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Distinction of nontronite from palagonite by thermal analysis and evolved-gas analysis: Application to Mars surface exploration[1]

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Abstract

Alternative models for the soils of Mars have invoked either the mineral nontronite (an iron-rich smectite clay) or the mineraliod palagonite (an oxidized, hydrated alteration product of basalt glass) as the major silicate component. Laboratory tests on representative terrestrial minerals demonstrate that nontronite is distinguishable from palagonite by their respective responses to combined thermal and evolved-gas analysis. When subjected to differential scanning calorimetry (DSC) or simultaneous thermogravimetric analysis and differential thermal analysis (SDT), combined with mass spectrometry (MS) of evolved gases, nontronite and palagonite differ in the onset temperatures, peak intensities, and peak profiles for their respective dehydration reactions. Using operating conditions apporpriate for a small planetary surface instrument (40°C min^{-1}, 50 ml Ar min^{-1}), nontronite dehydration peaks are sharply centered at ~ 120–125°C and ~ 460–490°C; equivalent peaks for palagonite occur more broadly at ~ 125–145°C and ~ 620°C. Further distinctions can be made from detailed shapes of the respective SDT profiles, especially at temperatures of 1000–1300°C. The SDT–MS data also reveal minor carbonates, sulfates, and nitrates naturally admixed with the major silicates.

Keywords: Evolved gas analysis; Soil; Thermal analysis

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1. Introduction

The development of flight instruments that would identify the phase composition, volatile compound contents, and oxidation state of iron in planetary surface materials has been recommended by the National Academy of Sciences [1]. Towards that goal, thermal analysis (TA) and evolved-gas analysis (EGA) experiments are being developed for combination into miniaturized, flight-qualified instruments [2, 3]. A major objective of this study is to evaluate how TA–EGA can address one of the key outstanding questions regarding martian soil mineralogy: Is the martian soil dominated by iron-rich smectite clays (for example, nontronite) or by the hydrous, clay-like mineraloid known as "palagonite" [3]? Palagonite is a yellow or orange mineraloid formed by hydration and devitrification of basaltic glass [4]. Our specific purpose was to identify the optimum TA–EGA operating conditions (heating rate, purge rate, etc.) for distinguishing nontronite from palagonite. Although planetary flight experiments are expected to be limited in capability [2, 3] relative to laboratory experiments, we employed a wide variety of methods to achieve sample characterization. Our approach included differential scanning calorimetry (DSC), modulated DSC (MDSC), differential thermal analysis (DTA), thermogravimetry (TG), derivative TG (DTG), simultaneous TG–DTA (SDT), and mass spectrometry (MS).

2. Experimental conditions

Five samples of Mars-analogous minerals and soils (NG-1, SWa-1, HWMK11, HWMK12 and HWMK13) were prepared at NASA Lyndon B. Johnson Space Center. NG-1 and Swa-1 are iron-rich smectite clays. HWMK11, 12, 13 are palagonite-bearing soils from Hawaii. The details of sample preparation are listed in Appendix 1.

Approximately 15–20 mg of each HWMK sample and around 5 mg of the NG-1 and SWa-1 samples were used in this study. A TA Instruments 2960 SDT system, combined with a VG Thermolab MS was used. This system gives information on the weight loss (TG), heat evolved (DTA) and gas evolved (MS) from the sample.

The experimental conditions for the SDT–MS are as follows: pan; alumina open cup without reference; heating rate, 40°C min^{-1}; flow rate, 50 ml min^{-1} of argon; MS range, 1–100 amu; sample size, $\sim$ 20 mg.

The TA 2920 MDSC was used to determine the usefulness of this technique for these samples. The MDSC provides information on the total, reversing and nonreversing heat flows and the heat capacity of the sample in a single experiment. Compared to the conventional DSC an MDSC increases resolution without loss of sensitivity. The MDSC curves were obtained under the following conditions: crimped alumnum pan (Al_2O_3 is the reference material), 50 ml min^{-1} of helium gas, 5°C min^{-1} heating rate (the maximum heating rate that can be used in an MDSC), 60 for one period (cycle), and 3°C amplitude.

The experimental conditions for the DSC are as follows: temperature range room temp. to 720°C; flow rate, 50 ml min^{-1} of argon or helium; heating rate, 20°C min^{-1} and 40°C min^{-1}; pan, platinum open pan with Al_2O_3 as reference.

3. Results and discussion

3.1. DSC

Fig. 1 shows the DSC curves for the five samples in argon at 40°C min^{-1}. The general features of the DSC curves for the five samples in argon at 20°C min^{-1}, in argon at 40°C min^{-1} and in helium at 40°C min^{-1} may be summarized as follows:

(i) NG-1 and SWa-1 give similar DSC curves and HWMK11, 12 and 13 give similar DSC curves.

(ii) All five samples have a first endothermic peak, due to sorbed water, in the temperature range between room temperature and 200°C.

(iii) NG-1 and SWa-1 give their main dehydroxylation peak in the 420°C region; this dehydroxylation is not well-defined in the HWMK11 and 12 palagonite samples. A slow process of dehydroxylation for the HWMK13 sample is observed between 380 and 550°C.

(iv) HWMK12 and 13 give an endothermic peak at around 600°C which does not appear in NG-1 or SWa-1.

(v) The fast heating rate (40°C min^{-1}) increases the sensitivity of heat flow compared to the slow heating rate (20°C min^{-1}).

(vi) There is no significant difference between using argon or helium as the purge gas.

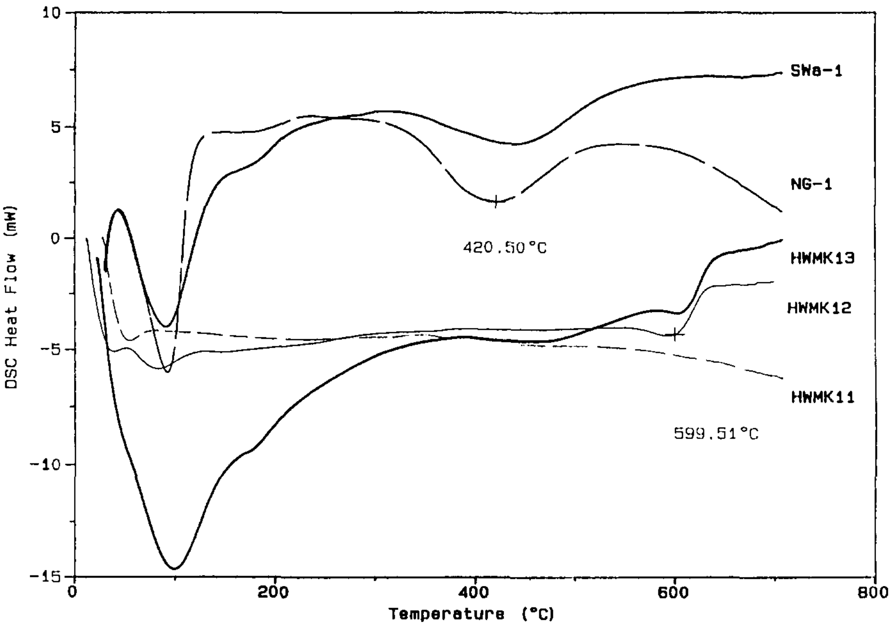

Fig. 1. DSC curves for NG-1, SWa-1, HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

3.2. MDSC

Samples NG-1 and HWMK12 both show significant features only in their nonreversible heat flows. In the case of NG-1, the first endothermic peak around 100°C is due to loss of interlayer water and the second at around 400°C is due to dehydroxylation of the octahedral layers. In the case of HWMK12, the first endothermic peak at around 60°C is not well-defined. HWMK12's DSC curve shows two more broad and not well-defined endothermic peaks in the 100 and 500°C region; this indicates that the dehydroxylation process is slow. Such a slow loss is not likely to produce a sharp DSC peak in the curve.

There is no useful information from the reversible heat flow curves. The MDSC is not recommended to be heated above 300°C and the heating rate must be below 5°C min^{-1}. This technique was therefore not applicable and was not pursued further.

3.3. SDT

The differential thermal curves for the five samples reproduced in Fig. 2 and Table 1 show the following.

(i) An endothermic peak between room temperature and 300°C represents the loss of sorbed moisture from the sample. The peaks for NG-1 and SWa-1 are sharper than those of HWMK11, 12 and 13.

(ii) A medium-small endothermic peak at about 450°C is due to dehydroxylation for the NG-1 and SWa-1 samples.

(iii) NG-1 and SWa-1 give a small endothermic peak at 660°C and this is followed by a relatively broad s-shaped endothermic-exothermic peak between 800 and 1400°C. The peak at about 660°C might be due to a change in the magnetic properties of hematite. The endothermic-exothermic peak may be due to some structural rearrangement and crystallization.

(iv) An endothermic peak at exactly 618°C is observed for the HWMK samples. This peak may be due to a phase change of natural, structurally disordered mineraloids, or devitrification of basalt glass, i.e., the unhydrated silicate-glass cores of the palagonite particles [3].

(v) An s-shaped endo-exothermic peak is also observed at around 1000°C in the HWMK samples; this peak, may be due to some structural rearrangement and crystallization.

(vi) The HWMK11 sample gives a sharp melting peak at 1303°C for α-Fe_2O_3.

3.4. TG and DTG

TG and DTG curves for the samples are shown in Figs. 3 and 4 and in Tables 2 and 3. Comparison of the DTA curves with the TG and DTG curves may be summarized as follows:

(i) NG-1 shows a clear distinction between the two inflections (sorbed water and dehydroxylation). SWa-1 shows a gradual continuous weight loss between the two

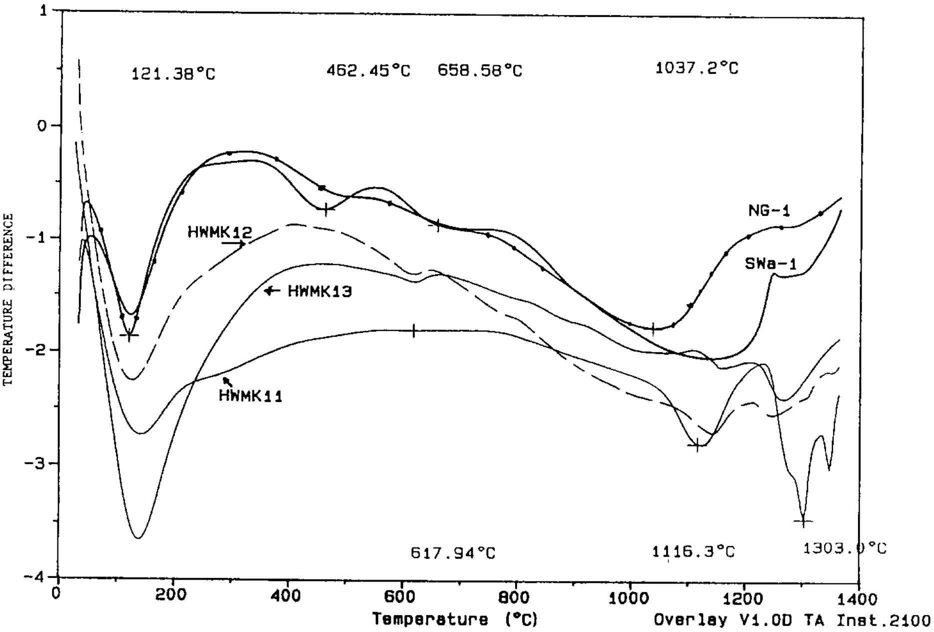

Fig. 2. DTA curves for NG-1, SWa-1, HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

Table 1
DTA peak maxima in argon (°C)

NG-1	SWa-1	HWMK11	HWMK12	HWMK13
121	125	146	126	139
458	485	617	617	618
660	693			
1037	1140	1120	1139	1152
		1269	1246	1263
1360(–)	1360(–)	1303		
		1343		

(–), Exothermic reaction.

inflections. The clear distinction between the two inflections is observed only with exchangeable cations of high hydration energy (such as Mg^{2+}).

(ii) The HWMK samples show a gradual continuous weight loss up to 800°C.

(iii) The total weight loss for NG-1, SWa-1, HWMK11, HWMK12, and HWMK13 are 85%, 79%, 99%, 99% and 96%, respectively.

(iv) The second DTG peak for NG-1 and SWa-1 is an overlapping peak. Both peaks start tailing at around 520°C; thus, the weight loss in this temperature range (200–700°C) is not only due to the dehydroxylation of the sample. In the case of the HWMK

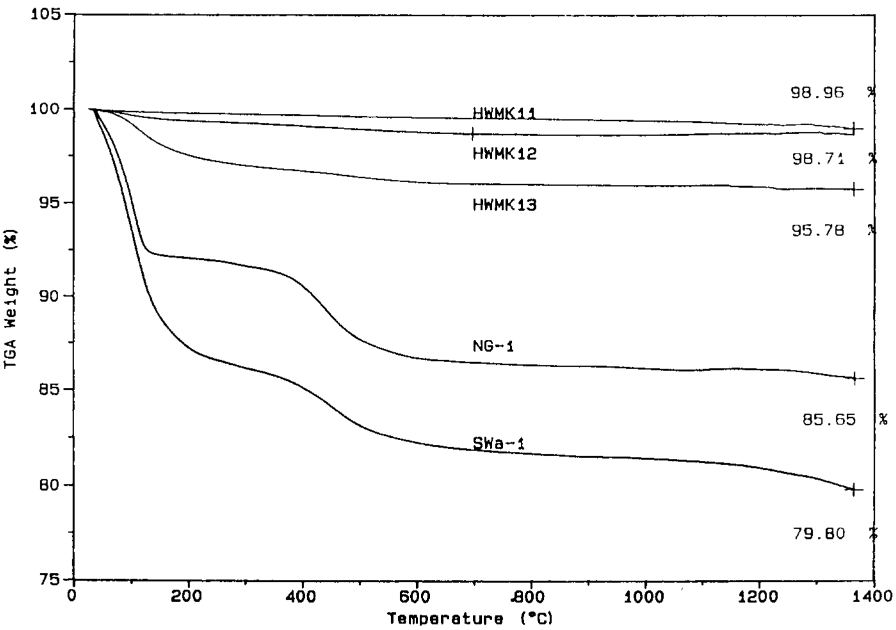

Fig. 3. TGA curves for NG-1, SWa-1, HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

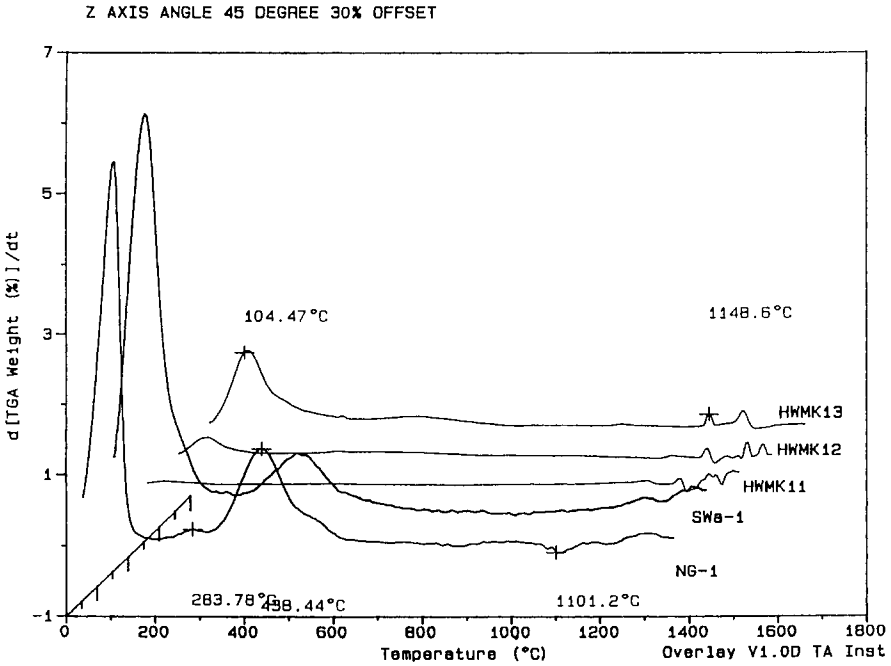

Fig. 4. DTG curves for NG-1, SWa-1, HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

Table 2
TGA in argon (weight loss %)

	NG-1	SWa-1	HWMK11	HWMK12	HWMK13
R–200°C	7.94	12.79	0.2	0.63	2.48
200–700°C	5.59	5.32	0.25	0.66	1.47
700–1000°C	0.31	0.43	0.13	0.07	0.09
1000–1360°C	0.51	1.63	0.46	−0.02	0.18

Table 3
DTG in argon (temperature of peak max/°C)

NG-1	SWa-1	HWMK11	HWMK12	HWMK13
104	103	69	90	103
438	450	400	(390)	(323)
			490	490
1080(+)				
1110(+)				
		1152	1139	1148
	1227	1229	1215	1224
		1248(+)	1235(+)	1256(+)
		1295	1290	
1309	1310	1311	1306	
-	1340	1355	1347	

(+), Weight gain.

samples, the DTG curve is not well-defined in this temperature range; this is due to the slow weight loss process of the samples.

(v) The DTG curve for all samples is not significant (no weight change) between 700 and 1000°C.

(vi) A negative DTG peak is observed in the case of NG-1 at 1100°C which indicates a weight gain; this is followed by a weight loss, indicating that the sample is starting to decompose.

(vii) The DTG curve for the HWMK samples is more complicated than those of NG-1 and SWa-1 in the higher temperature range. The HWMK samples have a weight loss that is followed by a weight gain in the 1215–1256°C region. After that, HWMK11 and 12 have additional weight loss peaks.

(viii) The DTG curve of HWMK11 is similar to that of HWMK12.

(ix) HWMK13 gives two clearly defined weight loss peaks at 1148 and 1224°C.

3.5. MS

Fig. 5 shows the mass soectrul data curves for NG-1. A summary of the gas-evolved MS data for each sample follows:

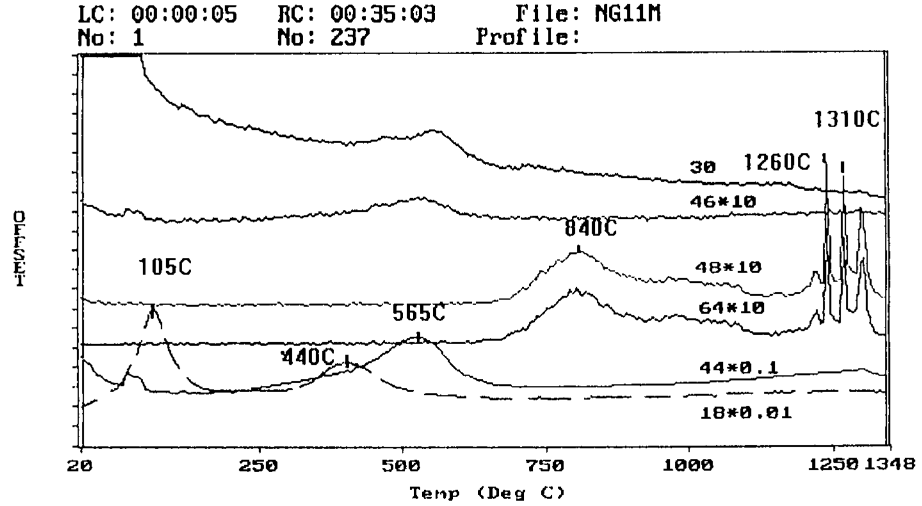

Fig. 5. MS curves for NG-1.

(i) Two water peaks ($m/e = 18$), one at 107°C and the other at 440°C, correspond to the removal of physically adsorbed water and the expulsion of water from the crystal structures. Both peaks match the DTG and DTA peaks in the case of NG-1 and SWa-1.

(ii) The CO_2 peak ($m/e = 44$) starts at 250°C and ends at 650°C with the peak maximum at 550°C in both samples (NG-1 and SWa-1). The CO_2 peak corresponds to the overlapping DTG peak mentioned above (under the TGA and DTG section and shown in Fig. 4). The CO_2 peak is due to the decomposition of carbonate that was naturally admixed with the silicate clay. The peak is also observed at 550°C in the case of NG-1. Both samples show peaks at $m/e = 30$ and $m/e = 46$ at about 650°C, indicating the possible presence of NO_2. This NO_2 data may comprise the first evidence of nitrates in these minerals.

(iii) HWMK11 gives a water peak between room temperature and 560°C; it corresponds to the slow weight loss of the sample. CO_2 evolution occurred between 750 and 1000°C. CO_2 evolution occurred again at 1200°C. The SO_2 peaks ($m/e = 64$) are well-defined in this sample. The first is an overlapping peak between 750 and 1200°C, and several sharp SO_2 peaks are defined at 1265, 1295 and 1350°C. The fragment ion at $m/e = 48$ is consistent with this interpretation. This is evidence for traces of sulfate minerals.

(iv) HWMK12 gives a well-defined sorbed water peak at 115°C and is followed by a gradual water release peak between 250 and 750°C. CO_2 continues to be gradually evolved above 500°C. The SO_2 peaks are again well-defined at 900°C, 1300°C and 1350°C.

(v) HWMK13 gives an overlapping water peak which is due to sorbed water, the other salt-mineral and the dehydroxylation of zeolite. The CO_2 peak is well-defined at 490°C and is again noted at 710°C.

3.6. Mixture of NG-1 with the HWMK samples

The purpose of this study is to distinguish smectite from palagonite. Thus, it is interesting to record the SDT–MS data for the mixture of NG-1 and the HWMK samples. The samples were physically mixed in 1 : 1 proportions. Some DTA, DTG and MS data are shown in Figs. 6–8. Combining DTA, DTG and MS data provide the following features of interest:

(i) The smectite (NG-1) shows its dehydroxylation peak at 455°C and the palagonite (HWMK11, 12, 13) has this structural change peak at 618°C.

(ii) The smectite has a high-temperature endothermic peak at 1040°C. The palagonite has high-temperature peaks at 1120 and 1250°C. The endothermic peak at 1328°C is complete.

(iii) HWMK11 has a melting peak at 1305°C.

(iv) All gas evolution peaks (CO_2, H_2O, SO_2 and NO_2) that are found in the individual samples are identified in the mixture sample.

4. Conclusions

Nontronite can be distinguished from palagonite by thermal analysis at a fast heating rate of 40°C min^{-1} in argon purge gas at 50 ml min^{-1}. The evolved-gas analysis provides additional information, including identification of trace carbonates, sulfates, and nitrates that might not be apparent by solid-state analysis alone.

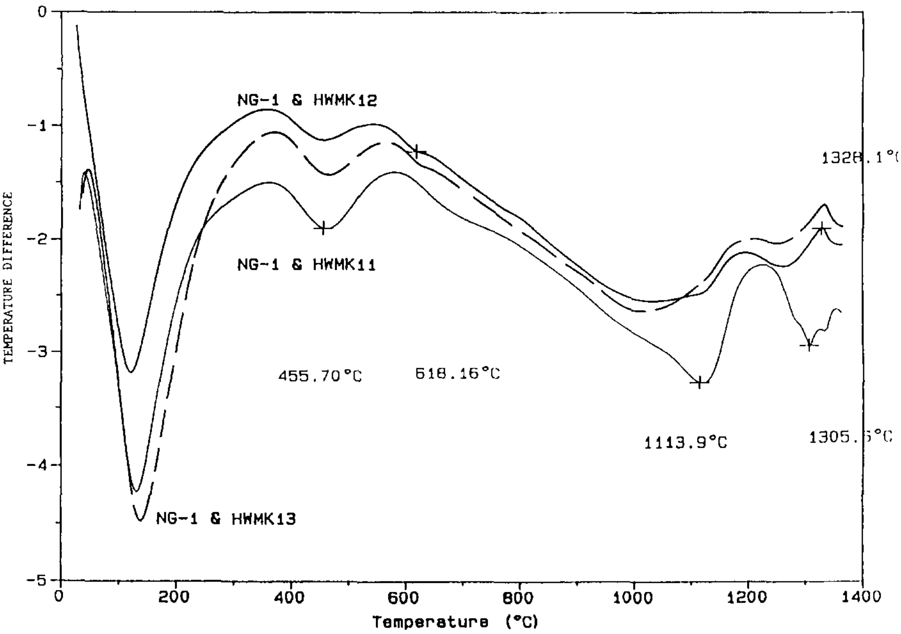

Fig. 6. DTA curves for NG-1 mixed with HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

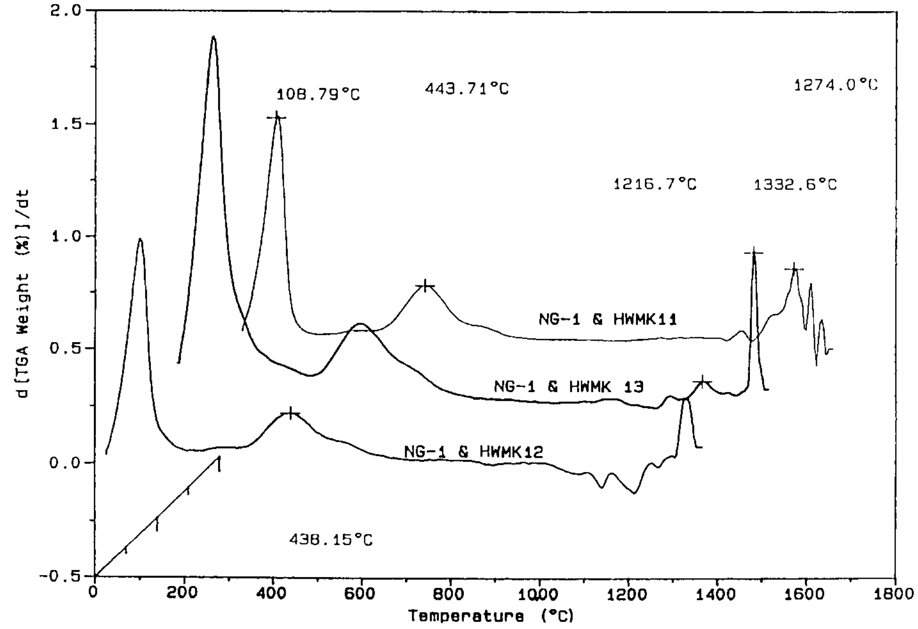

Fig. 7. DTG curves for NG-1 mixed with HWMK11, HWMK12 and HWMK13 in argon, 40°C min^{-1}.

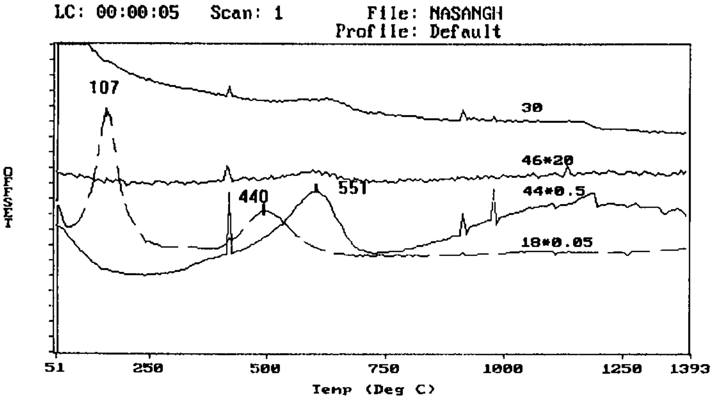

Fig. 8. MS curves for NG-1 mixed with HWMK11.

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Thermal Analysis Fellowship Grant. J.H. Allton and D.C. Golden prepared samples at NASA JSC.

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Appendix 1. Preparation of samples

NG-1 is nontronite (a specific iron-rich smectite clay) from Hohen Hagen, Germany. It is a standard reference clay from the Clay Minerals Society. The original material was nontronite-cemented sand (15–20% nontronite) from The Clay Mineral Society. The material was subsequently processed to purify nontronite as detailed below.

Swa-1 is an iron-rich smectite clay from Grant County, Washington, USA. The original material was obtained from The Clay Mineral Society and then processed as detailed below.

Both NG-1 and SWa-1 were air-dried and gently crushed. The crushed material was suspended in an aqueous solution of NaOH adjusted to a pH of 9.5. The suspension was sonicated for approximately 10 min, several times as needed, to break up and disperse clay particles. The supernatant liquid containing suspended particles was then centrifuged at 800 rpm for 4 min to precipitate the silt particles. The clay particles < 2 μm remained in suspension. These particles were flocculated by the addition of 10 g of salt. NaCl was used to precipitate NG-1 nontronite and $MgCl_2$ was used for the SWa-1 ferruginous smectite. Further centrifugation was used to concentrate the clay particles (3000 rpm for 5 min), because flocculation was not very efficient. Excess salt was removed from the resulting mud by placing the sample in dialysis tubing and soaking in deionized water for several days, until no more salts diffused out, as indicated by a negative silver nitrate test. The mud was placed in a freeze drier to remove the water. The resulting sample was a fluffy yellow powder.

HWMK11–13 are 0.02-mm sieves fractions of palagonite-bearing soils from Mauna Kea, Hawaii. These fractions contain little or no smectite but do contain traces of zeolites (erionite, a hydrous aluminosilicate), iron oxides (hematite, Ti-magnetite), and palagonite (hydrated Mg, Fe-rich rock glass) that is expected to be thermally active.