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THERMAL ANALYSES OF SODALITE, TUGTUPITE, DANALITE AND HELVITE

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ABSTRACT

Differential thermal analyses (DTA) and thermogravimetric analyses (TG) were carried out on sodalite, tugtupite, danalite, and helvite using a Netzsch STA 409 EP/3/D simultaneous TG–DTA apparatus. In the DTA and TG experimental run, a weighed amount of finely powdered sample was heated from 20 to 1450°C at a constant rate of 5°C/min. Sodalite, $Na_8[Al_6Si_6O_{24}]Cl_2$, melts at 1079°C. The NaCl component in the sodalite-derived melt is lost in two stages; about 4.5 wt.% of NaCl is lost slowly at about 1150°C, and about 7.0 wt.% of NaCl is lost at a faster rate at about 1284°C. The interpretation that the NaCl component behaves this way in sodalite is confirmed by DTA and TG analyses of halite. Tugtupite, $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, melts at 1029°C. The NaCl component in tugtupite is lost in two main stages; about 1.8 wt.% of NaCl is first lost at about 1007°C, and about 8.2 wt.% of NaCl is lost in several steps between about 1018 and about 1442°C. Danalite, ideally $Fe_8[Be_6Si_6O_{24}]S_2$, and helvite, ideally $Mn_8[Be_6Si_6O_{24}]S_2$, undergo an oxidation of $(Mn, Fe)^{2+}$ to $(Mn, Fe)^{3+}$ cations. This is followed by a loss of $S_2(g)$, and then melting at about 1060°C. Finally, there is another oxidation of Mn^{3+} to Mn^{4+}. These oxidations occur because the samples were heated in a static air environment. The first oxidation in danalite and helvite begins at about 771 and 705°C, respectively. Danalite gains 4.0 wt.%, whereas helvite gains 5.0 wt.% in the first weight-gain stage. In the weight-loss stage, danalite loses 5.7 wt.% of $S_2(g)$ from about 1029°C, whereas helvite loses 4.7 wt.% of $S_2(g)$ from about 883°C. The second stage of oxidation begins at about 1300°C in both the danalite- and helvite-derived melts. At this stage, the weight gain in the danalite-derived melt is about 0.7%, whereas that in the helvite-derived melt is about 0.2%.

Keywords: sodalite, tugtupite, danalite, helvite, differential thermal analysis, thermogravimetric analysis.

SOMMAIRE

Nous avons étudié la sodalite, la tugtupite, la danalite et la helvite par analyses thermique différentielle (ATD) et thermogravimétrique (TG) en utilisant un appareil Netzsch STA 409 EP/3/D. Pour ces expériences, nous nous sommes servis d'une quantité connue d'échantillon finement pulvérisé, chauffé à partir de 20 jusqu'à 1450°C à un taux constant de 5°C/min. La sodalite, $Na_8[Al_6Si_6O_{24}]Cl_2$, atteint son point de fusion à 1079°C. La composante NaCl du bain fondu se volatilise en deux étapes; environ 4.5% (poids) de NaCl est perdu lentement près de 1150°C, et environ 7.0% est perdu plus rapidement près de 1284°C. Notre interpretation à propos de la sodalite est confirmée par analyses ADT et TG de la halite. La tugtupite, $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, fond à 1029°C. La composante NaCl de la tugtupite se volatilise en deux étapes; environ 1.8% de NaCl se perd près de 1007°C, et environ 8.2% de NaCl se perd en plusieurs étapes entre 1018 et 1442°C. La danalite, dont la composition idéale est $Fe_8[Be_6Si_6O_{24}]S_2$, et la helvite, $Mn_8[Be_6Si_6O_{24}]S_2$, subissent une oxydation de $(Mn, Fe)^{2+}$ à $(Mn, Fe)^{3+}$. Cette transformation est suivie d'une perte de $S_2(g)$, et de la fusion à environ 1060°C. Enfin, il y a une oxydation plus poussée de Mn^{3+} à Mn^{4+}. Ces étapes d'oxydation sont le résultat du chauffage des échantillons dans l'air, dans un milieu statique. La première étape d'oxydation de la danalite et de la helvite débute à environ 771 et 705°C, respectivement. La danalite augmente en poids de 4.0%, tandis que la helvite augmente de 5.0%. Suit ensuite une perte de poids, 5.7% sous forme de $S_2(g)$ pour la danalite à partir de 1029°C, et 4.7% de $S_2(g)$ à partir de 883°C pour la helvite. Le second stade d'oxydation débute à environ 1300°C dans les liquides dérivés de la danalite et de la helvite. L'augmentation en poids à ce stade est d'environ 0.7% pour le cas de la danalite et 0.2% pour le cas de la helvite.

(Traduit par la Rédaction)

Mots-clés: sodalite, tugtupite, danalite, helvite, analyse thermique différentielle, analyse thermogravimétrique.

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Introduction

Our aim in this study is to determine the thermal behavior of sodalite, tugtupite, danalite, and helvite using differential thermal analysis (DTA) and thermogravimetry (TG) techniques. The types of volatiles liberated and the temperatures at which liberation occurs are determined, among other features.

In sodalite and tugtupite, Cl and possibly Na are important volatile constituents that may be liberated on heating. If the formula of sodalite is written as $Na_8[Al_6Si_6O_{24}]Cl_2$, then Cl_2 (g) could be expected to be liberated on heating; however, if the sodalite formula is written as $Na_6[Al_6Si_6O_{24}]{\bullet}2NaCl$, then NaCl could be liberated on heating; similarly for tugtupite, $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, which can be written as $Na_6[Al_2Be_2Si_8O_{24}]{\bullet}2NaCl$. This study was carried out to determine which chemical constituents are liberated on heating, to measure the temperature where changes take place, and to compare the results for sodalite and tugtupite. If NaCl is liberated, then it would be of interest to compare the results for sodalite and tugtupite with those for halite, NaCl. For this purpose, halite also was analyzed by the differential thermal analysis (DTA) and thermogravimetric analysis (TG) techniques.

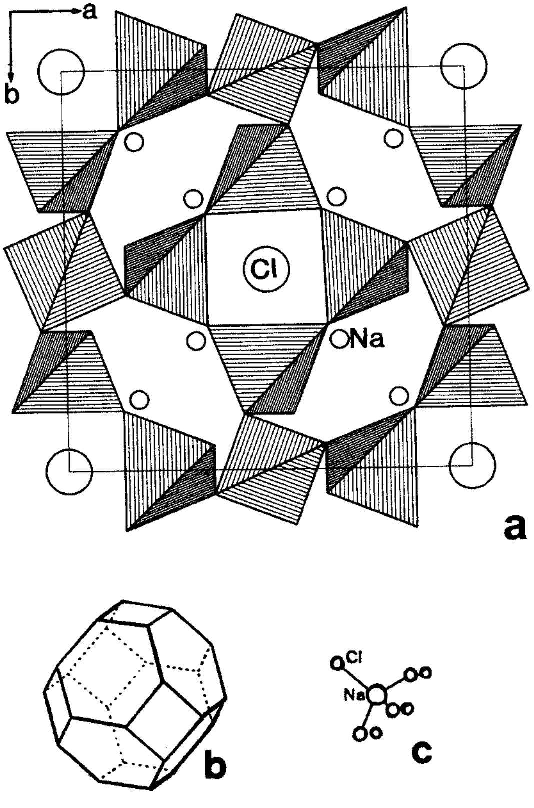

FIG. 1. (a) Projection of the unit cell of the sodalite structure down [001], drawn using the program STRUPLO. (b) The truncated cubo-octahedral or β-cage in sodalite. (c) Fourfold (trigonal pyramid) coordination of the Na site in sodalite.

From the chemical composition of danalite and helvite, S is an important volatile that could be liberated on heating. Therefore, this study on danalite and helvite was carried out to determine the temperature where S_2(g) is liberated, and to determine the temperatures at which other structural changes may occur.

Review of the Structural Aspects

The frameworks of tugtupite, danalite, helvite, lazurite, nosean, and haüyne, which has the sodalite structure, consist of TO_4 tetrahedra ($T = Si^{4+}$, Al^{3+}, and Be^{2+}), which are linked at the corners and give rise to large cages (Fig. 1). These tetrahedra are fully ordered. The aluminosilicate framework of cubic sodalite, ideally $Na_8[Al_6Si_6O_{24}]Cl_2$, is characterized by parallel six-membered rings consisting of alternating AlO_4 and SiO_4 tetrahedra. The cubic symmetry is the result of the stacking of such six-membered rings in an *ABCABC*... sequence, which leads to large cages that are bounded by eight six-membered rings parallel to {111} planes and six four-membered rings parallel to {001} planes. The four-membered rings also consist of alternating AlO_4 and SiO_4 tetrahedra (Fig. 1a). The sodalite or β-cages enclose $[Na_4{\bullet}Cl]^{3+}$ clusters (Figs. 1b, c). The structure of tugtupite (tetragonal), ideally $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, is isotypic with that of sodalite. The β-cages in tugtupite also enclose $[Na_4{\bullet}Cl]^{3+}$ clusters, as in sodalite (Hassan & Grundy 1991). The sodalite-group minerals were studied by several researchers (*e.g.*, Pauling 1930, Löns & Schulz 1967, Taylor 1967, 1968, Danø 1966, Peterson 1983, Hassan & Grundy 1984, 1991).

The helvite-group minerals, $(Mn,Fe,Zn)_8[Be_6Si_6O_{24}]S_2$, are also isotypic with sodalite. The Mn-rich member is helvite, the Fe-rich member is danalite, and the Zn-rich member is genthelvite. These minerals were also studied by several researchers (*e.g.*, Hassan & Grundy 1985, Barth 1926, Burt 1980, Dunn 1976). The β-cages in the helvite-group minerals enclose clusters of $[(Mn,Fe,Zn)_4{\bullet}S]^{6+}$. Because these clusters are highly charged (*i.e.*, 6+ valence units), they have smaller sizes than the $[Na_4{\bullet}Cl]^{3+}$ clusters of sodalite and tugtupite (Hassan & Grundy 1985, 1991). The dimensions of the framework tetrahedra in the helvite-group minerals are constant regardless of the nature of the interframework cation because of the rotational freedom of the framework tetrahedra (Hassan & Grundy 1985). In particular, pure danalite consists of 100% $[Fe_4{\bullet}S]^{6+}$ clusters, and pure helvite consists of 100% $[Mn_4{\bullet}S]^{6+}$ clusters. These two minerals are investigated in this study.

EXPERIMENTAL

The samples of sodalite, tugtupite, danalite, and helvite were crushed, and pure crystals were handpicked and crushed to a powder using an agate mortar and pestle. A portion of the powder was used for the DTA and TG analyses, and another portion was used for high-temperature X-ray-diffraction (XRD) analyses. The results will be published elsewhere (Antao & Hassan, in prep.). The samples used in this study were also used by Hassan & Grundy (1984, 1985, 1991) to refine their crystal structures; they thus are well characterized. The composition of the samples used is presented in Table 1.

The experiments were carried out with a Netzsch STA 409 EP/3/D simultaneous TG–DTA instrument. The data were analyzed using software programs supplied with the instrument (Hassan 1996). The thermogravimetric (TG) curve was corrected for buoyancy effect, and the differential thermal analysis (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.

RESULTS AND DISCUSSION

Sodalite, $Na_8[Al_6Si_6O_{24}]Cl_2$

The blue sodalite sample used in this study is from the Princess mine, Bancroft, Ontario. Its chemical composition is given in Table 1. For the thermal analyses, 98.7 mg of finely powdered sodalite sample was used. The TG and DTA curves and their corresponding derivative curves (DTG and DDTA, respectively) for sodalite are shown in Figure 2. The temperature range from 20 to 850°C did not lead to any significant change in weight or peaks, and is therefore left out of Figure 2. The DTG and DDTA curves are obtained from the raw TG and DTA data, respectively, using a narrow window for filtering the measured raw data. The differentiation was done by using a modified Golay–Savitzky algorithm of second order. Sodalite data obtained from these curves are summarized in Table 2.

Four peaks are observed in the DTA curve; peaks 1, 3, and 4 are well defined in both the DTA and DDTA curves, but peak 2, although visually detectable, is less obvious in the DTA curve, but is clearly seen in the DTG curve (Fig. 2, Table 2). At 1079°C, peak 1 occurs only in the DTA trace, but there is no loss in weight in the TG curve. Peak 1 thus is related to melting (Fig. 2a). At 1347°C, peak 4 also occurs only in the DTA trace, and there is no loss in weight; we have no explanation for the cause of peak 4 (Fig. 2a). After the experiment, the residue in the crucible was found to be a porous powder that was easily removed just by tapping the crucible on a desk. This is in contrast to the residue observe for the other minerals, where the product of melting is a glass. Wellman (1970) studied the stability of sodalite in the range of 500–700°C and 600–2000 bars fluid pressure and indicated that sodalite is stable on the vapor-saturated liquidus, so sodalite can be a magmatic mineral.

There are two well-defined DTG peaks, 2 and 3 (Table 2, Fig. 2b). A continuous loss in weight occurs over peaks 2 and 3 and corresponds to a net loss in

TABLE 1. CHEMICAL COMPOSITION OF SODALITE, TUGTUPITE, DANALITE, AND HELVITE

	Sodalite			Tugtupite			Danalite			Helvite		
	wt.%		*apfu*†	wt.%		*apfu*‡	wt.%		*apfu**	wt.%		*apfu*§
SiO_2	36.55	Si	5.93	51.58	Si	7.98	30.56	Si	5.83	32.47	Si	6
Al_2O_3	31.78	Al	6.07	11.15	Al	2.03	0.10	Al	0.02			
BeO				5.40	Be	2.00	13.40	Be	6.14	13.52	Be	6
Na_2O	25.30	Na	7.95	25.52	Na	7.62						
CaO	0.25	Ca	0.04				0.05	Ca	0.01			
K_2O	0.10	K	0.02	0.12	K	0.02						
Fe_2O_3	0.19	Fe	0.02									
MnO	0.01	Mn	0.00				24.97	Mn	4.04	51.12	Mn	8
FeO							24.00	Fe	3.83			
ZnO							4.13	Zn	0.58			
MgO	0.19	Mg	0.05	0.20	Mg	0.05						
Cl	7.17	Cl	1.97	7.28	Cl	1.90						
S	0.02	S	0.01	0.33	S	0.09	5.73	S	2.05	5.78	S	2
O=Cl,S	–1.62			–1.99			–2.86			–2.88		
Total	99.54			99.59			100.08			100.01		

† Composition from Hassan & Grundy (1984), based on Al + Si = 12 atoms per formula unit (*apfu*). ‡ Composition from Danø (1966), based on Al + Be + Si = 12 *apfu*. * Composition from Dunn (1976), based on Al + Be + Si = 12 *apfu*. § Theoretical composition of pure helvite. Tugtupite: sample ROM # M32790. Danalite: sample ROM # M37261.

weight of about 11.5%. This continuous weight-loss can be somewhat arbitrarily divided into two steps, with a slow loss of about 4.5 wt.% for peak 2, and a more rapid loss of about 7.0 wt.% for peak 3 (Fig. 2b). In the sodalite formula, $Na_6[Al_6Si_6O_{24}]•2NaCl$, the 2NaCl component constitutes 12.1 wt.%, which is comparable to the total loss in weight of about 12.2% obtained experimentally (Table 2). According to the chemical data on sodalite, Cl constitutes 7.17 wt.% (Table 1), so 4.93 wt.% loss of Na is required for the total weight-loss to be about 12.1%. Moreover, the TG results indicate that NaCl was lost at two different rates. To investigate the results of sodalite further, halite was thermally analyzed.

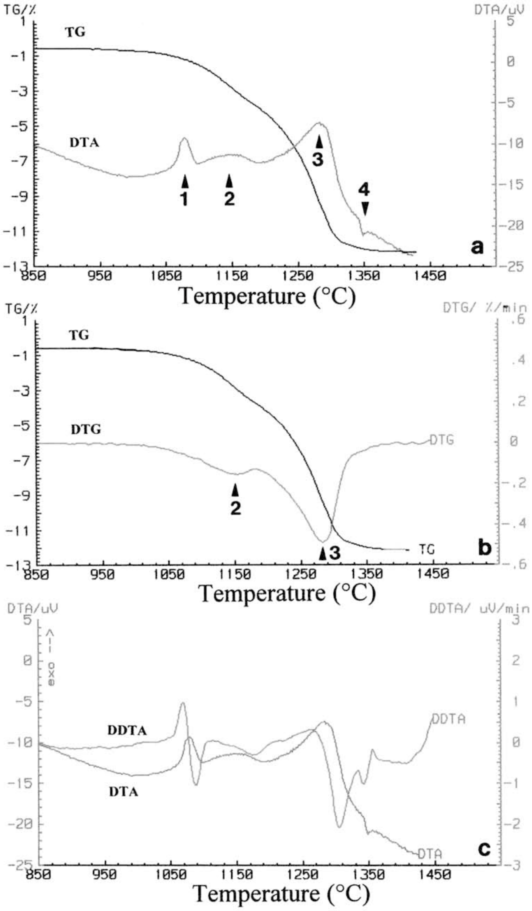

FIG. 2. Thermal curves for sodalite: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves. Corresponding peaks at a particular temperature are given the same number and are labeled on the DTA and DTG curves in this and the other figures that contain thermal curves.

Halite, NaCl

For the thermal analyses of halite, 43.0 mg of the sample was used. The thermal curves for halite are shown in Figure 3, and the data from these curves are summarized in Table 3. Three peaks are observed in the DTA curve (Figs. 3a, c); peaks 1 and 3 are well defined in both the DTA and DDTA curves, but peak 2, although visually detectable, is less obvious in the DTA curve, but is clearly seen in the DTG curve. At 803°C, peak 1 occurs only in the DTA trace, and there is no loss in weight. Peak 1 is thus attributed to the melting of NaCl. This melting point is very close to that reported, 800°C, in the literature (*e.g.*, Neuman 1977).

Peaks 2 and 3 in the thermal curves correspond to loss of volatiles. The TG curve of NaCl shows that practically all the mass is lost (Table 3). A continuous loss of weight occurs over peaks 2 and 3 and corresponds to a net loss in weight of about 98.5%. This continuous weight-loss may somewhat arbitrarily be divided into two steps, with losses of about 38.7 wt.% for peak 2 and 59.5 wt.% for peak 3 (Fig. 3b); the loss of NaCl is slower in the first step compared to the second step.

The DTA and TG results for halite and sodalite are similar to each other with regard to the three peaks (1, 2, and 3). In both samples, NaCl is liberated at two different rates. Peaks 2 and 3 in both samples are attributed to the loss of NaCl at different rates; peak 2 corresponds to a slow rate of loss, and peak 3, to a more rapid rate of loss.

TABLE 2. DATA DERIVED FROM TG, DTG, DTA, AND DDTA ANALYSES OF SODALITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1	Onset T (°C)			1064	1068	
(+) ve†	Peak T (°C)			1079		
	End T (°C)			1093	1088	Melting
	% wt. loss	----				
	Enthalpy (J/g)			59.94		
Peak 2	Onset T (°C)	933	1019	1093		
(+) ve	Peak T (°C)		1150	1148		Loss of
	End T (°C)	1224	1180	1190	1173	NaCl is
	% wt. loss	4.5				slow
	Enthalpy (J/g)			69.72		
Peak 3	Onset T (°C)	1224	1180	1190	1261	
(+) ve	Peak T (°C)		1284	1287		Loss of
	End T (°C)	1384	1322	1319	1306	NaCl is
	% wt. loss	7.0				more
	Enthalpy (J/g)			2.68		rapid
Peak 4	Onset T (°C)			1342	1342	
(–) ve	Peak T (°C)			1347		
	End T (°C)			1354	1356	?
	% wt. loss	----				
	Enthalpy (J/g)			–0.07		
Total*	Peaks 2 and 3: 11.5 wt.%					

* Total % wt. loss from beginning to end is 12.2, including 0.7 at the beginning.

† Positive: exothermic peak, negative: endothermic peak in this and other similar tables.

Tugtupite, $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$

The red tugtupite sample is from Ilímaussaq, Narssaq Kommune, South Greenland (Royal Ontario Museum, ROM #M32790). Table 1 contains the chemical data for a sample from the same locality (Danø 1966). For the thermal analyses, 103.0 mg of the finely powdered tugtupite sample was used. The thermal curves for tugtupite are shown in Figure 4. The temperature range from 20 to 850°C did not show any significant change in weight or peaks, and are therefore left out of Figure 4. Data for tugtupite obtained from these curves are summarized in Table 4. Many peaks are observed in the DTA and DDTA curves. At 1029°C, peak 2 occurs only in the DTA trace, and there is no loss in weight in the TG curve. Peak 2 thus is related to melting. Note that peak 2 in the DTA curve also encloses peak 1, which corresponds to a weight-loss step. Thus, peaks 1 and 2, which are well separated in sodalite, overlap in tugtupite (Figs. 2a, 4a). It should be noted that both the DTA and DTG curves are mirror images of each other. However, the DTG curve only contains peaks corresponding to weight loss, whereas the DTA curve contains these peaks in addition to peaks corresponding to transitions. Signs of melting (*i.e.*, glass) were observed in the crucible after the experiment.

Several DTG peaks were observed (Fig. 4b). The weight loss can be divided into two main steps, with losses of about 1.8 wt.% for peak 1 and 8.2 wt.% for all the other peaks beyond 1250°C. All the TG peaks correspond to a net loss in weight of about 10.0%. These weight losses are attributed to the escape of NaCl. According to the chemical analyses, Cl constitutes 7.28 wt.% (Table 1), so 2.72 wt.% loss of Na is required for the total weight loss to be about 10.0%. In the tugtupite formula, $Na_6[Al_2Be_2Si_8O_{24}]$•2NaCl, theoretically the 2NaCl component constitutes 12.49 wt.%, which is comparable to the net loss in weight of about 10.0% obtained from the TG curve of tugtupite. Note that at the end of the experiment, weight loss was still taking place, as indicated by peak 4 in the DTG curve (Fig. 4b). However, this weight loss is not reflected in the corrected TG curve because the blank correction curve was truncated before 1450°C, but the uncorrected TG curve (not shown) indicates the corresponding weight-loss peaks 4a, b; these data are included in Table 4. In tugtupite, each weight-loss step is attributed to NaCl, escaping at different rates. The tugtupite sample was run a second time, and the results obtained were the same.

In both tugtupite and sodalite samples, NaCl is liberated at different rates. In sodalite, the loss of NaCl

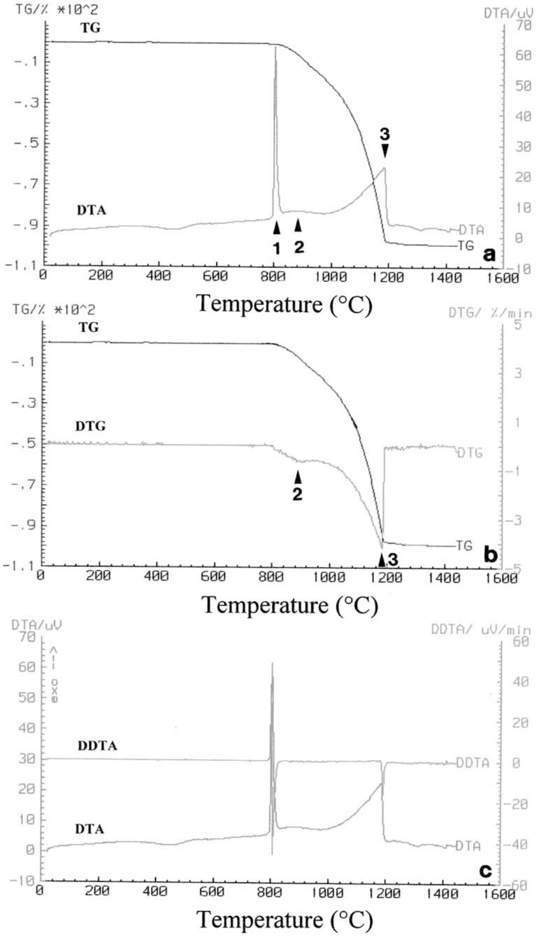

FIG. 3. Thermal curves for halite: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves.

TABLE 3. DATA DERIVED FROM TG, DTG, DTA, AND DDTA ANALYSES OF HALITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1 (+) ve†	Onset T (°C)			795	801	
	Peak T (°C)			803		
	End T (°C)			821	806	Melting
	% wt. loss	---				
	Enthalpy (J/g)			639.89		
Peak 2 (+)ve	Onset T (°C)	766	802	844	---	
	Peak T (°C)		900	877		Loss of NaCl is slow
	End T (°C)	1083	949	923	---	
	% wt. loss	38.7				
	Enthalpy (J/g)			21.84		
Peak 3 (+)ve	Onset T (°C)	1083	1018	1005	---	
	Peak T (°C)		1182	1182		Loss of NaCl is more rapid
	End T (°C)	1261	1194	1193	1188	
	% wt. loss	59.5				
	Enthalpy (J/g)			14.52		
Total*	Peaks 2 and 3: 98.2 wt.%					

* Total % wt. loss (from start to end) is 99.0, including 0.8 at the beginning.

occurs in two continuous steps; in the first step, the loss of NaCl is slow, but in the second step, it is more rapid. However, in tugtupite, NaCl escapes in several steps at different rates. This difference in behavior may be related to the number of bonds with different strengths that have to be broken to liberate NaCl. In sodalite, there are three Na–O bonds of equal strength that have to be broken, but in tugtupite there are four Na–O bonds with different strengths that have to be broken to liberate NaCl (Fig. 5). Moreover, the escape of NaCl from sodalite may occur more easily because of the larger β-cages (V = 701 Å^3) in sodalite compared to those in tugtupite (V = 662 Å^3).

In tugtupite, melting occurs at 1029°C, which is 50°C lower than in sodalite. This difference in temperature may be attributed to more strain in the tugtupite framework, which contains three different types of T atoms (Al, Be, Si) compared to two different types of T atoms (Al, Si) in sodalite. The temperature at which tugtupite (926°C) begins to lose NaCl is about the same as that in sodalite (933°C), but the loss from the sodalite melt is stopped at about 1384°C, whereas in the experiment on the tugtupite, the melt continues to lose NaCl beyond 1442°C.

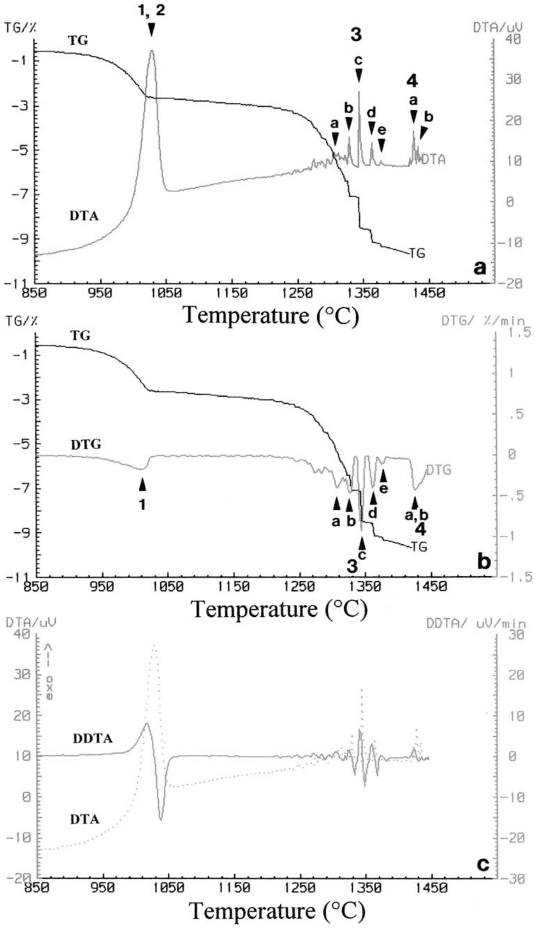

FIG. 4. Thermal curves for tugtupite: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves.

TABLE 4. DATA DERIVED FROM THE TG, DTG, DTA, AND DDTA ANALYSES OF TUGTUPITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1	Onset T (°C)	926		Encl.		
	Peak T (°C)		1007	in		
	End T (°C)	1019		Peak 2		Loss of
	% wt. loss	1.8				NaCl
(+) ve†	Enthalpy (J/g)			----		
Peak 2	Onset T (°C)			991	1016	
	Peak T (°C)		----	1029		
	End T (°C)			1047	1038	Melting
	% wt. loss	----				
(+) ve	Enthalpy (J/g)			707.25		
----	Starting T (°C)	1019				
	End T (°C)	1257	----	----	----	Gradual
	% wt. loss	0.9				loss
Peak 3	Onset T (°C)	1257		----	----	
(a)	Peak T (°C)		1311	1311		Loss of
	End T (°C)	1323		----	----	NaCl
	% wt. loss	2.9				
(+) ve	Enthalpy (J/g)			10.80		
Peak 3	Onset T (°C)	1325		1325	1319	
(b)	Peak T (°C)		1326	1328		
	End T (°C)	1331		1336	1332	Loss of
	% wt. loss	0.7				NaCl
(+) ve	Enthalpy (J/g)			18.32		
Peak 3	Onset T (°C)	1339		1341	1340	
(c)	Peak T (°C)		1343	1344		
	End T (°C)	1347		1355	1350	Loss of
	% wt. loss	1.4				NaCl
(+) ve	Enthalpy (J/g)			43.94		
Peak 3	Onset T (°C)	1358		1359	1359	
(d)	Peak T (°C)		1362	1362		
	End T (°C)	1365		1370	1372	Loss of
	% wt. loss	0.6				NaCl
(+) ve	Enthalpy (J/g)			23.77		
Peak 3	Onset T (°C)	1372		1375		
(e)	Peak T (°C)		1362	1376		
	End T (°C)	1381		1384		Loss of
	% wt. loss	0.2				NaCl
(+) ve	Enthalpy (J/g)			4.59		
Peak 4	Onset T (°C)	1411		1418	1419	
(a)	Peak T (°C)		1425	1427		
	End T (°C)	1429		1431	1432	Loss of
	% wt. loss	0.8				NaCl
(+) ve	Enthalpy (J/g)			8.91		
Peak 4	Onset T (°C)	1429		1431		
(b)	Peak T (°C)		1432	1434		Loss of
	End T (°C)	>1442		1436		NaCl
	% wt. loss	>0.7		2.24		
Total*	All peaks: –10.0 wt.%					

* Total wt. loss from start to end is 10.4%. Note that peak 1 is enclosed in peak 2.

Danalite, $Fe_8[Be_6Si_6O_{24}]S_2$

A sample of danalite from Mt. Francisco granitic pegmatite, Ribawa area, Western Australia (ROM #M37261) was used is this study. The chemical data for a sample from the same locality are given in Table 1. This material was studied by Hassan & Grundy (1985). For the thermal analyses, 102.0 mg of the finely powdered sample was used. The thermal curves for danalite are shown (Fig. 6). In general, the TG curve indicates three main events, first a weight-gain event, followed by a weight-loss event, and finally another small weight-gain event (Fig. 6a). The other thermal curves (Fig. 6) are more complex and contain many peaks, unlike the TG curve. Data obtained from these curves are summarized in Table 5.

Peaks 1, 2, and 3 in the DTA trace correspond to various rates of increase in weight as indicated by the TG curve (Fig. 6). Peaks 4, 5, 6, and 7 in the DTA curve are attributed to the loss of volatiles at different rates because of the continuous decrease in weight in the TG curve. The onset and end temperatures for all the peaks are better defined by the DDTA curve. Peak 7 at about 1274°C in the DTA trace is also related to the melting of danalite and is close to the end of the weight-loss event. Melt was observed in the crucible after the experiment.

Peaks 1, 2, and 3 in the DTG curve correspond to the first weight-gain stage, and from the TG curve a net gain of 4.0 wt.% is obtained (Fig. 6, Table 5). The gain in weight results from oxidation because the sample was heated in a static air environment. Therefore, divalent Fe^{2+} and Mn^{2+} oxidize to trivalent Fe^{3+} and Mn^{3+}, respectively, at different rates. With complete oxidation, the theoretical formula of danalite (initially consisting only of Fe^{2+}) would change from $Fe^{2+}_8[Be_6Si_6O_{24}]S_2$ to $Fe^{3+}_8[Be_6Si_6O_{28}]S_2$, and the theoretical increase due to the extra four O atoms would be 5.7 wt.%. If the theoretical formula changed to $Fe^{2+}_2Fe^{3+}_6[Be_6\,Si_6O_{27}]S_2$, the theoretical increase due to the extra three O atoms would be 4.3 wt.%. From the TG curve, a weight gain of 4.0 wt.% is obtained, which corresponds to a theoretical increase of 2.8 O atoms. This sample of danalite contains about equal amounts of Fe and Mn, and a small

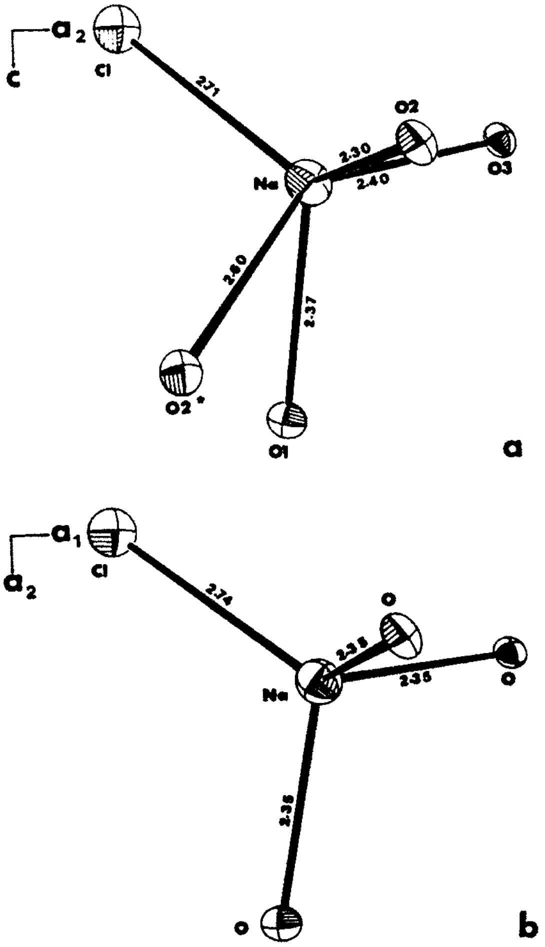

FIG. 5. Na atom coordinations: (a) five coordination in tugtupite, and (b) four coordination in sodalite.

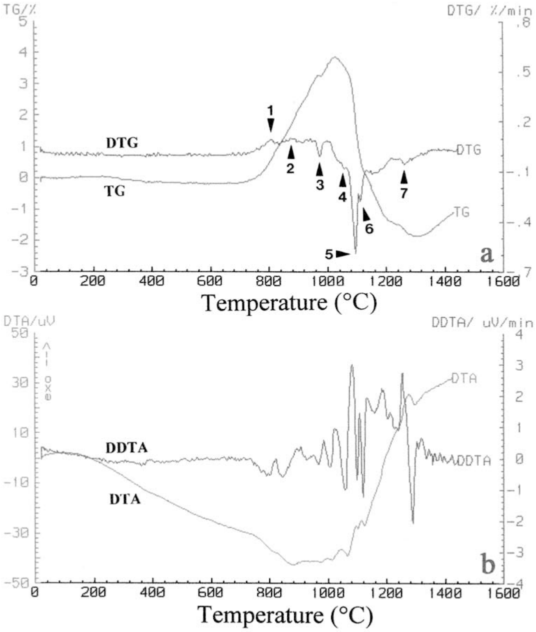

FIG. 6. Thermal curves for danalite: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves.

amount of Zn, which will not be oxidized (Table 1). The Fe^{2+} first begins to oxidize to Fe^{3+} because of its lower oxidation potential (+0.77 V for $Fe^{2+} \rightarrow Fe^{3+}$ and +1.51 V for $Mn^{2+} \rightarrow Mn^{3+}$; Bard *et al.* 1985). Weight loss occurs over peaks 4, 5, 6, and 7 in the DTG curve, and from the TG curve a net loss of 5.7 wt.% is obtained (Fig. 6, Table 5). Sulfur constitutes 5.73 wt.% of danalite (Table 1), which is comparable to the weight loss obtained from the TG curve. Therefore, this weight loss is attributed to the loss of S_2(g) at different rates. In the weight-gain stage, O atoms are incorporated into the danalite structure, and in the succeeding weight-loss stage, instead of losing the incorporated O atoms, S atoms are lost as S_2(g).

Beyond about 1297°C, the TG curve begins to increases in weight again (incomplete peak 8 in the TG curve, Fig. 6a). An increase of 0.7 wt.% is obtained up to 1450°C (Table 5). Possibly the trivalent Mn^{3+} begins to oxidize to tetravalent Mn^{4+}. The peak temperature for this weight gain is beyond the experimental limit of 1450°C; therefore, the DTG or DTA curve did not give a peak to indicate this increase in the TG curve.

In danalite, there is a weight gain caused by oxidation of $(Fe, Mn)^{2+}$ to $(Fe, Mn)^{3+}$ followed by a loss of S_2 (g), melting, and finally another weight-gain stage, possibly caused by further oxidation of Mn^{3+} to Mn^{4+} in the melt. During the first weight-gain event, which begins at about 771°C, the O atoms incorporated possibly enter the cubo-octahedral cavities, and occupy a general site such that they are within bonding distance to the Mn or Fe atoms. Such a general site was found for the O atoms of OH and H_2O in basic sodalite (Hassan & Grundy 1983). If the Mn and Fe atoms fully oxidize to $(Fe, Mn)^{3+}$, two O atoms are expected to enter each cubo-octahedral cavity. Thus, the original four-fold coordination of the Mn or Fe atom (tetrahedrally coordinated to three O atoms of the framework and one central S atom), probably increases to six, and the structure of danalite still remains intact. From about 1029°C, each Mn or Fe atom, which is now bonded to one central S atom, three O atoms from the framework, and two incorporated O atoms, cannot retain the coordination number of six. The distance of the interframework cation, *IC* (*IC* = Mn, Fe) to S, is longer than the *IC*–O bond distance [*IC*–S = 2.413(1) Å, *IC*–O = 2.033(3) Å; Hassan & Grundy 1985]. Therefore, the longer *IC*–S bonds are broken, and S_2 (g) is liberated. The coordination of the *IC* cation is now five, all the anions being oxygen atoms. The incorporated O atoms, however, do not occupy the positions of the S atoms, *i.e.*, at the center and corners of the unit cell, because the *IC*–S bond in danalite is too long [*IC*–S = 2.413(1) Å] to allow for reasonable *IC*–O bond distances. The incorporated O atoms are probably located off the center of the unit cell and are closer to the *IC* cation to give proper *IC*–O bond distances. More O atoms can be incorporated into the danalite-derived melt with further oxidation of Mn^{3+} to Mn^{4+}. Thus, the contents of some of the cages of tetrahedra change from $[(Mn,Fe)^{2+}{}_4 \bullet S]^{6+}$ to $[(Mn,Fe)^{3+}{}_4 \bullet SO_2]^{6+}$ in the first stage of oxidation, with the net charge on the cage cluster remaining at +6 valence units. When danalite loses all of the S atoms, the cage clusters change to $[(Mn,Fe)^{3+}{}_4 \bullet O_2]^{8+}$. In this case, the net charge on the clusters (+8 valence units) does not balance the net change on the framework (–6 valence units), so the danalite structure becomes unstable and the sample melts. To balance the excess of +2 valence units, more O atoms are required. Therefore, with further oxidation of the melt ($Mn^{3+} \rightarrow Mn^{4+}$), the O atom content increases, the charge balances, and the melt becomes stable.

TABLE 5. DATA DERIVED FROM TG, DTG, DTA, AND DDTA ANALYSES OF DANALITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1	Onset T (°C)	771			794	
(–)ve†	Peak T (°C)		809	811		
	End T (°C)				819	
	Enthalpy (J/g)			–14.27		
Peak 2	Onset T (°C)				846	Peaks 1–3: weight gain caused by the oxidation of Fe^{2+} to Fe^{3+} and Mn^{2+} to Mn^{3+} at different rates
(–)ve	Peak T (°C)		879	880		
	End-T (°C)				893	
	Enthalpy (J/g)			–79.58		
Peak 3	Onset T (°C)				966	
(–)ve	Peak T (°C)		973	974		
	End T (°C)	1029			984	
	Enthalpy (J/g)			–7.03		
	% wt. gain*	4.0				
Peak 4	Onset T (°C)	1029			1025	
(+)ve	Peak T (°C)		1058	1045		
	End T (°C)				1058	
	Enthalpy (J/g)			80.31		
Peak 5	Onset T (°C)				1082	
(+)ve	Peak T (°C)		1092	1095		
	End T (°C)				1099	Peaks 4–7: loss of S_2 (g) at different rates
	Enthalpy (J/g)			24.28		
Peak 6	Onset T (°C)				1108	
(+)ve	Peak T (°C)		1112	1116		
	End T (°C)				1119	
	Enthalpy (J/g)			28.35		
Peak 7	Onset T (°C)				1255	
(+)ve	Peak T (°C)		1263	1274		
	End T (°C)	1298			1286	Melting
	Enthalpy (J/g)			0.67		
	% wt. loss**	5.7				
Peak 8	Onset T (°C)	1298				Weight gain caused by oxidation of Mn^{3+} to Mn^{4+}
(+)ve	Peak T (°C)					
	End T (°C)					
	% wt. gain	0.7				

* Total wt. gain over peaks 1, 2, and 3 is 4.0%. ** Total wt. loss over peaks 4, 5, 6, and 7 is 5.7%. Concerning the oxidation of Mn^{3+} to Mn^{4+}, see the text.

Helvite, $Mn_8[Be_6Si_6O_{24}]S_2$

The helvite sample is from Sunnyside, San Juan County, Colorado (ROM #M36390). In the thermal ex-

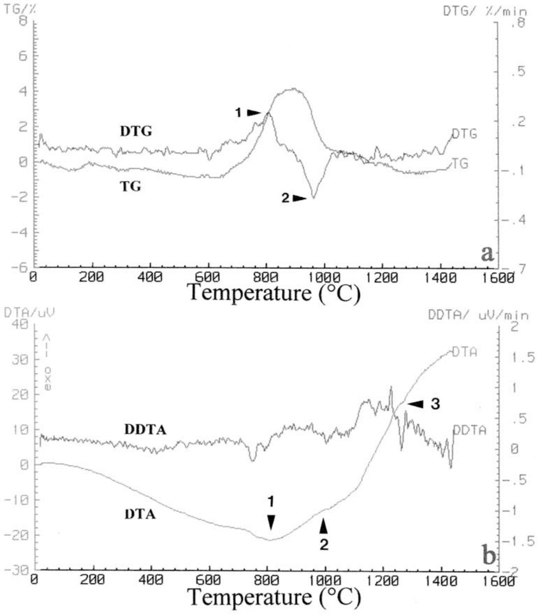

FIG. 7. Thermal curves for helvite: (a) TG and DTA curves, (b) TG and DTG curves, and (c) DTA and DDTA curves.

TABLE 6. DATA DERIVED FROM TG, DTG, DTA, AND DDTA ANALYSES OF HELVITE

Peaks	Miscellaneous	TG	DTG	DTA	DDTA	Changes
Peak 1 (–)ve†	Onset T (°C)	705			793	Weight gain caused by oxidation of Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
	Peak T (°C)		810	810		
	End T (°C)	883			828	
	% wt. gain	5.0				
Peak 2 (+)ve	Onset T (°C)	883			992	
	Peak T (°C)		965	996		
	End T (°C)	996			1004	Loss of S_2 (g)
	% wt. loss*	3.5				
Peak 3 (+)ve	Onset T (°C)				1225	
	Peak T (°C)			1260		Melting
	End T (°C)				1261	

* Weight loss over peak 2 is 3.5%, but it is a slow continuous loss, which occurs until about 1333°C giving a total of 4.7 wt.%. Beyond 1333°C, there tends to be a small gain in weight (about 0.2 wt.%).

periment, only 20.7 mg was used instead of about 100 mg of helvite, as more sample was unavailable. The theoretical chemical composition of pure helvite, $Mn_8[Be_6Si_6O_{24}]S_2$, is given in Table 1. The thermal curves for helvite are shown in Figure 7. Data obtained from these curves are summarized in Table 6. In general, from the TG curve, there are two main stages; a weight-gain stage is followed by a weight-loss stage, as was found also in danalite. Two sharp peaks (1 and 2) in the DTG curve correspond to these two events. The DTA curve contains three small peaks (1, 2 and 3) possibly because of the small amount of sample. Peaks 1 and 2 in the DTA curve are related to weight gain and weight loss, respectively, because of the change in weight in the TG curve. Peak 3 occurs in the DTA trace at about 1260°C, and there is no loss in weight in the TG curve; peak 3 thus is related to melting.

Peaks 1 and 2 are well defined in the DTG curve. The TG curve shows that there is a weight gain of 5.0 wt.% over peak 1 (Fig. 7, Table 6). This gain in weight is caused by the oxidation of divalent Mn^{2+} and Fe^{2+} to trivalent Mn^{3+} and Fe^{3+}, respectively. With complete oxidation, the theoretical formula of pure helvite (consisting only of Mn) would change from $Mn^{2+}_8[Be_6Si_6O_{24}]S_2$ to $Mn^{3+}_8[Be_6Si_6O_{28}]S_2$; the theoretical increase due to the extra four O atoms is 5.8 wt.%. From the TG curve, a weight gain of 5.0 wt.% is obtained. This indicates a theoretical increase of 3.4 extra O atoms. Therefore, similar to the case for danalite, helvite undergoes oxidation, and contains extra incorporated O atoms. The TG curve gives a total weight loss of 4.7 wt.% over peak 2. This weight loss is attributed to the loss of S_2 (g), as in danalite. S constitutes 5.78 wt.% in the theoretical chemical composition of helvite (Table 6), but from the TG curve a weight loss of 4.7 wt.% is obtained. Beyond about 1333°C, the TG curve shows a small gain in weight of 0.2 wt.%. At the maximum temperature, the DTG and DDTA curves also seem to indicate peaks corresponding to this weight-gain stage. However, since the experiment was terminated at 1450°C, this weight-gain stage is not well defined. Therefore, in this minor weight-gain stage, possibly Mn^{3+} further oxidizes to Mn^{4+}.

The DTG curve contains small peaks in addition to the two major peaks 1 and 2 (Fig. 7b); however, these small undulations are not really peaks, but noise, which arises because of the small amount of sample used (20.7 mg). Larger filters (*e.g.*, 101p) can smooth the DTG curve and eradicate most of the noise, but the peak temperatures obtained would not be accurate, so the use of larger filters was avoided.

In both danalite and helvite, first there is a weight-gain stage, which begins at a temperature of about 705°C in helvite and about 771°C in danalite. This weight gain is caused by the oxidation of (Fe, Mn)$^{2+}$ to (Fe, Mn)$^{3+}$. Following this event there is a loss of S_2 (g), which begins at 883°C in helvite and 1029°C in danalite. The weight gain and weight loss in danalite occur in several steps and at different rates, unlike those observed in helvite. The weight-gain stage in danalite was expected to occur at a lower temperature than that for helvite because of the lower oxidation potential of Fe^{2+} compared to that of Mn^{2+}. However, the onset temperatures for both the weight loss and weight gain in helvite are lower than those observed for danalite. Melting occurs at about 1260°C in both samples. Finally, beyond about 1300°C there is further weight-gain, possibly caused by further oxidation of Mn^{3+} to Mn^{4+} in both melts formed. As helvite is Mn-rich, a larger weight-gain is expected for helvite in the second stage of oxidation, compared to danalite, because only the Mn^{3+} (not Fe^{3+}) can further oxidize to the +4 oxidation state. However, in this second stage of oxidation, the observed weight-gain in danalite (0.7 wt.%) is more than that observed in helvite (0.2 wt.%). The mechanism of incorporating O atoms into the structure, and losing S atoms, is the same in both danalite and helvite. Finally, this study shows that thermal techniques may be used to determine volatiles, oxidation states, and transition temperatures in minerals. This type of study may also have implications for studies concerning the degassing of magmas.

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