

NOTE

EFFECTS OF SAMPLE SIZE AND PACKING
IN THE THERMOGRAVIMETRIC ANALYSIS OF
CALCIUM MONTMORILLONITE STx-1

Key Words—Derivative thermogravimetry, Sample size, Sample packing, Smectite, Thermogravimetric analysis.

In thermogravimetric analyses (TGA) of Ca-montmorillonite (STx-1) from the Source Clays Repository of The Clay Minerals Society, discrepancies were observed between data collected in the author's laboratory and corresponding curves found in the clay data handbook of van Olphen and Fripiat (1979). Specifically, the three weight-loss steps associated with loss of water are as much as 115°C higher in the handbook. The differences in temperature may be attributable to the effects of sample size and packing. It is well known in the field of thermal analysis that sample size and preparation can have a pronounced effect on thermoanalytic data (see, e.g., Wendlandt, 1974). The purpose of this note is to report how these parameters affect TGA curves of this smectite clay.

EXPERIMENTAL

TGA and derivative thermogravimetry (DTG) data were recorded using a Mettler TG50 thermobalance equipped with a TC10A controller. Samples were examined over the range 20° to 1000°C using a heating rate of 10°C/min. The furnace was purged with ultra high purity nitrogen at a flow rate of 50 ml/min. An empty 150- μ l alumina crucible was analyzed as a blank.

The equipment was calibrated using identical measuring conditions against the known Curie temperatures of standard Mettler alumel, mumetal, and trafoperm. In this procedure, a magnet was placed around the furnace, and pieces of each metal standard were contained in an empty crucible for analysis. During analysis, when a metal standard reached its Curie temperature, the force exerted by the magnet on the standard decreased, producing a minimum in the DTG curve. A three-point calibration of the temperature axis was thereby obtained using this method.

Calcium montmorillonite, STx-1, was obtained from the Source Clays Repository of The Clay Minerals Society. The clay was not pre-treated prior to analysis. TGA was performed on samples of loosely packed powder and on powder pressed into the crucible, which

simulated the method of preparation reported in the clay handbook by Mackenzie and Caillère (1979). Initial sample weights were measured on the balance pan outside of the purged furnace. This procedure was found necessary because, even at constant ambient temperature, water slowly desorbed from clay samples inside the purged furnace, causing the initial weight reading to decrease gradually.

To evaluate the effects of diffusion and thermal lag in TGA of clays, pieces of the Mettler calibration standards about 1 mg in weight were placed into 10- and 100-mg samples of packed clay for analysis, utilizing the aforementioned experimental conditions and calibration procedure.

The data reported in the clay handbook were acquired using a variety of DTA and TGA equipment. Samples of clay weighing about 360 mg were pressed into sample crucibles and analyzed at a heating rate of 10°C/min.

RESULTS

Figures 1 and 2 present the TGA and DTG results, respectively, for sample STx-1. The DTG data, summarized in Table 1 for the entire set of samples, exhibited a marked dependence on sample size. To a first approximation, peak temperatures increased linearly

Table 1. Derivative thermogravimetry peak temperature vs. sample size and packing for montmorillonite STx-1.

Weight (mg)	Sample preparation	Peak temp (°C)		
		Adsorbed water	Chemical water	Hydroxyl water
10	powder	70	130	670
50	powder	86	142	660
50	packed	93	150	665
100	packed	120	180	685
359 ¹	packed	185	240	720

¹ Data for 359-mg sample taken from Mackenzie and Caillère (1979).

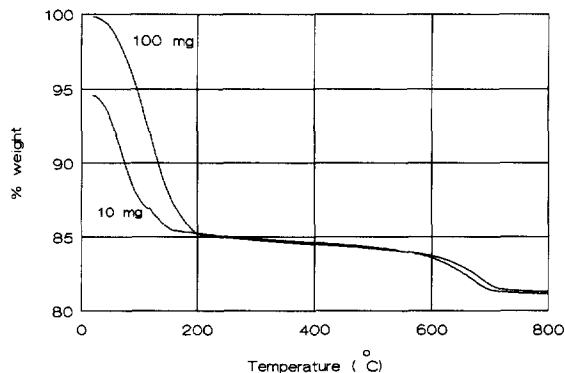


Figure 1. Thermogravimetric analysis curves for montmorillonite STx-1, illustrating shift in data for 100-mg tightly packed sample relative to 10-mg loosely packed sample. Starting weight for 10-mg sample is less than 100% due to desorption of water in laboratory atmosphere during initial weighing.

with sample weight. Sample preparation also influenced peak temperatures, as shown in Table 1. In general, higher peak temperatures were exhibited by tightly packed samples than loosely packed samples of the same weight.

For all runs, however, DTG peak temperatures were lower than the data reported in the clay handbook (Mackenzie and Caillère, 1979). In fact, the first weight-loss step for the 10-mg sample was 115°C below the value given in this reference. DTG peak temperatures reported by Earnest (1988) were also lower than the data in the clay handbook, but no explanation was provided for the discrepancy.

Figure 3 shows graphically results obtained from the analysis of Curie standards packed in clay. Experimentally derived Curie temperatures are listed in Table

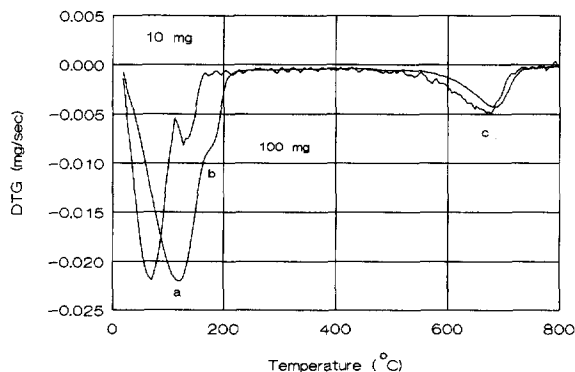


Figure 2. Derivative thermogravimetric curves for data from Figure 1, rescaled for overlay. Note minima for weight-loss steps associated with: (a) loss of adsorbed water; (c) loss of water formed by dehydroxylation. Shoulder in curves at point (b) is due to loss of water chemically bound to exchangeable calcium ions.

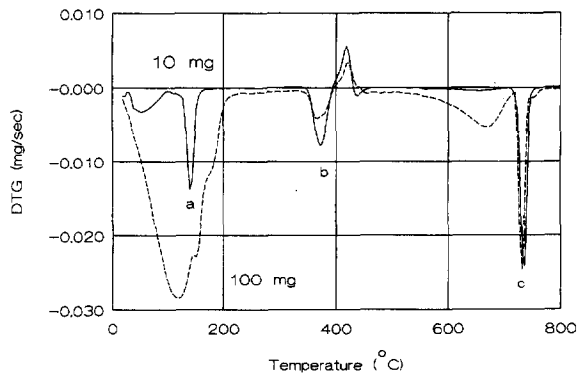


Figure 3. Derivative thermogravimetric curves for montmorillonite STx-1 packed with three Curie point standards, rescaled for overlay. Minima indicate Curie transitions of: (a) alumel; (b) mumetal; (c) trafoperm. Upwardly pointing peak was caused by the Curie transition of thermobalance heater coils. Measurements of Curie temperature were reproducible to 3°C.

2 and reflect the magnitude of thermal lag at three given temperatures as a function of clay mass.

DISCUSSION

TGA of sample STx-1 shows three weight-loss steps in the range 20° to 1000°C; in order of increasing temperature, they correspond to the loss of adsorbed water, chemically bound water associated with exchangeable calcium ions, and structural water (Greene-Kelly, 1957; Mackenzie, 1970). According to a table in the clay handbook, DTA curves exhibit minima for these events at 185°, 240°, and 720°C, respectively (Mackenzie and Caillère, 1979).

As the data in Table 1 shows, these values are not constant but increase with sample size. The increase in DTG peak temperatures with sample size is attributed to the effects of thermal lag and diffusion of water vapor through the clay. An estimate of the magnitude of thermal lag can be obtained from the increase in apparent Curie temperature with clay mass, as shown in Table 2. In general, the magnitude of thermal lag appears to be small compared with the temperature differences listed in Table 1, indicating that other factors contributed to the DTG peak-temperature shifts.

Although thermal lag is a major disadvantage that

Table 2. Apparent Curie temperature of metal standards versus sample size of montmorillonite STx-1.

Weight of clay (mg)	Curie temp (°C)		
	Alumel	Mumetal	Trafoperm
None	138	367	732
10	140	370	735
100	155	392	745

occurs if large samples are employed, it is by no means the only one. Large samples release volatile reaction products more slowly into the purge gas stream of the furnace, resulting in broader DTA and DTG peaks that are shifted in temperature. These results are evident in Figure 2 for the 100-mg sample. Similar effects have also been observed for tightly packed samples, because diffusion of gaseous products is retarded by the reduction in void volume between clay particles.

SUMMARY AND CONCLUSIONS

The results of this brief study show sample size and preparation to be important parameters to control in thermoanalytical studies of clays. Increases in DTA and DTG peak temperatures with sample size were attributed to the effects of thermal lag. Tight sample packing impedes the diffusion of volatiles through the clay, resulting in broader DTG peaks that are shifted in temperature. The results suggest that for a given substance both sample size and preparation must be considered when evaluating DTG data.

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