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Controlled rate thermal analysis of nontronite

Z. Ding, R.L. Frost*

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology,
2 George Street, G.P.O. Box 2434, Brisbane, Qld 4001, Australia

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Abstract

The thermal decomposition of a series of nontronites and a ferruginous smectite has been studied using a combination of high-resolution thermogravimetric analysis (TGA) with a controlled heating rate and the mass spectrometry (MS) of evolved water vapour. The temperature–mass spectrum curve follows the differential TGA (DTGA) curve with precision, thus providing a second means of calculating the percentage weight loss. Three dehydration steps were observed in the controlled rate thermal analysis (CRTA) experiment at around 86, 117 and 245 °C depending on the nontronite sample. Two overlapping dehydroxylation steps were observed at approximately 350 and 400 °C with a weight loss ratio of 1:2. A comparison is made between the between the results obtained from the dynamic DTGA experiment and the CRTA experiment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nontronite; Ferruginous smectite; Controlled rate thermal analysis; Differential thermogravimetric analysis

1. Introduction

Smectites belong to the group of hydrous clay minerals, which expand upon contact with water and other solvents [1,2]. Smectites may be either di- or trioctahedral [3–5]. The dioctahedral smectites can be divided into two principal groups: (a) aluminium smectites; (b) the iron-rich varieties including ferruginous smectites and nontronites [4–6]. It is this group of dioctahedral clays that the thermal decomposition we are reporting in this manuscript. Montmorillonites and beidellites have Fe^{3+} <1 mol%. The term nontronite is used for dioctahedral smectites when Fe^{3+} is >3 mol% and when the layer charge originates from the tetrahedral sheet. The ideal structural formula for aluminium smectites with octahedral charge (montmorillonites) is $(X^+)_{0.85}(Al_{3.15}Mg_{0.85})(Si_{8.0})$-$O_{20}(OH)_4$, where X is a monovalent cation that counterbalances the layer charge [1]. Two types of dioctahedral smectites exist depending on the site of the layer charges: (a) montmorillonites where the charge arises from divalent cations usually Mg which substitutes for Al in the octahedral sites; (b) beidellites where the charge arises from the aluminium substitution for silicon in the tetrahedral sites. Ferruginous smectites have partial substitution of the aluminium by iron. In nontronites, almost all of the Al in the octahedral layer is replaced with ferric iron (Fe^{3+}). In this case, the structural formula is given by $((M^+)_x\cdot nH_2O)(Fe^{3+})_4(Si_{4x}Al_x)O_{20}(OH)_4$. This clay is the end member and is known as nontronite [5,6]. Two nontronites from Garfield (Spokane County, Washington, USA) and Hohen-Hagen (Germany) have been extensively used as reference clays [7] but are becoming

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* Corresponding author. Tel: +61-7-3864-2407;
fax: +61-7-3864-1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

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difficult to obtain. Recently, two nontronites from Port Lincoln, South Australia, have replaced these two standards [8]. Mineralogical and chemical analyses studies indicate that the Uley green nontronite is similar in chemistry and structure to the Garfield nontronite, whereas the Uley brown nontronite appears to be significantly lower in aluminium and possibly contains tetrahedrally coordinated iron [8].

Thermal analysis of clay minerals can provide valuable information about the chemical composition of clay minerals [9], particularly in the lower temperature regime (<700 °C). The study of the dehydroxylation of smectites can be complicated by a nearly continuous evolution of water at temperatures below about 400 °C [10]. These waters include surface-sorbed waters of hydration and coordination waters of interlayer cations. In addition, the dehydroxylation event often occurs over a range of temperatures [11]. For the aluminium-enriched smectites, the loss of hydroxyls typically commences at temperatures >700 °C, however, for the iron-enriched smectites, the temperatures in which dehydroxylates are formed is often as low as 450 °C. Thus, significant overlap can occur between dehydration and dehydroxylation of ferruginous smectites. For nontronites, these reactions are further complicated by the formation of ancillary phases: maghemite when heated under air or argon and fayalite when heated under H_2/N_2 [9]. The aim of this paper is to describe the thermal decomposition of nontronites, including the Uley nontronites and a ferruginous smectite in terms of dehydration and dehydroxylation and to utilise controlled rate thermal analysis (CRTA) techniques combined with mass spectrometry (MS) of evolved water vapour [12,13] to further our understanding of the similarities and differences between the two Uley nontronites with each other and with reference nontronites.

2. Experimental techniques

2.1. Origin of samples

The clay minerals used are the Clay Mineral Society standards: the ferruginous smectite SWA1, the Garfield nontronite from Spokane County, Washington, USA labelled as API-H33a or sometimes H33a [5] and the nontronite NG-1 from Hohen-Hagen, Germany [7]. The two Australian samples are from Uley Graphite Mine, Eyre Peninsula, South Australia. The calcium exchanged, <1 μm size fractionated portions were used. Samples were analysed for purity by X-ray diffraction. Infrared spectrometry was also used to detect low levels of other phases, particularly kaolinite and amorphous phases. The Uley green nontronite (NAu1) sample contained traces of kaolinite and the Uley brown nontronite (NAu2) contained calcite and ferrihydrite. The contaminants were at very low levels and were not detected by XRD. Both the Uley nontronites are now available from the source Clay Minerals Repository at the University of Missouri.

The ferruginous smectite SWA1 from the Clay Mineral Repository (Grant County, Washington) has a structural formula of $(M^{+})_{0.95}[Al_{1.10}Fe_{2.61}Mg_{0.25}]$-$[Si_{7.40}Al_{0.60}]O_{20}(OH)_4$. The nontronite from Hohen-Hagen, Germany (CMR NG-1) has a structural formula of $(M^{+})_{0.95}[Al_{0.86}Fe_{3.08}Mg_{0.05}][Si_{7.12}Al_{0.11}$-$Fe_{0.76}]O_{20}(OH)_4$. It should be noted that titanium as anatase occurs as an admixture in this nontronite and some of the Fe (≈20%) is in the tetrahedral layers. The Garfield nontronite from Spokane County, Washington, has a formula $(M^{+})_{1.07}[Al_{0.23}Fe_{3.71}Mg_{0.03}][Si_{7.03}$-$Al_{0.97}]O_{20}(OH)_4$. It should be noted that there is another nontronite from Spokane, Washington County, titled Spokane nontronite. This is an extremely rare mineral and was not used in this work. The Uley Green (NAu1) nontronite has a formula of $(M^{+})_{1.05}[Al_{0.26}Fe_{3.71}Mg_{0.03}][Si_{6.97}Al_{1.03}]O_{20}(OH)_4$ and the Uley brown (NAu2) nontronite has a formula of $(M^{+})_{0.83}[Al_{0.42}Fe_{3.43}Mg_{0.04}][Si_{7.52}Al_{.06}Fe_{.42}]O_{20}$-$(OH)_4$. Nontronites contain Fe predominantly in the trivalent state [5,9,11]. The above analyses were conducted on ignited, Ca-saturated purified fractions (nominally <0.15 μm) of each nontronite.

The minerals were selected to provide a range of total Fe^{3+} and Al contents. The Fe content (ignited, Fe_2O_3 basis) are: SWA1, 24.4%; Uley green, 36.49%; Garfield, 36.4%; NG-1, 37.5%; Uley brown, 38.1%. The aluminium content are: SWA1, 11.04%; Garfield, 7.54%; NG-1, 6.06%; Uley green, 8.15%; Uley brown, 3.02%. It should be noted that NG-1 and the Uley brown nontronite each contains significant amounts of ferric iron in the tetrahedral sheet. However each of the nontronites studied here contain most of the iron as ferric iron in the octahedral sheet. The SWA1 is usually referred to as a ferruginous smectite rather than a nontronite due to its elevated Mg content, low tetrahedral Al substitution and high proportionate charge residing in the octahedral layer. Thus, based on chemical composition, the Uley smectites are members of the smectite series in which the octahedral aluminium has been replaced by octahedral ferric iron.

2.2. Thermal analysis

2.2.1. The dynamic experiment

Thermogravimetric analysis (TGA) and differential TGA (DTGA) on ~50 mg of the size fractionated smectite minerals was obtained using a Setaram DTGA/TGA instrument, operating at 2.0 °C/min from ambient temperatures to 1000 °C in a nitrogen atmosphere. The fact that the DTGA experiment is conducted in an inert atmosphere means that the samples cannot oxidise during thermal treatment.

2.2.2. The CRTA experiment

Thermal decomposition of the nontronite was carried out in a TA high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min) at a pre-set, constant decomposition rate of 0.15 mg/min (below this threshold value the samples were heated under dynamic conditions at a uniform rate of 0.5 °C/min). The 50 mg samples were heated in an open cylindrical platinum crucible at a rate of 1.0 °C/min up to 1000 °C. With the quasi-isothermal, -isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfieffer) mass spectrometer for gas analysis. Only selected gases were analysed.

3. Results and discussion

In this work two types of experiments are undertaken: (a) the dynamic experiment where the sample is heated at a constant heating rate; (b) the sample is heated at a controlled heating rate determined by the rate of weight loss. In this latter experiment, the thermal analysis instrument is coupled to a mass spectrometer and the weight loss is monitored by mass spectrum of the water vapour [12–14].

A recent study by the authors have explored the dehydration and dehydroxylation of nontronites and ferruginous smectites using the dynamic technique which employs a constant heating rate [12–14]. It has been found that by using the controlled rate heating method, that much more information with better resolution of the thermal decomposition steps can be obtained [15–18]. This research is an extension of this work [15], where we use CRTA to determine if the dehydration and dehydroxylation of nontronites occurs in steps [15–18].

3.1. Dehydration in the dynamic DTGA experiment (constant heating rate)

The DTGA patterns for the series of nontronites and ferruginous smectite are shown in Fig. 1and the results of the DTGA reported in Table 1. The dehydration steps are complex with up to three dehydration steps, which appear to overlap. The first three endotherms are observed for both reference nontronites at 62, 97 and 151 °C and are attributed to the loss of adsorbed water (62 and 97 °C) and the loss of coordinated water (151 °C). For the Hohen-Hagen nontronite, 12.9% of the total energy of dehydration and dehydroxylation is utilised at 62 °C and is attributed to the energy required to remove the adsorbed water and 38% of the total energy is utilised at 97 °C and is attributed to water of hydration of the cation. The values for the Garfield nontronite are 6.0 and 28.0%. The ferruginous smectite showed two water desorption endotherms at 60 and 91 °C with 17.7 and 28.0% relative areas. Such thermal values are not unexpected as smectites containing hydrated cations contain large amounts of water. The Uley nontronite (NAu1) did not show the low temperature endotherm at ~60 °C. However, a large water desorption endotherm at 89 °C was observed with a relative area of 47%. The Uley nontronite (NAu2) showed desorption isotherms at 72 and 100 °C with 14.9 and 10.9% relative thermal energies. The difference in thermal energies for the water adsorption between the two Australian nontronites suggests differences in chemical structure. This is also exemplified by the cation water of hydration endotherms. The NAu1 sample has an endotherm at 156 °C, that is, 3.0% of the total thermal energy. The NAu2 shows no endotherm at ~150 °C, but does have a broad endotherm at 289 °C with 18.3% of the total

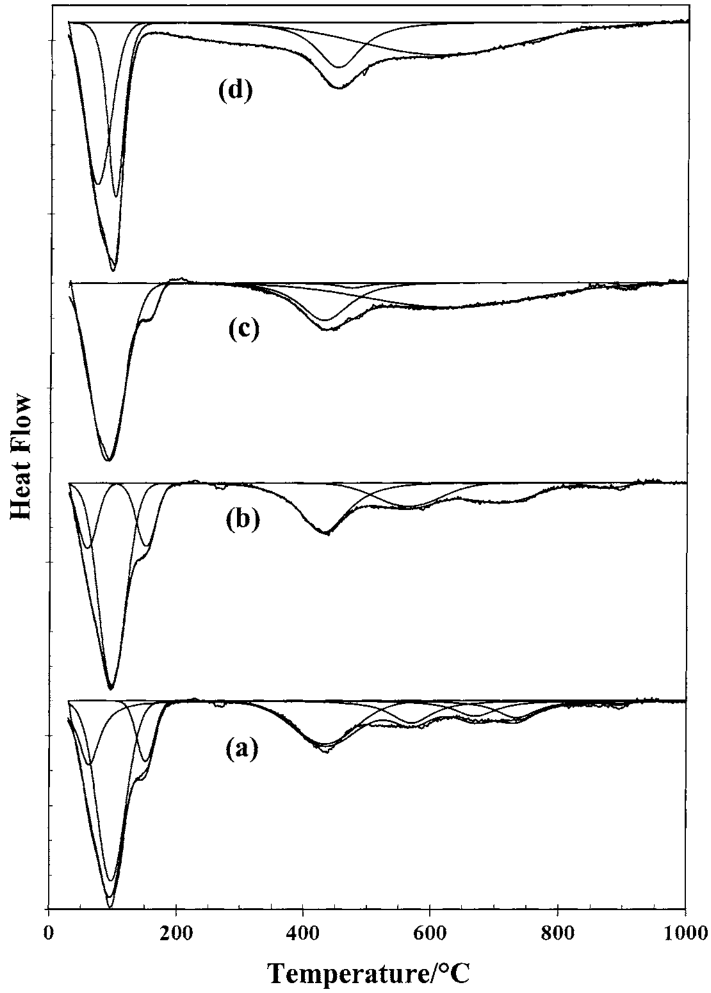

Fig. 1. DTA (constant heating rate) patterns of the nontronites: (a) Hohen-Hagen; (b) Garfield; (c) NAu1; (d) NAu2.

thermal energy. This broad endotherm is attributed to the presence of some ferrihydrite impurity in this nontronite. The low temperature thermal behaviour of the two Uley nontronites suggests that the two minerals are different, resulting from different diagenetic origins in agreement with the chemical and geological analyses [8].

3.2. Dehydroxylation in the dynamic DTGA experiment (constant heating rate)

A sequence of dehydroxylation endotherms as determined by DTGA is observed at 433, 567, 670 and 735 °C for the Hohen-Hagen nontronite (Table 1). The relative areas of these endotherms are 20.4, 9.5, 5.1 and 5.1%. The principal dehydroxylation temperature is 433 °C. The series of endothermic steps suggests that the dehydroxylation of this nontronite is occurring in steps. For the Garfield nontronite, dehydroxylation endotherms were observed at 430, 563 and 708 °C with relative areas of 27.6, 16.0 and 13.1%. A minor endotherm was observed for both the Hohen-Hagen and Garfield nontronites at ~880 °C and is attributed to a phase change. The dehydroxylation of the Garfield nontronite is similar to that of the Hohen-Hagen nontronite except that the third dehydroxylation step is not resolved. However, the last step in the dehydroxylation is broad, thus there is likely

Table 1
Results of the thermal analysis of the DTA patterns of nontronites and a ferruginous smectite as measured by the dynamic experiment

	Nontronite				
	Hohen-Hagen	Spokane	SWA1	NAu1	NAu2
Dehydration (°C)	62	59	6.0		72
Step 1 (%)	12.9	60	17.7		14.9
Dehydration (°C)	97	98	91	89	100
Step 2 (%)	38.0	28.4	28.0	47	10.9
Dehydration (°C)	151	151	144	156	289
Step 3 (%)	7.9	6.3	6.3	3.0	18.3
Dehydroxylation (°C)	433	430	440	434	451
Step 4 (%)	20.4	27.6	19.9	18.0	17.5
Dehydroxylation (°C)	567	563	606	626	613
Step 5 (%)	9.7	16.0	26.0	26.0	38.5

little difference between the thermal evolution of these two nontronites. The ferruginous smectite shows two dehydroxylation steps similar to the Garfield nontronite with endotherms at 440 and 606 °C. The relative areas of these two endotherms are 19.9 and 26.0%.

It is noteworthy that the relative areas of the two dehydroxylation steps of Garfield nontronite and the ferruginous smectite are reversed (27.6 and 16.0% compared with 19.9 and 26.0%). The major difference between the two minerals is the amount of aluminium in the octahedral sheet. The ferruginous smectite contains more aluminium. Thus the two steps at ~430 and 565 °C are attributed to the dehydroxylation of firstly the OH associated with Fe/Fe pairs and secondly the OH associated with Fe/Al pairs [11]. The Uley green nontronite shows a sharp dehydroxylation endotherm at 434 °C and a broad endotherm centred at 629 °C. The relative areas of these two endotherms are 18.0 and 31.4%. These two endotherms for the Uley brown nontronite are observed at 451 and 613 °C with areas of 17.5 and 38.5%. Distinct steps of dehydroxylation were not resolvable for the Uley nontronites, as they were for the Hohen-Hagen nontronite and it can be concluded that the dehydroxylation of the Uley nontronites is occurring as a continuous process. The exact reasons for the difference in thermal behaviour of the two Uley nontronites compared to the reference nontronites are unclear. One possible reason for this could be the very small particle size of the two Uley nontronites. A second possibility is that these are not dehydroxylation steps but rather possible phase changes.

3.3. Dehydration in the dynamic DTGA experiment (constant heating rate)

The DTGA curves for the series of nontronites are shown in Fig. 2. The bulk of the water is lost in the first dehydration step, which occurs over the 60–20 °C temperature range. The percentage weight loss varies between samples but is between 12.1 and 15.0%. The second dehydration step starts at ~20 °C and is complete by 160 °C and the weight change varies between 2.5 and 4 wt.%. The third dehydration step is ~160 °C and a loss of around 1% is observed. For the Uley brown nontronite, only one dehydration step could be observed. A small weight loss of 0.90% is observed over the 200–300 °C temperature range. This small weight loss is quite often observed for smectites and may be attributed to the overlap of the dehydration and dehydroxylation steps.

The results presented here are in agreement with previously published data [9]. Greater weight losses are observed in this work and we have differentiated steps in the dehydration process. The weight loss during the dehydroxylation step is around 4% and is consistent for all samples. The theoretical weight loss of the dehydroxylation step for a nontronite is 3.96%. Thus, the experimentally observed dehydroxylation weight loss values for the two Uley nontronites are close to the theoretical value and agree with

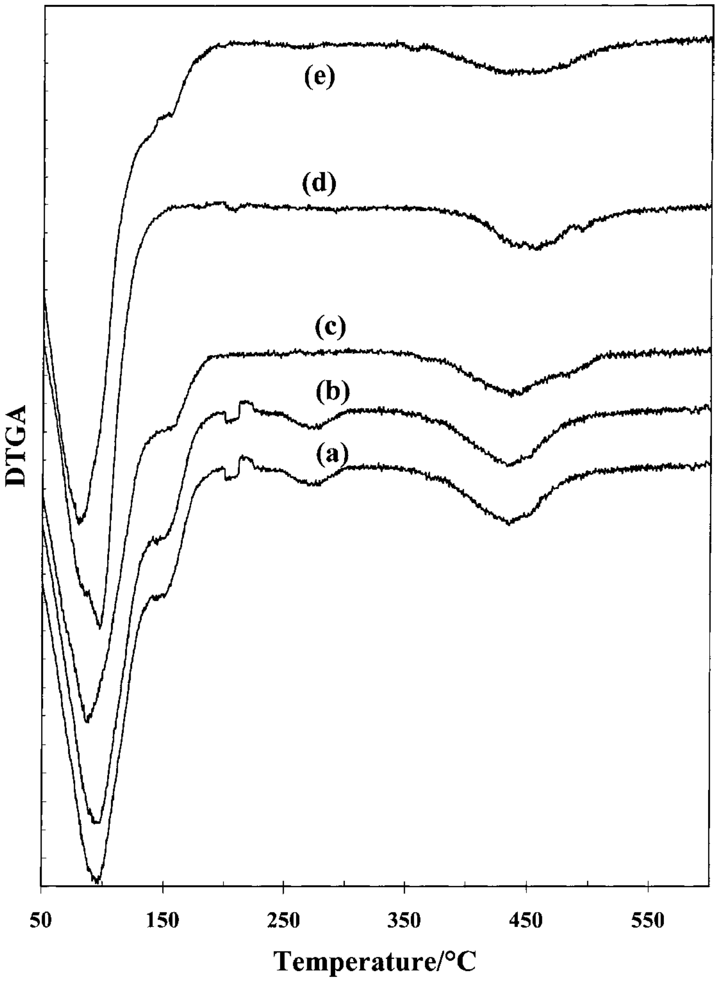

Fig. 2. DTGA patterns of the nontronites: (a) Hohen-Hagen; (b) Garfield; (c) NAu1; (d) NAu2; (e) ferruginous smectite.

published value [10]. The TGA patterns show that the thermal behaviour of the two South Australian nontronites closely follows the behaviour of the more well-known nontronites from Hohen-Hagen and Garfield.

3.4. Dehydroxylation in the dynamic DTGA experiment (constant heating rate)

Fig. 2 shows one differential weight loss centred around 440 °C with basically a single weight loss step. The weight loss for the ferruginous smectite is broad, probably indicative of a range of structures. Some higher temperature transitions may be also observed.

3.5. Relationship between the mass spectrum of water and the DTGA in the controlled rate experiment

Fig. 3 shows the DTGA curve for the Garfield nontronite and the mass spectrum of evolved water. One conclusion that is made is that the mass spectrum follows the DTGA curve with absolute precision. This is as expected as both measurements determine weight loss as a function of the temperature. Indeed, the DTGA curve is the differential of the TGA curve. Thus, a series of peaks are obtained as may be observed in Fig. 3. Thus, the integration of these peaks when normalised should be the percentage weight

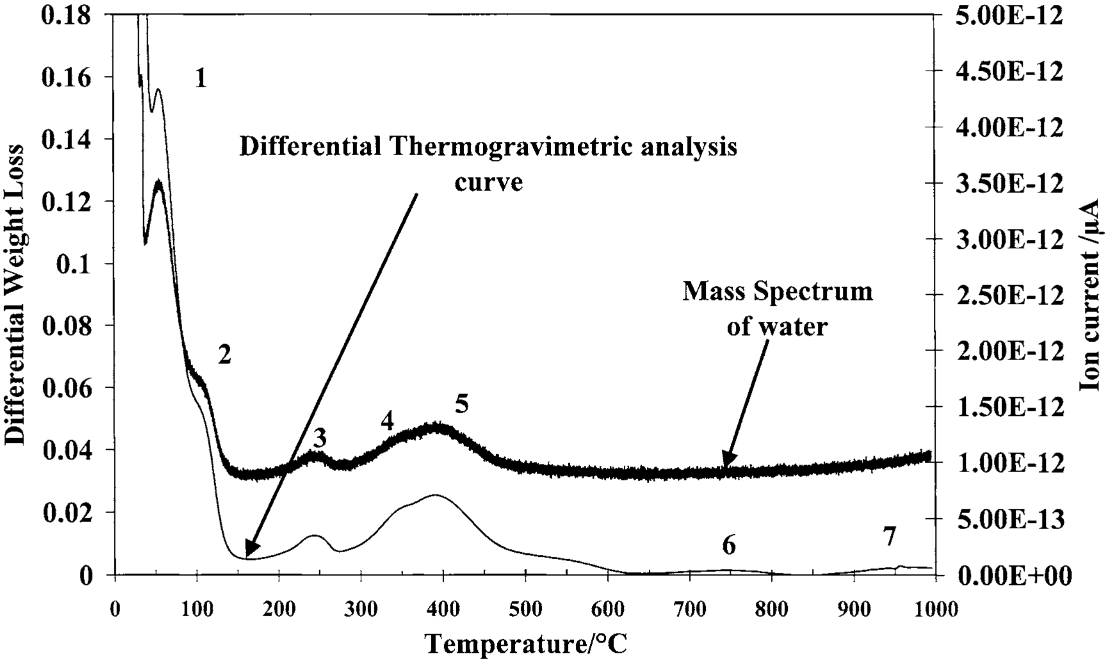

Fig. 3. Relationship between the mass spectrum of water and the DTGA curve in the CRTA experiment.

losses for that thermal change. Similarly the percentage weight loss may also be determined using the MS data. This then gives a second method of determining the weight loss for a particular thermal step.

Both the MS and DTGA results are reported in Table 2. In the controlled rate experiment, two distinct dehydration steps in both the MS and DTGA curves are observed at around 60–70 °C and at around 110–125 °C. There is a further weight loss around 240 °C. Both the mass spectrum and the DTGA curves show two distinct dehydroxylation steps at around 402 and 350 °C. In the DTGA patterns, there is a small weight loss at 540 °C, which is not associated with water but is associated with a loss of oxygen.

3.6. DTGA in the controlled rate experiment

The DTGA curves for the nontronites studied in this research using the CRTA technique are shown in Fig. 4. A number of observations can be readily made: (a) the dehydration steps appear to be resolved; (b) these dehydration steps are different for the different nontronites; (c) some nontronites such as the Garfield nontronite and the ferruginous smectite have an additional dehydration step at around 240 °C, as confirmed by MS; (d) each nontronite has two dehydroxylation steps; (e) higher temperature weight losses are observed which are not associated with the loss of hydroxyl units; (f) overall there is excellent agreement with the results obtained from DTGA and MS methods.

The first dehydration step is observed around 80–90 °C and is resolved from the other dehydration steps (step marked 1 in Fig. 4). The weight loss appears to vary between the nontronites, which is not unexpected as these numbers simply measure the amount of adsorbed water. The second dehydration step (step 2, Fig. 4) occurs in the 110–125 °C region for the nontronites and at 103 °C for the ferruginous smectite. The percentage weight loss appears reasonably constant for the nontronites for this step, which is accountable in terms of the cation water of hydration. This step is assigned to water surrounding the cation in the interlayer space. The values as determined by DTGA and MS are in good agreement for this step. The third dehydration step (step 3 in Fig. 4) occurs around the 225–245 °C temperature range. The values appear to vary between the DTGA and MS techniques. This may be accounted for by the difficulty in curve fitting the noisy MS patterns.

Table 2
Results of the thermal analysis of the DTGA patterns of nontronites and a ferruginous smectite as measured by the controlled rate heating experiment

	Nontronite									
	Hohen-Hagen		Spokane		SWA1		NAu1		NAu2	
	DTGA	MS	DTGA	MS	DTGA	MS	DTGA	MS	DTGA	MS
Dehydration (°C)	86	90.9	60.6	60.4	82	85	81	82	85	85
Step 1 (%)	2.0	2.9	11.6	5.4			9.5	13.9		
Dehydration (°C)	117	117	110	113	103	103	126		125	
Step 2 (%)	3.9	4.5	3.9	2.8	3.7	2.0	2.8		2.7	
Dehydration (°C)	241	245	242	243	233	234	243	242	245	
Step 3 (%)	8.0	11.7	8.7	14.5	15.0	16.9	3.1	15.2	2.1	
Dehydroxylation (°C)	344	347	350	352	357	350	336	337	355	348
Step 4 (%)	25.9	33.5	21.7	26.2	34.7	15.6	20.4	15.9	21.3	35.2
Dehydroxylation (°C)	393	390	402	402	413	401	380	398	402	412
Step 5 (%)	47.5	27.4	47.8	43.7	44.9	39.9	32.7	41.7	68.2	54.9
Deoxygenation (°C)		533	540		568	530	434	592	522	
Step 6 (%)		4.0	6.2		1.6	6.5	31.4	9.6	7.9	

The CRTA experiment clearly shows two overlapping dehydroxylation steps (steps 4 and 5 in Fig. 4). The temperature of the first dehydroxylation step varies from 340 to 350 °C and the second from 390 to 412 °C. The temperature values as determined by MS are in excellent agreement with the DTGA results. The average value for the dehydroxylation step at around 350 °C is 24.1% and the average value for

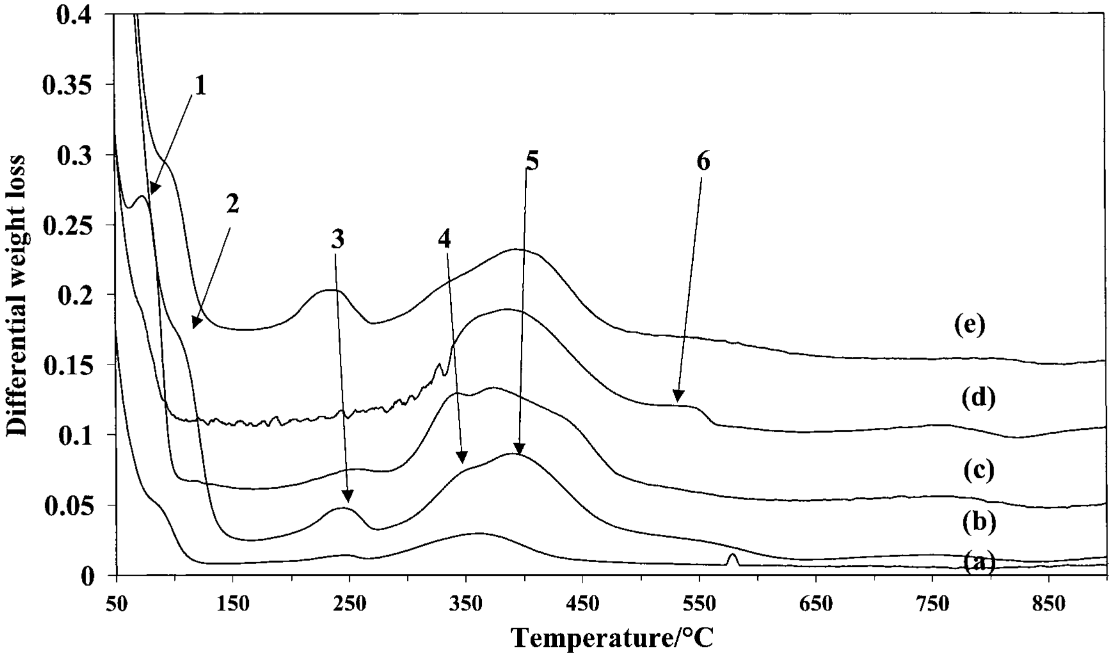

Fig. 4. DTGA patterns obtained using controlled heating rates of the nontronites: (a) Hohen-Hagen; (b) Garfield; (c) NAu1; (d) NAu2; (e) ferruginous smectite.

the second dehydroxylation step is 47.8%. In other words, the ratio of dehydroxylation steps 1 and 2 is 1:2. Such a number may be attributed to the arrangement of the hydroxyls on the octahedral Fe. The ratio of Fe/dioctahedral space to Fe/Fe is 1:2.

3.7. Comparison of the dynamic and CRTA experiments

It is interesting to compare the data in Tables 1 and 2, which reflect the DTGA dynamic experiment and the CRTA DTGA/MS experiment. The use of CRTA enables the weight changes to be more easily separated. Differences in the temperatures of dehydration occur in the two experiments. In the dynamic experiment, the dehydration steps overlap and occur at temperatures below those measured in the CRTA experiment. For example the first two dehydration steps occur at 62 and 97 °C for the Hohen-Hagen nontronite in the DTGA experiment and occur at 86 and 117 °C in the CRTA experiment. Similarly, the third dehydration step occurs at around 150 °C in the dynamic experiment and at 240 °C for the CRTA experiment. Thus, in the controlled rate heating experiment the temperatures of the dehydration steps occur at significantly higher temperatures. In the DTGA experiment, only one dehydroxylation step was observed, two overlapping dehydroxylation steps are observed in the CRTA experiment. Heating at a constant rate appears to displace the dehydroxylation step to higher temperatures.

4. Conclusions

A number of conclusions may be drawn.

(a) The mass spectrum of water for the nontronites follows with precision the DTGA curves in the CRTA experiment.
(b) The CRTA experiment enables the separation of the weight losses for the dehydration steps of nontronite.
(c) The CRTA experiment enables the separation of the weight losses for the dehydroxylation steps of nontronite.
(d) Two dehydroxylation steps are observed in the CRTA experiment.
(e) The ratio of weight loss for these two steps is 1:2.
(f) Significant differences in the results as determined by the dynamic and CRTA experiment are observed.

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