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BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: THERMAL ANALYSIS

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INTRODUCTION

Thermal analysis involves a dynamic phenomenological approach to the study of materials by observing the response of these materials to a change in temperature. This approach differs fundamentally from static methods of analysis, such as structural or chemical analyses, which rely on direct observations of a basic property of material (*e.g.* crystal structure or chemical composition) at a well-defined set of conditions (*e.g.* temperature, pressure, humidity). Clay minerals are highly susceptible to significant compositional changes in response to subtle changes in conditions. For example, changes in the fugacity of water affect the stability of interlayer H_2O in a clay mineral (see below). Therefore, care must be taken that all experimental conditions are known with accuracy and precision.

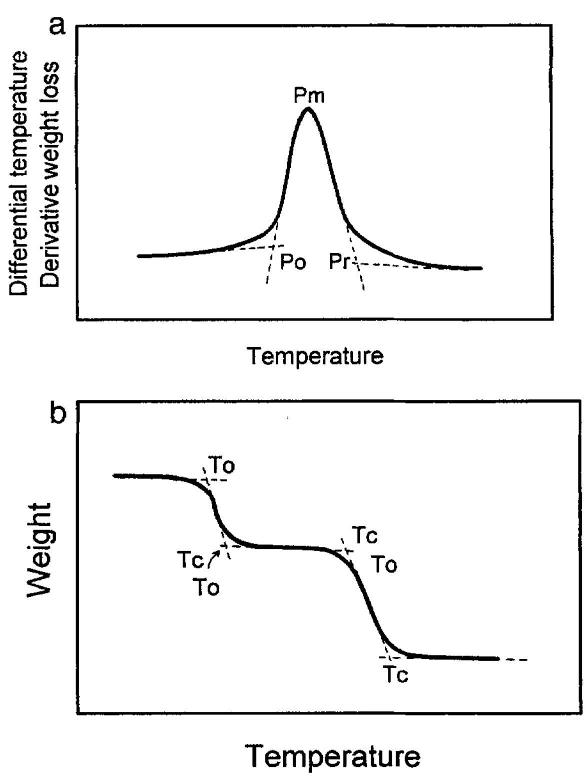

Figure 1. Parameters defined for a simple DTA or DTG peak (a) and for a TG curve (b).

Differential thermal analysis (DTA), thermal gravimetric analysis (TG or TGA), and derivative thermal gravimetric (DTG) analysis are reported for each of the eight Source Clay minerals using commonly available commercial instruments. The DTA curves show the effect of energy changes (endothermic or exothermic reactions) in a sample. For clays, endothermic reactions involve desorption of surface H_2O (*e.g.* H_2O on exterior surfaces) and dehydration (*e.g.* interlayer H_2O) at low temperatures (<100°C), dehydration and dehydroxylation at more elevated temperatures, and, eventually, melting. Exothermic reactions are related to recrystallization at high temperatures that may be nearly concurrent with or after dehydroxylation and melting. Discriminating between desorption and dehydration or dehydration and dehydroxylation may be problematic. The TG curves ideally show only weight changes during heating. The derivative of the TG curve, the DTG curve, shows changes in the TG slope that may not be obvious from the TG curve. Thus, the DTG curve and the DTA curve may show strong similarities for those reactions that involve weight and enthalpy changes, such as desorption, dehydration and dehydroxylation reactions.

In thermal analytical studies of clay minerals, results from different laboratories often show significant variations in the desorption and dehydration properties of these minerals. Koster van Groos, Guggenheim and co-workers (for a summary, see Guggenheim and Koster van Groos, 1992a,b), found that the temperature of an event involving H_2O is greatly affected by the fu-

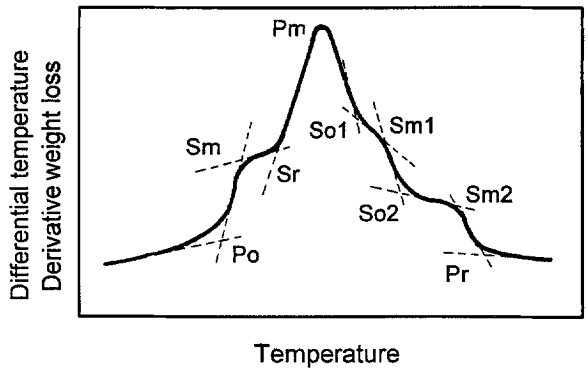

Figure 2. Parameters defined for complex DTA or DTG peaks.

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Table 1. Themogravimetric analysis.

Sample	Adsorbed water/Dehydration/Other									Other			Dehydroxylation					
	To	Tc	Δ wt.%	To	Tc	Δ wt.%	To	Tc	Δ wt. %	To	Tc	Δ wt.%	To	Tc	Δ wt.%	To	Tc	Δ wt.%
KGa-1b*	<20	—	—	—	—	—	—	—	—	—	469	0.40	468	567	12.66º	—	—	—
KGa-1b^	<20	—	—	—	—	—	—	—	—	—	474	1.68	474	566	12.26º	—	—	—
KGa-2*	<20	—	—	—	—	—	—	—	—	—	457	0.55	457	541	12.08º	—	—	—
KGa-2^	<20	—	—	—	—	—	—	—	—	—	462	2.07	462	561	12.19º	—	—	—
SWy-2^	<20	69	6.22	69	151	1.32	—	—	—	151	631	1.70	631	719	3.20	—	—	—
SWy-2″	<20	74	8.26	74	158	1.46	—	—	—	158	619	1.39	619	713	3.47	—	—	—
SAz-1*	<20	90	7.39	90	155	2.80	—	—	—	155	541	1.05	541	683	2.93	—	—	—
SAz-1^	<20	100	13.65	100	165	3.90	—	—	—	165	575	2.01	575	674	2.44	—	—	—
SAz-1″	<20	92	15.22	92	162	4.00	—	—	—	162	567	2.32	567	666	2.82	—	—	—
STx-1*	<20	107	5.04	107	173	7.40	—	—	—	173	598	1.00	598	709	2.73	—	—	—
STx-1^	<20	93	10.61	93	165	2.66	—	—	—	165	617	1.45	617	706	2.63	—	—	—
STx-1″	<20	76	8.97	76	148	2.89	—	—	—	148	545	1.82	545	703	2.89	—	—	—
Syn-1^	<20	70	3.81	—	—	—	—	—	—	70	409	2.69	409	531	4.81	531	643	2.72
Syn-1″	<20	64	5.01	—	—	—	—	—	—	64	408	2.75	408	523	4.81	523	639	2.66
SHCa-1^	<20	78	7.85	—	—	—	—	—	—	78	562	1.62	562	658	0.64	858	711	0.19
SHCa-1″	<20	73	6.70	—	—	—	—	—	—	73	564	1.70	564	717	1.20	717	743	0.60
PFl-1*	<20	71	2.12	71	115	4.73	187	245	2.24	245	361	0.49	361	506	4.30	—	—	—
PFl-1^	<20	64	3.92	64	97	4.31	191	247	2.20	247	382	1.01	382	497	3.77	—	—	—
PFl-1″	<20	86	6.33	86	170	1.51	170	220	2.37	220	354	0.94	354	510	4.53	—	—	—

See Figure 1b and text for definition of column headings and other abbreviations.
* UIC, nitrogen purge; ^ UT, no nitrogen purge; ″ UT, nitrogen purge.
º Δ wt.% based on sample weight just prior to dehydroxylation.
SHCa-1^ Four additional dehydroxylation events are at: To = 711°C, Tc = 741°C; Δ wt.% = 0.63; To = 741°C, Tc = 806°C, Δ wt.% = 0.73; To = 806°C, Tc = 850°C, Δ wt.% = 0.92; To = 850°C, Tc = not available, Δ wt.% > 1.78.
SHCa1″ Three additional dehydroxylation events are at: To = 743°C, Tc = 809°C, Δ wt.% = 0.90; To = 809°C, Tc = 848°C, Δ wt.% = 0.80; To = 848°C, Tc = 894°C, Δ wt.% = 0.60.
PFl-1* Additional dehydration occurred at: To = 115°C, Tc = 187°C, Δ wt.% = 1.16.
PFl-1^ Additional dehydration occurred at: To = 97°C, Tc = 191°C, Δ wt.% = 1.59.
PFl-1″ Additional dehydration occurred at: To = 115°C, Tc = 187°C, Δ wt.% = 1.16.

Table 2. Derivative thermal gravimetry.

Sample	Adsorbed water/Dehydration																Dehydroxylation						
	Peak (1)									Peak (2)													
	Po	Sm	Sr	Pm	So1	Sm1	So2	Sm2	Pr	Po	Sm	Sr	Pm	So	Sm	Pr	Po	Sm	Sr	Pm	So	Sm	Pr
KGa-1b*	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	448	—	—	519	—	—	581
KGa-1b^	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	462	—	—	517	—	—	575
KGa-2*	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	437	—	—	506	—	—	553
KGa-2^	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	462	—	—	509	—	—	549
SWy-2^	<20	—	—	51	106	115	123	139	165	—	—	—	—	—	—	—	592	622	640	689	—	—	734
SWy-2"	<20	—	—	59	109	119	127	148	164	—	—	—	—	—	—	—	598	612	628	685	—	—	726
SAz-1*	<20	—	—	78	112	136	—	—	175	—	—	—	—	—	—	—	512	—	—	633	—	—	680
SAz-^	<20	—	—	65	72	80	121	144	172	—	—	—	—	—	—	—	546	—	—	639	—	—	691
SAz-1**	<20	—	—	64	70	76	117	146	174	—	—	—	—	—	—	—	542	—	—	633	—	—	689
STx-1*	<20	—	—	82	—	—	—	—	122	126	—	—	150	—	—	173	457	503	553	669	—	—	722
STx-1^	<20	—	—	69	—	—	—	—	113	122	—	—	146	—	—	169	595	—	—	679	—	—	719
STx-1^	<20			51	—	—	—	—	89	104	—	—	130	—	—	153	451	485	547	663	—	—	712
Syn-1^	<20	—	—	37	—	—	—	—	84	—	—	—	—	—	—	—	378	441	473	494	554	600	669
Syn-1"	<20	—	—	33	52	61	—	—	85	—	—	—	—	—	—	—	366	—	—	483	544	602	666
SHCa-1^	<20	—	—	64	—	—	—	—	85	—	—	—	—	—	—	—	617	—	—	636	—	—	663
SHCa-1"	<20	—	—	54	—	—	—	—	78	—	—	—	—	—	—	—	528	—	—	617	—	—	711
PFl-1*	<20	—	—	93	—	—	—	—	128	163	—	—	215	—	—	260	311	—	—	441	—	—	530
PFl-1^	<20	43	57	81	113	130	—	—	146	169	199	207	220	237	250	270	344	—	—	442	—	—	527
PFl-1"	<20	43	52	67	114	120	—	—	128	150	—	—	196	—	—	225	305	—	—	444	—	—	538

See Figures 1a and 2 and the text for definition of column headings and other abbreviations.
* UIC, nitrogen purge; ^ UT, no nitrogen purge; " UT, nitrogen purge.
STx-1^ One additional dehydroxylation peak at: Po = 474°C, Pm = 505°C, Pr = 529°C.
SHCa-1^ Three additional dehydroxylation peaks with: Po = 708°C, Pm = 729°C, Pr = 752°C; Po = 798°C, Pm = 827°C, Pr = 867°C; Po = 867°C, Pm = 890°C, Pr = 945°C.
SHCa-1" Three additional dehydroxylation peaks with: Po = 711°C, Pm = 735°C, Pr = 756°C; Po = 784°C, Pm = 829°C, Pr = 868°C; Po = 868°C, Pm = 908°C, Pr, not available.

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Table 3. Differential thermal analysis.

Sample	Dehydration												Dehydroxylation							Melting			Recrystallization				
	Peak (1)									Peak (2)																	
	Po	Sm	Sr	Pm	So1	Sm1	So2	Sm2	Pr	Po	Pm	Pr	Po	Sm	Sr	Pm	So	Sm	Pr	Po	Pm	Pr	Po	Pm	So	Sm	Pr
KGa-1b*	—	—	—	—	—	—	—	—	—	—	—	—	483	—	—	575	—	—	618	—	—	—	974	990	—	—	994
KGa-1b^	—	—	—	—	—	—	—	—	—	—	—	—	452	—	—	518	—	—	577	—	—	—	980	993	—	—	997
KGa-2*	—	—	—	—	—	—	—	—	—	—	—	—	474	—	—	568	—	—	604	—	—	—	961	977	—	—	981
KGa-2^	—	—	—	—	—	—	—	—	—	—	—	—	439	—	—	513	—	—	557	—	—	—	965	984	—	—	994
SWy-2*	90	—	—	135	—	—	170	185	209	234	332	374	601	—	—	684	—	—	737	—	—	—	889	923	948	960	976
SAz-1*	<70	—	—	178	204	228	269	327	368	—	—	—	548	—	—	641	695	704	721	815	854	883	950	979	992	1013	1106
STx-1*	<70	—	—	167	198	217	249	327	351	—	—	—	593	—	—	681	—	—	730	829	894	931	982	1008	1023	1080	1106
Syn-1*	90	—	—	139	—	—	—	—	188	251	319	353	392	458	502	532	563	578	673	—	—	—	939	990	—	—	1009
SHCa-1*	<70	—	—	156	—	—	200	250	265	265	331	360	727	741	758	827	—	—	888	1122	1175	1196	—	—	—	—	—
PFL-1*	97	—	—	152	—	—	—	—	196	209	272	307	377	—	—	455	—	—	526	—	—	—	850	872	—	—	915

See Figures 1a and 2 and the text for definition of column headings and other abbreviations.
* TK; ^ UT.
Syn-1* Two additional dehydroxylation peaks are at 489°C and 626°C
SHCa-1* One small additional dehydroxylation peak with: Po = 645°C, Pm = 695°C and Pr = 717°C was observed.

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Table 4. Comments on color changes after thermal analysis for samples analyzed at UIC.

Sample	Comments
KGa-1b	no change
KGa-2	change from tan to orange
SWy-2	change from tan to red-brown
SAz-1	change from brown-white to orange
STx-1	no change
Syn-1	no change
SHCa-1	no change
PFl-1	tan to dark red-brown

gacity of water, f_{H_2O}, at the hydrated site. Hence, the response of materials during thermal analysis will be strongly influenced by a variety of factors, including the humidity surrounding the sample at the time of the experiment. Evidence for this is shown by the effect of purging the atmosphere surrounding the sample with nitrogen. In addition, the grain size of clay aggregates, as well as the size of the individual crystals, will affect the diffusivity of H_2O and, consequently, f_{H_2O} at the hydrated site. More uniform experimental conditions may be obtained using high-pressure thermal analysis (HP-DTA), because the sample capsule may be sealed after water is added, thus controlling f_{H_2O}.

Other experimental variables which influence the apparent temperatures of water-loss reactions include sample size, packing, sample holder configuration, heating rate, particle distribution, contaminants, *etc.* Most of these affect the ability of water to equilibrate around the clay sample during a dynamic experiment. Although the storage of samples over a saturated solution of $Mg(NO_3)_2{\cdot}6H_2O$ prior to thermal analysis maintains constancy of relative humidity at 55% and thus helps in maintaining a fixed water pressure early in the thermal analysis, this technique is only effective during the procedure at the very lowest temperature range near room temperature. For a more complete discussion on the importance of each variable, see Mackenzie (1972). Shipment of samples to the participating laboratories precluded maintaining these samples at 55% relative humidity. Thus, the samples were stored under ambient humidity conditions at each laboratory.

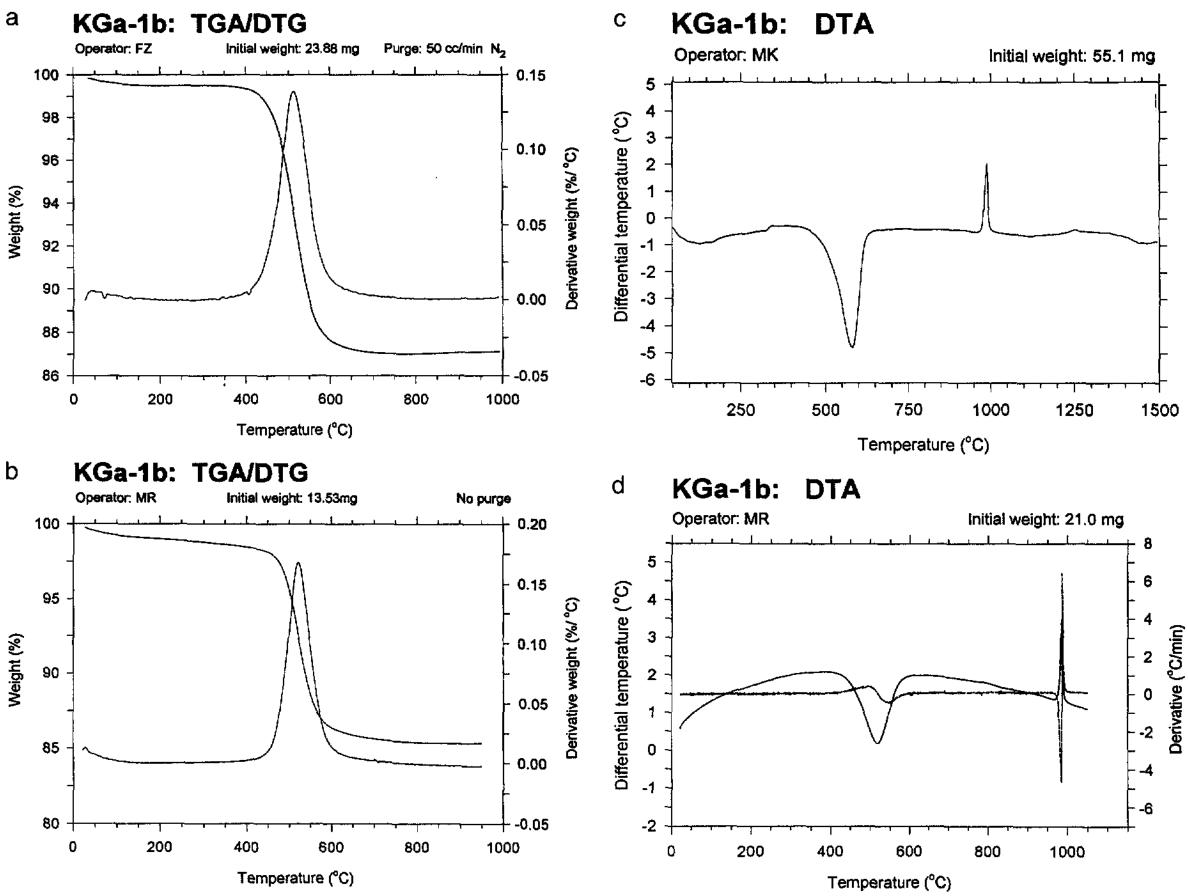

Figure 3. Experimental curves for KGa-1b: (a) TGA/DTG (UIC), N_2 purge; (b) TGA/DTG (UT); (c) DTA (TK); (d) DTA (UT).

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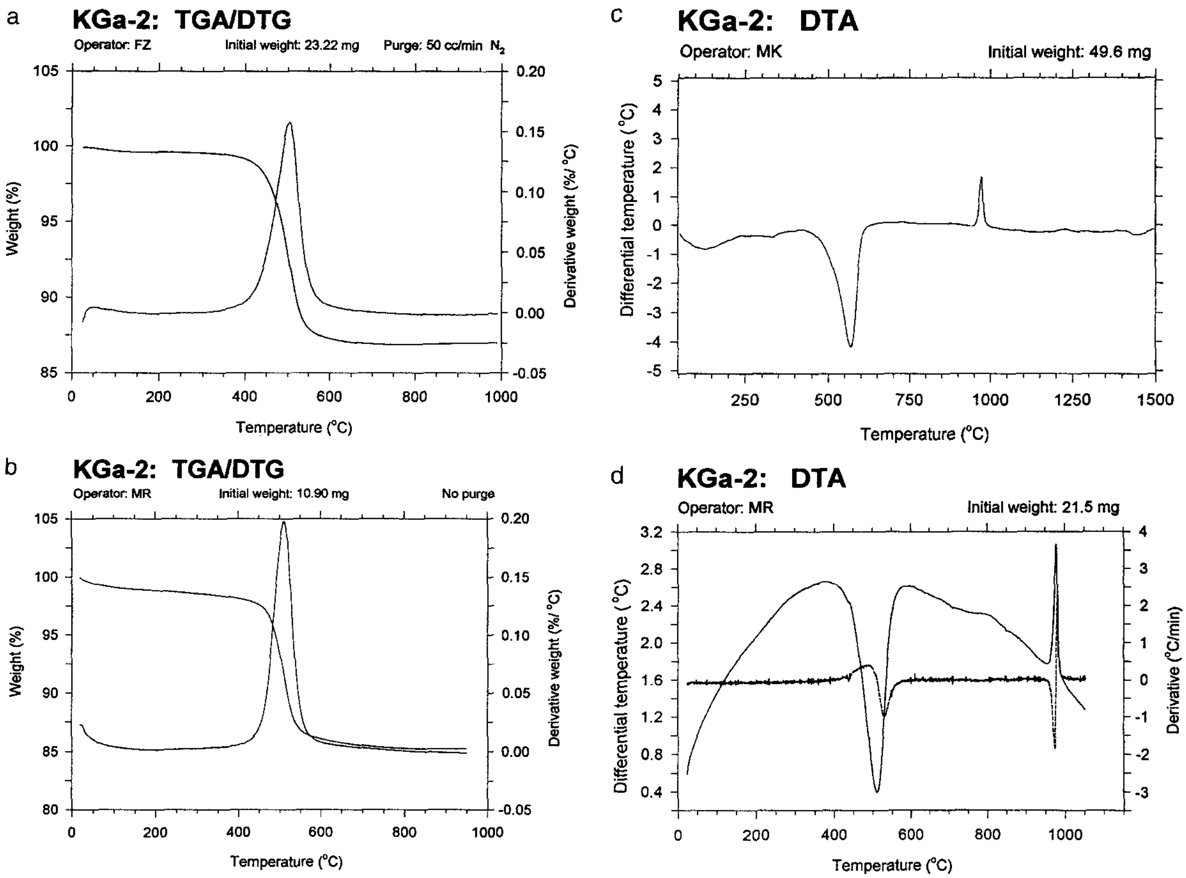

Figure 4. Experimental curves for KGa-2: (a) TGA/DTG (UIC), N_2 purge; (b) TGA/DTG (UT); (c) DTA (TK); (d) DTA (UT).

EXPERIMENTAL METHOD

Samples were prepared as described by Costanzo (2001) and distributed for thermal analysis to several different laboratories with different instruments. Three laboratories were involved: University of Utrecht (UT), University of Illinois at Chicago (UIC), and Thiele Kaolin Company (TK). The UT laboratory used a Du Pont Thermal Analysis System 1090 for the DTA experiments and a TA Instruments 2000 system controller with a 2950 TGA module. Du Pont and TA Instruments were previously affiliated and are run using the same software. The UIC laboratory used a TA Instruments 1600 for the DTA experiments and a module 51 (TA Instruments) for TGA; the software is identical to that used by UT. The TK instrumentation was a Perkin-Elmer 7 Series Thermal Analysis System.

The UT and UIC laboratories used platinum crucibles with Pt/Pt13%Rh thermalcouples adjacent to the bottom of the pans. The TK laboratory used alumina crucibles with Pt/Pt10%Rh thermalcouples. Samples were pressed by hand into the crucibles at UT, compressed using a Puritan applicator at TK, and tapped into the crucibles at UIC. At UIC, however, samples SWy-2, SHCa-1 and Syn-1 were first wetted with water and then dried before placing into the crucible owing to difficulty in handling the freeze-dried ('fluffy') material. The N_2 flow rate was 50 cc/min for DTA experiments and either the same flow rate or no N_2 flow for TG experiments. At TK, the purge gas was air with a flow rate of ~26 psi. The DTA experiments used an α-alumina powder as the reference. For all experiments, a heating rate of 10°C/min was maintained.

RESULTS

The DTA experiments from the TK laboratory and the TG and DTG curves from the UT and UIC laboratories are reported here. Temperatures for 'simple' DTA and DTG peaks are defined (Figure 1a) with an extrapolated onset (Po), peak maximum (Pm), and ex-

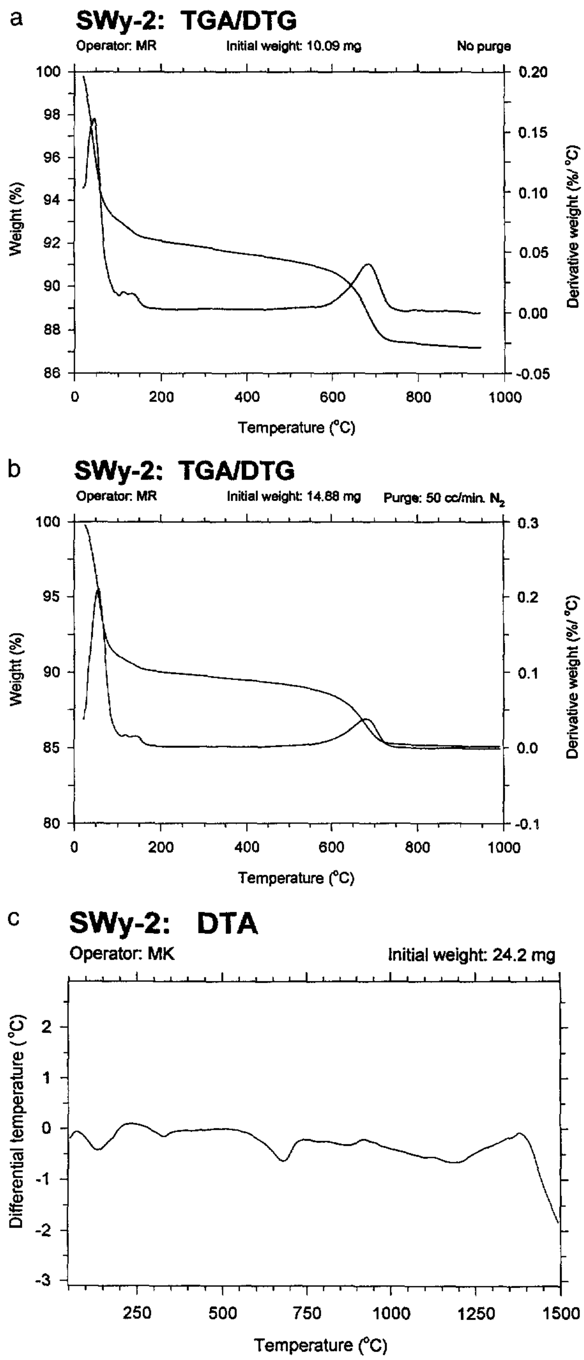

Figure 5. Experimental curves for SWy-2: (a) TGA/DTG (UT); (b) TGA/DTG (UT); N_2 purge, (c) DTA (TK).

trapolated return (Pr = Peak return) to baseline. The TG curves have an extrapolated onset (To) and extrapolated completion (Tc), as shown in Figure 1b. Composite peaks, where peak shape is difficult to define owing to the complexity of two or more nearly superimposing peaks are illustrated in Figure 2. Thus, in addition to the main peak (Pm), simple shoulder peaks are shown on the low-temperature limb, with the maximum (Sm) and the associated return temperature (Sr). On the high-temperature limb, the parameters So1, So2, *etc.* and Sm1, Sm2, *etc.* define the onset and maximum temperatures of the shoulder peaks. Experimental curves are given in Figures 3–10 and significant temperatures for the curves are tabulated in Tables 1–3.

Table 4 provides color-change information for the samples after thermal analysis at UIC.

DISCUSSION

The use of several laboratories with different equipment and different operators shows the variability of results for thermal analysis. As is common for samples not stored at constant-humidity conditions prior to thermal analysis, variations will occur at temperatures below ~100°C owing to surface-adsorbed H_2O. Different techniques in purging (*e.g.* with N_2, air, or no purge) will also produce variations at these temperatures. Above ~100°C, differences in packing of the sample may produce significant differences in the results. In these cases, evolving water vapor affects f_{H_2O} around the sample, with results depending on the ability of this vapor to disperse away from the sample. Therefore, caution must be exercised in comparing results to those presented here.

Mackenzie and Callière (1979) noted that weight loss is affected by the presence of ammonia in the synthetic mica-montmorillonite (Syn-1). Figure 8 shows a slow and continuous loss in weight from 200 to 400°C, a significant loss in weight from 400 to 600°C, and a DTA event near 320°C. Although a determination of ammonium loss at any of these temperatures would require additional study, ammonia loss is certainly a possible explanation. It is noteworthy that the DTA curve for SWy-2 also shows an event at ~330°C.

Mineralogical analysis of the samples as determined by X-ray diffraction (Chipera and Bish, 2001) indicates the presence of impurities in the studied fractions. We see no evidence of impurities affecting the thermal analysis, except possibly in SHCa-1, in which a 740°C peak in the TGA could represent dolomite decarbonation, and in Syn-1, in which the 430°C event in TGA and the 570°C event in the DTA could mask a response from boehmite. However, in SHCa-1, no corresponding evidence for dolomite was observed in DTA. In addition, visual examination of SAz-1 prior to thermal analysis showed white and brown flakes, clearly indicating inhomogeneity of the sample.

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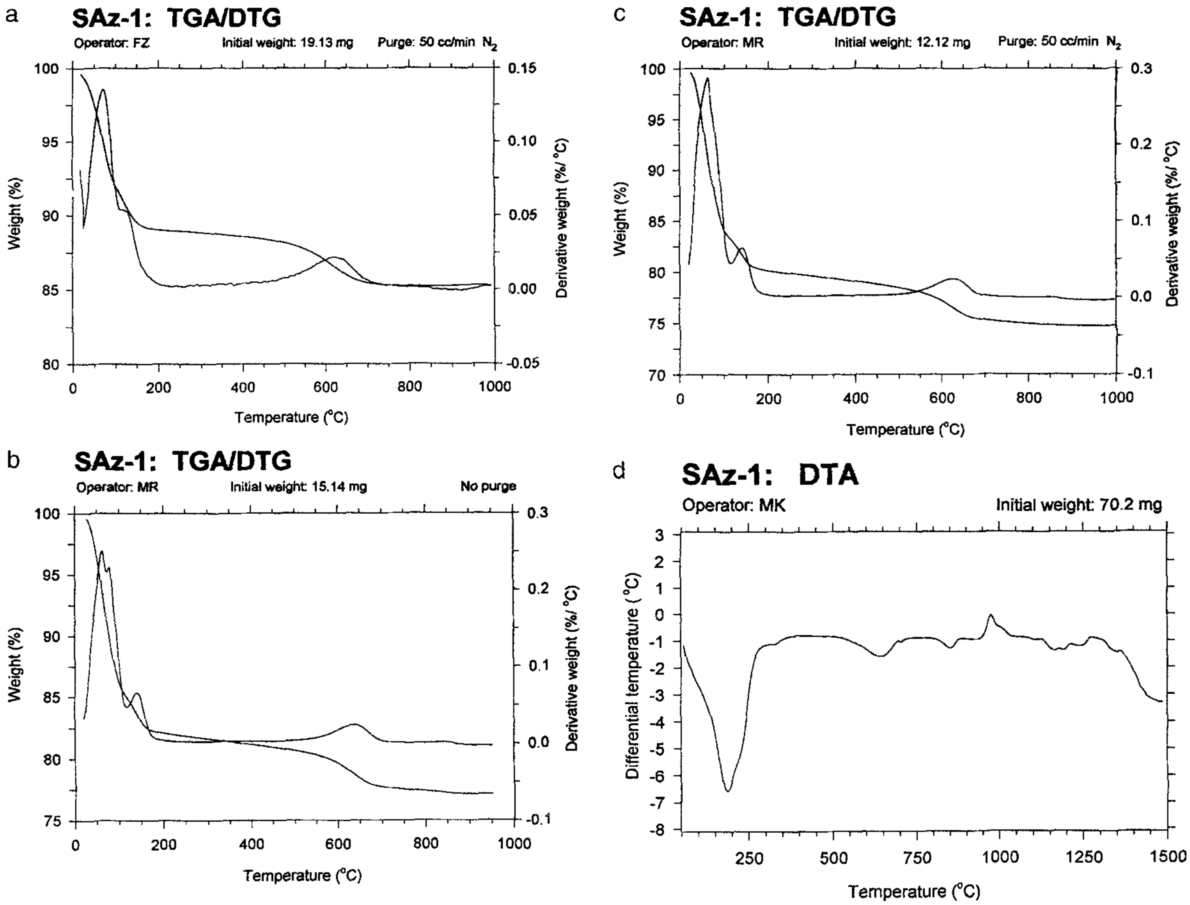

Figure 6. Experimental curves for SAz-1: (a) TGA/DTG (UIC), N_2 purge; (b) TGA/DTG (UT); (c) TGA/DTG (UT); N_2 purge; (d) DTA (TK).

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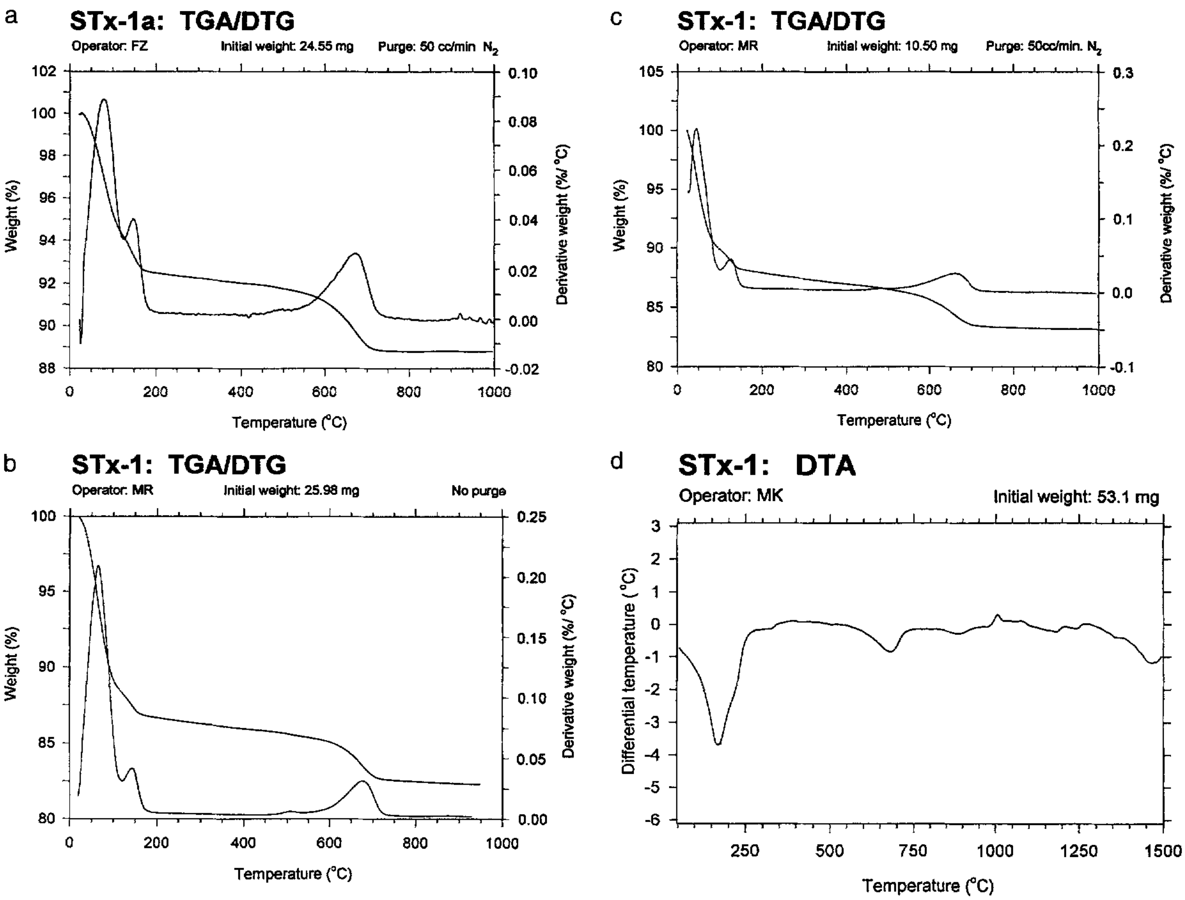

Figure 7. Experimental curves for STx-1: (a) TGA/DTG (UIC), N_2 purge; (b) TGA/DTG (UT); (c) TGA/DTG (UT), N_2 purge; (d) DTA (TK).

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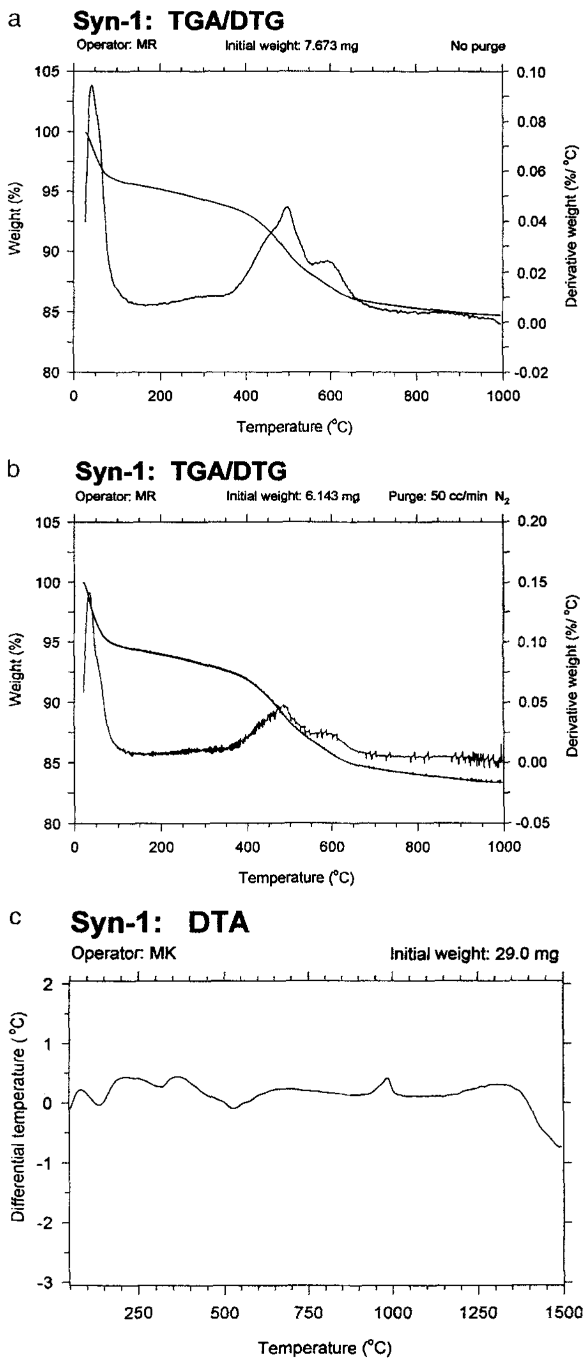

Figure 8. Experimental curves for Syn-1: (a) TGA/DTG (UT); (b) TGA/DTG (UT), N_2 purge; (c) DTA (TK).

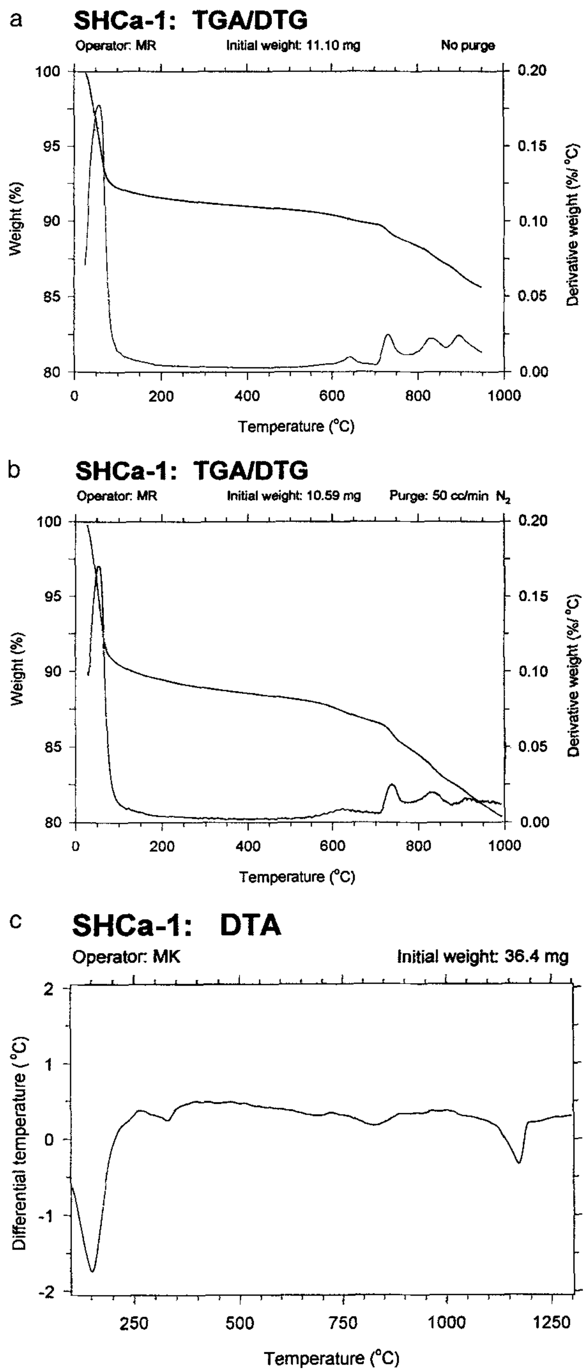

Figure 9. Experimental curves for SHCa-1: (a) TGA/DTG (UT); (b) TGA/DTG (UT), N_2 purge; (c) DTA (TK).

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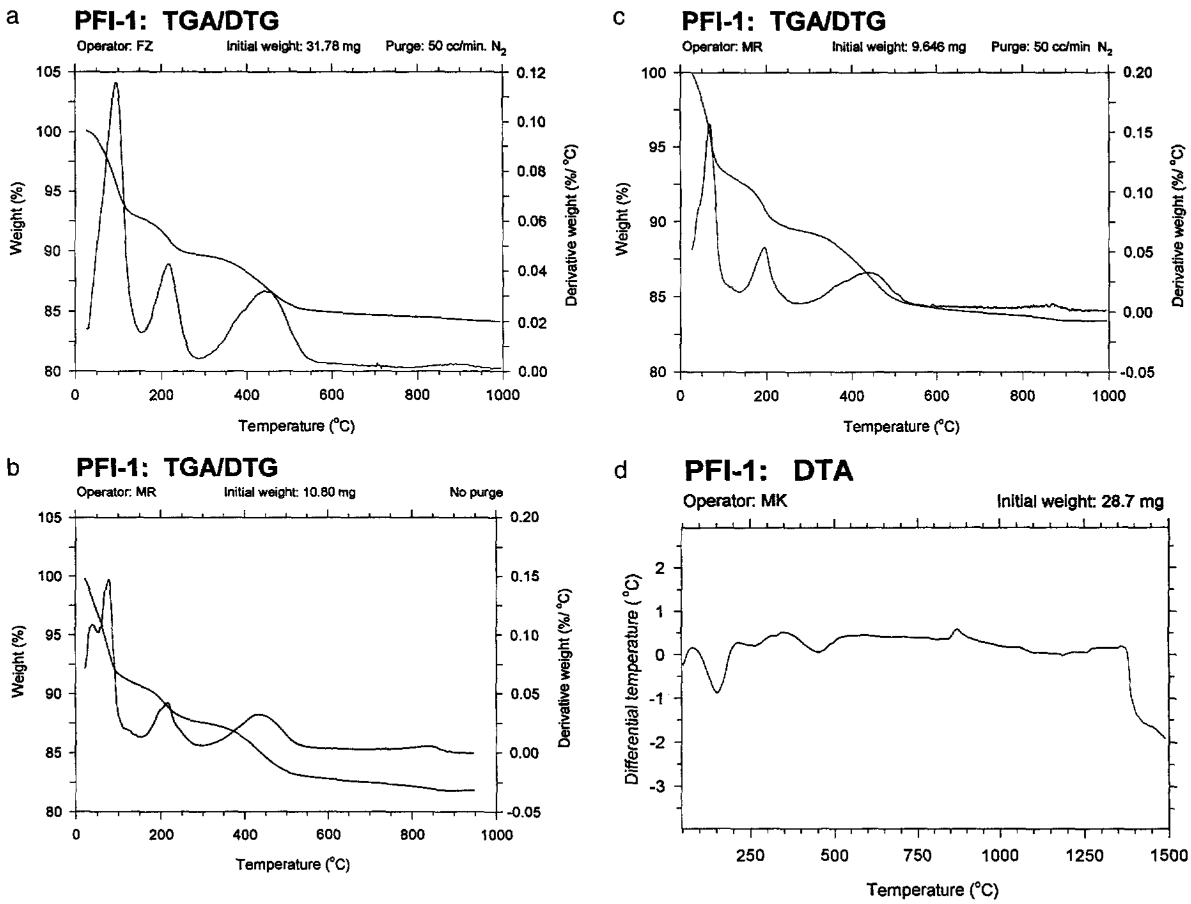

Figure 10. Experimental curves for PFl-1: (a) TGA/DTG (UIC), N_2 purge; (b) TGA/DTG (UT); (c) TGA/DTG (UT), N_2 purge; (d) DTA (TK).