (Fig. 2), but in $Me_{33,3}$, the DTA curve drops from the baseline with increasing temperature (Fig. 3). The DTA peaks in $Me_{33,3}$ are exothermic, whereas those in $Me_{79,6}$ are endothermic. The clusters $[NaCa_3 \cdot CO_3]^{5+}$ and $[Ca_4 \cdot CO_3]^{6+}$ in $Me_{79,6}$ are disordered (Hassan & Buseck 1988), so no transition is expected. The cage clusters $[Na_4 \cdot Cl]^{3+}$ and $[NaCa_3 \cdot CO_3]^{5+}$ in $Me_{33,3}$ are ordered (Hassan & Buseck 1988), but the DTA result does not indicate disordering of the cage clusters on heating, probably because the DTA technique is not sensitive enough, and possibly the energy involved in this transition is very small. Therefore, DSC, a technique more sensitive than DTA, was used to observe this transition.

The DSC and TG curves for $Me_{33,3}$ and $Me_{79,6}$ are shown in Figure 4, which also contains some characteristic data. A weight loss of 5.1 wt.% was obtained over

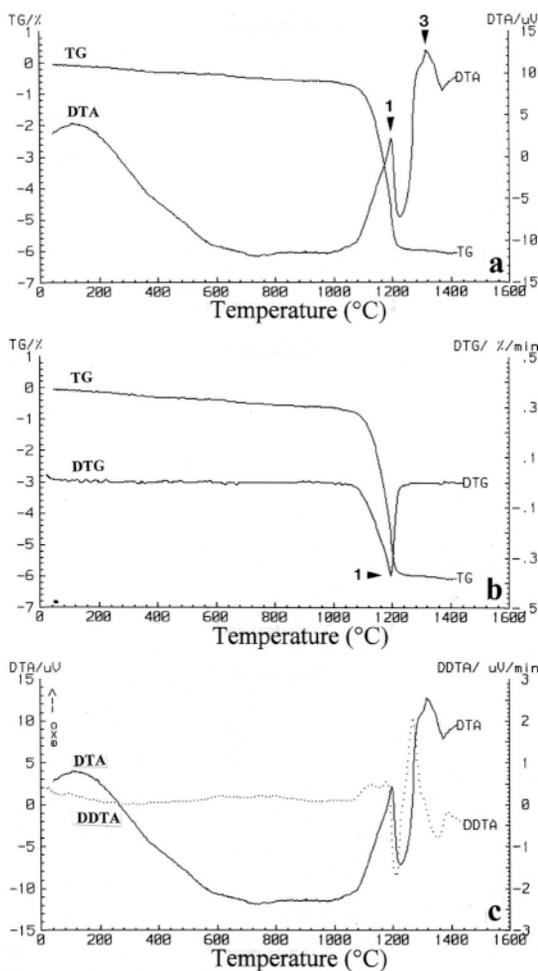


FIG. 3. Scapolite $Me_{33,3}$: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves. The exothermic direction is shown in c, along the vertical axis.

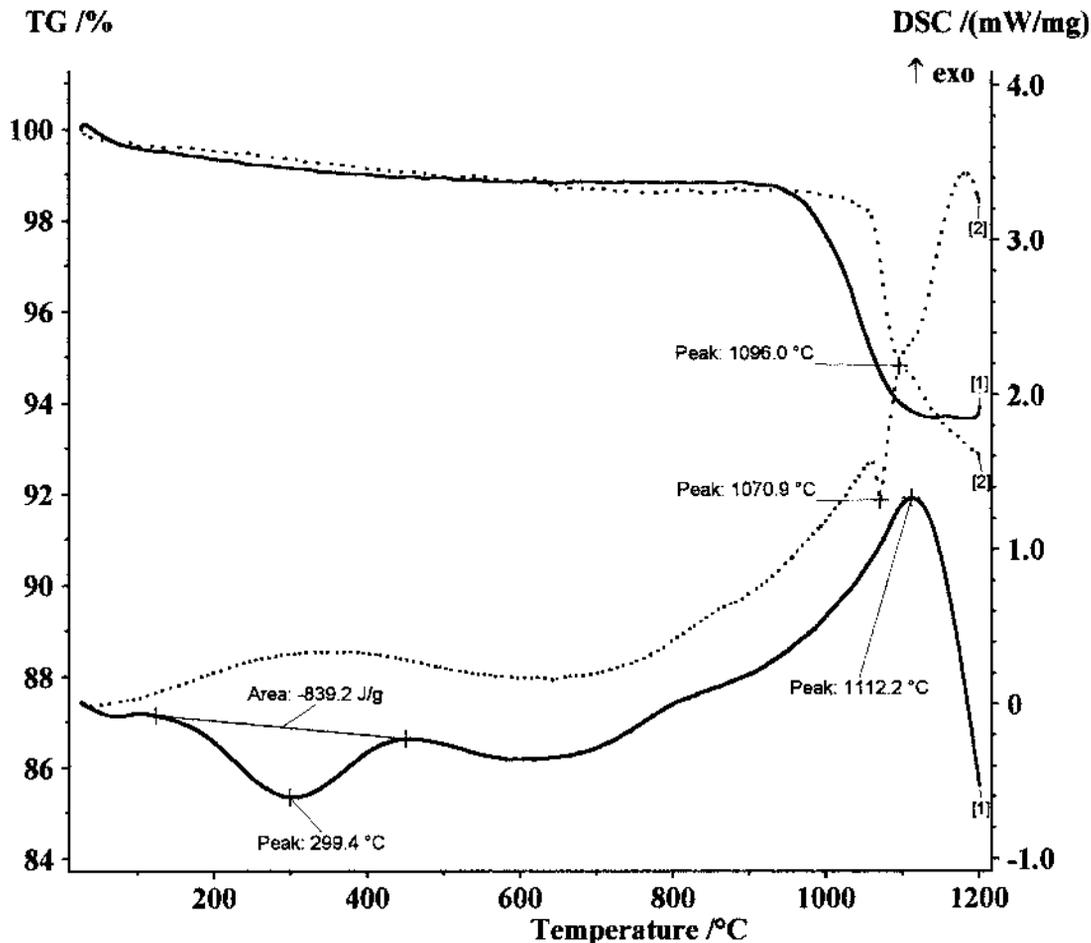


Fig. 4. TG and DSC curves for Me_{33.3} ([1], solid) and Me_{79.6} ([2], dotted). The TG curves are at the top and start at 100% on the TG axis (left). The DSC curves are at the bottom and start at 0 on the DSC axis (right). The exothermic direction is shown. For Me_{79.6}, the peaks at 1071° and 1096°C are referred to as peaks 1 and 2, respectively, for comparison to the DTA peaks. For Me_{33.3}, the peak at 1112°C is referred to as peak 1 for comparison with the DTA peak, and the peak at 299°C is an endothermic peak due to the disordering of clusters with a total enthalpy of -839 J/g.

peak 1 at 1112°C from the DSC-TG data for Me_{33.3}. This loss is comparable to the weight loss of 5.2 wt.% obtained from the DTA-TG data for Me_{33.3} at 1199°C (peak 1). Peak 3 in the DTA curve was not observed in the DSC experiment for Me_{33.3} because the experiment was stopped at 1200°C. Peak 1 in both the DTA and DSC experiments is an exothermic peak. A total weight-loss of 5.7 wt.% was obtained for Me_{79.6} over peak 1 at 1071°C and peak 2 at 1096°C from the DSC-TG data, and the same amount was obtained over peaks 1 and 2 at 1171 and 1232°C, respectively, from the DTA-TG data. Peak 3 in the DTA curve was not observed in the DSC experiment for Me_{79.6} because the experiment was run to 1200°C. At 1182°C, there appears to be a peak,

but by comparison with the DTA curve for Me_{79.6}, the DSC curve is dropping to form an endothermic peak 3, as in the DTA curve. Peaks 1 and 2 in both the DTA and DSC experiments are endothermic peaks. The temperatures obtained for the corresponding peaks using DSC and DTA are different and may be related to sample size. A smaller amount of sample is used in the DSC than in the DTA experiment.

Comparing the DSC curves for Me_{33.3} and Me_{79.6}, the Me_{33.3} sample contains a peak at about 299°C, which is absent in the Me_{79.6} sample. This peak is attributed to the disordering of the cage clusters, [Na₄•Cl]³⁺ and [NaCa₃•CO₃]⁵⁺ in the Me_{33.3} sample. The corresponding peak is absent in the Me_{79.6} sample because the clus-

ters [NaCa₃•CO₃]⁵⁺ and [Ca₄•CO₃]⁶⁺ are initially disordered. These order–disorder observations are consistent with the HRTEM results of Hassan & Buseck (1988). In a recent study of nepheline (Hassan *et al.* 2002), the DTA curve did not show peaks corresponding to order–disorder of atoms and vacancies. However, the DSC curve showed two peaks corresponding to these events in a temperature range from 20 to 500°C. These results indicate that the DSC technique is more sensitive than the DTA technique in monitoring disordering.

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