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Cover Picture

DEVIL'S CANYON

Located between Flat Top and Soldier's Spring Mountains in the Wichitas, Devil's Canyon is in Kiowa County, about 3 miles southeast of the Lake Altus dam (SE $\frac{1}{4}$ sec. 1, T. 4 N., R. 20 W.). In this north-eastward view, Flat Top Mountain is on the left, Soldier's Spring Mountain on the right.

The first recorded visit to the mile-long canyon was by a dragoon expedition, under the command of General Henry Leavenworth, sent from Fort Gibson in 1834 to contact the Wichita Indians. Approaching from the north, the party found it between two mountains with nearly inaccessible summits and excellent possibilities for defense along a well-worn trail running the length of the canyon. Lieutenant T. B. Wheelock, an officer with the expedition, described it as a narrow defile with precipitous granite walls several hundred feet high, equaling the Alps in grandeur. At the south end of the canyon they found a well-constructed village inhabited by about 500 Wichita Indians, who were excellent farmers with extensive fields.

The next recorded visit was by the R. B. Marcy expedition in 1852, which found that the Wichitas had deserted their strategic location, probably driven out by Comanches and Kiowas, and had re-located about 70 miles to the east, near Rush Springs. Their mode of living, however, was the same, and they had again erected comfortable dwellings with "well tilled fields, neatly enclosed."

Dr. G. G. Shumard, physician and geologist for the group, described the surrounding mountains as "composed of huge masses of loose granite, thrown together in such confusion that it is seldom any portion can be seen in its original position. There are veins of quartz, greenstone, and porphyry running through these that characterize the gold bearing formations of California." Two small pieces of gold were actually found, but no vein was ever discovered, leading to the conclusion that the vast gypsum deposits to the west were of greater economic potential than was the trace of gold in the mountains.

Flat Top and Soldier's Spring Mountains are peaks of reddish to reddish-brown Reformatory Granite (Middle Cambrian?), which floor the canyon with granite boulders and arkosic gravel as they are weathered. The peaks are sculptured from what C. A. Merritt, in *Igneous Geology of the Lake Altus Area, Oklahoma* (Okla. Geol. Survey, Bull. 76) described as a batholithic structure elongated north-westward. In an area of abundant cross-cutting structures, joints, faults, and dikes, Devil's Canyon probably formed along a zone of weakness created by jointing, faulting, emplacement of dikes, or a combination of these processes.

—Phil O. Cannon

(Photograph courtesy of A. J. Myers)

CLAY-MINERAL DEHYDRATION

RAYMOND L. KERNS, JR.

INTRODUCTION

Weight-loss determinations of clay minerals, as well as of other mineral and rock samples, provide essential chemical and mineralogical information. The percent weight loss on drying is used as a measure of the absorbed water content (H_2O) and is routinely measured at 105-115 °C. If samples contain expandable clay minerals, such as montmorillonite and vermiculite, interlayer water will contribute to the weight-loss value; the weight loss, therefore, has special significance for clay mineralogists. The 105-115 °C range is usually sufficient to remove the interlayer water from the clay-mineral lattice. However, the tenacity with which interlayer water is held by the lattice depends in part on the interlayer cations present. Of the more common interlayer cations in naturally occurring clay minerals, magnesium possesses a higher retentive capacity for interlayer water than does potassium, sodium, or calcium.

Differential thermal analysis patterns of most clay minerals show endothermic reactions between 500 and 700 °C. These endotherms are generally attributed to dehydroxylation of the octahedral layers. In many cases, a slight endotherm occurs in the 900 °C range; this endotherm may be due to the loss of the last traces of hydroxyls from the structure, but it can also be attributed to relaxation or stretching of chemical bonds within the lattice before the formation of high-temperature phases, which may be represented by an exothermic peak closely following the high-temperature endothermic loop.

Samples are ordinarily heated to 1,000 °C to determine the total weight loss from the evolution of vapor phases. In clay minerals, the total weight loss comprises the low-temperature water loss plus the loss of hydroxyls from the octahedral layers. It is not yet known at what temperature this reaction is completed, but it is certainly below 1,000 °C. The interpretation of total-weight-loss data may be complicated by the presence of carbonates, sulfates, sulfides, organic matter, or other phases that also lose evolved components at high temperatures.

LOW-TEMPERATURE WEIGHT-LOSS DETERMINATION

To achieve reasonable accuracy, all weight-loss determinations should be made in triplicate, with weights measured in grams. The first step in the procedure is preheating the furnace to the desired temperature (100-225 °C). Pyrex weighing bottles and caps with ground-glass joints should be washed and rinsed with distilled water. The glass should be dried with a lint-free towel and placed in the furnace with the cap off. The bottle and cap should be dried for 1 hour and the cap placed on the bottle before they are removed from the oven. The capped bottle should be allowed to cool in a desiccator for at least 0.5 hour before weighing. Balance manipulations should be made immediately after removal from the desiccator to determine the weight

of the bottle in a dry-air environment. This value is recorded as the weight of the weighing bottle and cap.

A sample weighing at least 1 gram is placed in the bottle and the total weight (sample, bottle, and cap) determined and recorded. The sample, in the bottle with cap off, is placed in the oven and dried at temperature for a minimum of 4 hours. After drying, the bottle is capped before being removed from the oven and again allowed to cool in a desiccator. The assemblage is weighed with the cap on and the value recorded as the weight of dry sample plus bottle and cap.

The initial weight of the sample is determined by subtracting the weight of the dry bottle and cap from the weight of the air-dry sample plus the weight of the bottle and cap. The weight loss is calculated by subtracting the weight of the oven-dry sample plus bottle and cap from the weight of the air-dry sample plus bottle and cap. Weight loss is usually reported as a percentage of the initial weight. This is calculated by dividing the measured weight loss in grams by the initial sample weight and multiplying by 100.

Samples dried at less than 300 °C will usually reabsorb water when returned to atmospheric conditions, so the sample should probably not be reused for determination of cation-exchange capacity or weight loss on firing. However, the sample would still be usable for chemical analyses, and probably for X-ray and DTA analyses.

DTA DATA

Some of the effects of interlayer cation composition on the dehydration of clay minerals are observable from differential thermal analysis data (Barshad, 1948, 1949, 1950). Thermograms in the low-temperature range (less than 300 °C) for two samples of montmorillonite (A, B) and one sample of vermiculite (C) are shown in figure 1. The three samples were first converted to potassium, sodium, calcium, and magnesium forms with H⁺ resin and the appropriate chloride-salt wash treatment. The dried powders were humidified at about 50 percent relative humidity and analyzed on a Robert L. Stone DTA unit (model 13M).

The endothermic loops in figure 1 indicate the range over which adsorbed (0-100 °C) and absorbed water (0-200 °C) are driven out of the sample. Changes in the shapes of the loops reflect progressive stages of dehydration; Mg-vermiculite and Mg-montmorillonite generally lose interlayer water in three distinct steps (Walker, 1956; Rowland, Weiss, and Bradley, 1956). The point at which the endothermic curve returns to the base line marks the temperature at which almost all low-temperature water has been removed from the sample. Magnesium-saturated samples retain part of their interlayer water to temperatures above 200 °C; potassium-, sodium-, and calcium-saturated samples lose almost all interlayer water in the 100-200 °C range.

DIFFRACTOMETER FURNACE

A Norelco X-ray diffraction unit equipped with a Robert L. Stone diffractometer furnace was used to determine the temperatures at which clay minerals with different interlayer cation compositions would

be completely dehydrated. The heating control system is designed so that the temperature can be changed at a programmed rate while the diffractometer is oscillated across a particular d -value range. Changes in intensity or d spacing may be correlated directly to temperature changes.

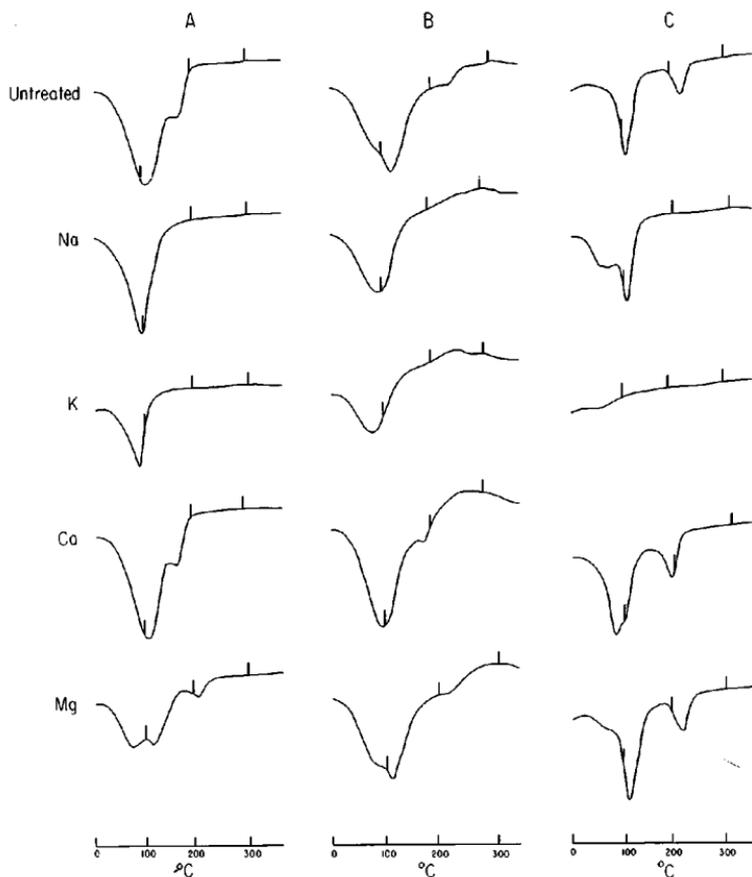


Figure 1. DTA curves for sodium-, potassium-, calcium-, and magnesium-exchanged clay samples.

A. Plum Bentonite montmorillonite

B. Less-than-0.5-micron fraction of iron-rich montmorillonite

C. 4-8-micron fraction of vermiculite

(Purging gas: nitrogen; heating rate: 10 °C/min; calibration: 1.0 @ 150 μ V)

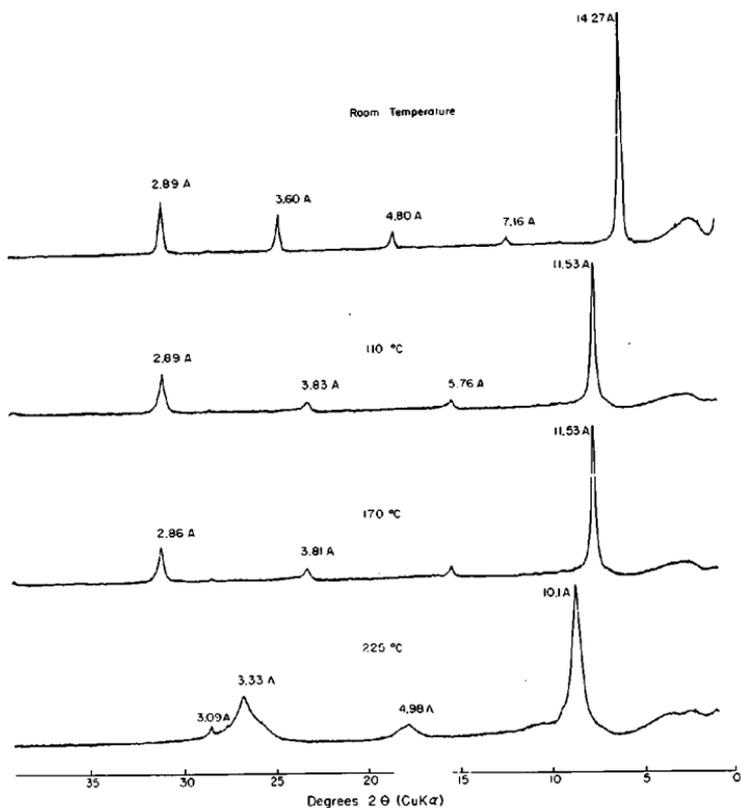


Figure 3. X-ray diffractometer scans of a 4-8-micron fraction of vermiculite at room temperature, at 110 °C, at 170 °C, and at 225 °C. Scans were made after allowing 4 hours for equilibration at elevated temperatures.

The potassium-, sodium-, and calcium-saturated montmorillonites were observed to collapse from expanded states (12.5-14 Å) to about 10 Å at temperatures slightly above 100 °C, indicating complete dehydration of the interlayer region. Magnesium-saturated samples did not collapse to 10 Å until the temperature exceeded 200 °C. The diffractometer furnace scans for a magnesian vermiculite (A) and montmorillonite (B) are reproduced in figure 2. Diffractograms traced under equilibrium conditions, after holding at temperature for 4 hours, are shown in figures 3 and 4. It is evident from figures 2, 3, and 4 that part of the interlayer water is tenaciously held in magnesium-interlayered clay minerals.

DEHYDRATION AND MEASUREMENT AT INTERVALS

A sample of vermiculite was measured for successive weight losses at intervals of about 20 °C from 50 to 1,000 °C. These data are presented in figure 5. Curve A of figure 5 shows the cumulative weight loss in percent over the temperature range; curve B shows weight loss over an increment of temperature increase. These graphs may be compared with the DTA pattern for the same sample, shown in figure 5-C. These data indicate that weight losses generally occur in three distinct temperature ranges: 0-220 °C, 500-600 °C, and 700-850 °C.

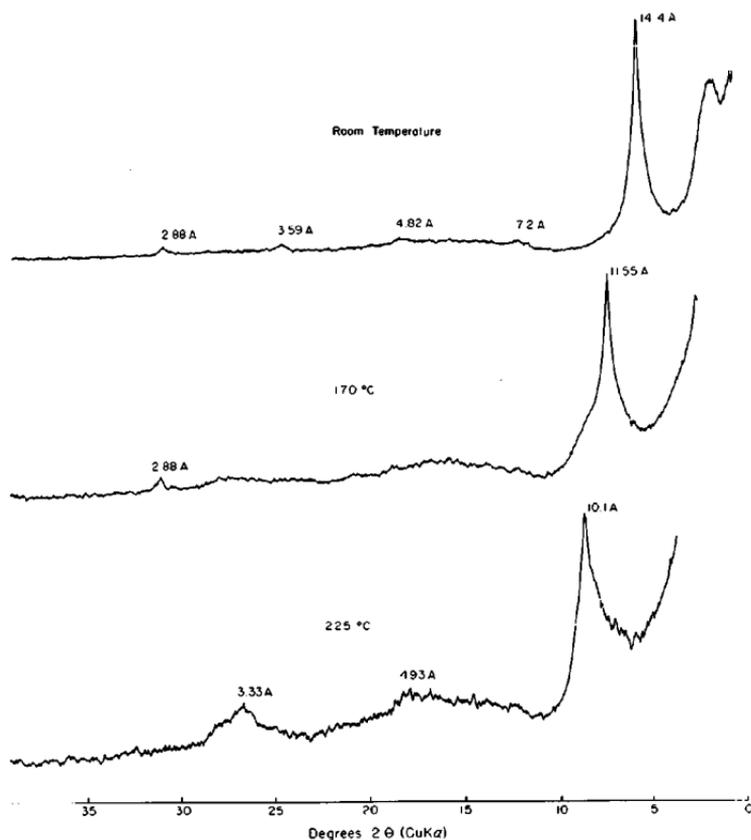


Figure 4. X-ray diffractometer scans of a -0.5-micron fraction of an iron-rich montmorillonite at room temperature, at 170 °C, and at 225 °C. Scans were made after allowing 4 hours for equilibration at elevated temperatures.

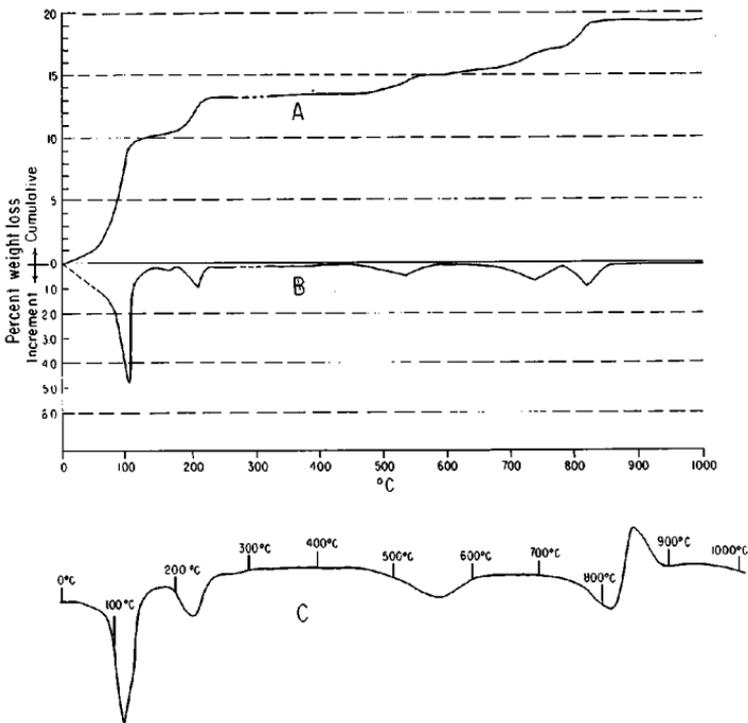


Figure 5. Progressive percent weight loss and corresponding DTA curve of a vermiculite sample heated from room temperature to 1,000 °C.

- A. Cumulative weight loss plotted at 15-25 °C intervals**
- B. Incremental weight loss plotted at 15-25 °C intervals**
- C. DTA curve**

TOTAL WEIGHT LOSS ON FIRING

The total weight loss should be made on cuttings of the same material used to measure the low-temperature weight loss, but not on the samples heated for that measurement. Either platinum or porcelain crucibles may be used as containers. The dry weight of the crucible is determined after drying in an oven or furnace at 200 °C for 1 hour. The crucible is removed and cooled for 0.5 hour in a desiccator, then weighed and the weight recorded. A sample of approximately 1 gram is placed in the crucible and the total weight of the sample, plus crucible, is recorded. The difference between the two weights is recorded as the initial weight of the sample before firing.

The sample and crucible should then be placed in the furnace and the temperature selector set at 1,000 °C. The sample is held at this

temperature for at least 4 hours, and the furnace is then turned off and allowed to cool to less than 500 °C. Cooling of the crucible and fired sample to room temperature is completed in a desiccator, and the weight after firing is then determined. The weight loss is calculated by subtracting the weight after firing from the weight of the air-dry sample plus dry crucible. The total percent weight loss on firing is calculated by dividing this number by the initial sample weight and multiplying by 100.

If the sample contains only clay minerals, the low-temperature weight loss, in percent, is reported as H_2O^- . H_2O^+ may be calculated by subtracting the H_2O^- value from the total percent weight loss on firing at 1,000 °C. The fired sample should be retained for X-ray analysis to see if any high-temperature mineral phases have formed.

EXPERIMENTAL TECHNIQUE

Weighing bottles and crucibles should be thoroughly washed and rinsed with distilled water before using. Containers should not be handled with bare hands, as fingerprinting can cause significant errors in weights measured to the fourth decimal place on an analytical balance. Hot samples may be handled with a pair of clean tongs, cooler samples may be handled with lint-free tissue.

The samples should always be cooled to room temperature in a desiccator before weighing, as hot or warm samples may cause thermal expansion of the balance which will introduce significant errors. The cap of a weighing bottle is ground to fit the bottle it came with; both have the same number and should be used together, not interchangeably with other weighing bottles and caps. It is important to have a good seal on the weighing bottle when dealing with dry clay. Clay minerals rehydrate readily when exposed to even the lowest relative-humidity conditions. Fired samples are less susceptible to water absorption, and weight gains of desiccator-cooled fired samples are considered well within the limits of precision for the technique.

The accuracy of the method is increased considerably if weight losses are determined in triplicate. Reproducible results are easily obtained to ± 1.0 percent of the reported value. Table I is a sample data sheet for three different specimens, and the data represent a triplicate determination of weight loss for the same mineral.

CONCLUSIONS

Weight-loss-determination techniques are quite simple, compared with other, more intricate types of analysis. However, the techniques must not be considered "cook-book" if meaningful data are to be obtained for clay-mineral characterizations and interpretations.

Routine drying temperatures of 105 to 115 °C are suitable for most clay minerals. However, clays having expandable lattices with a high-magnesium interlayer cation composition cannot be completely dehydrated at temperatures below 200 °C. For example, a 32.5-percent error would have resulted from estimating the interlayer-water content of the vermiculite sample in figure 5 from the H_2O^- value at 115 °C rather than at 225 °C. The H_2O^+ content would have been calculated

TABLE I.—TYPICAL COMPUTATIONS FOR WEIGHT-LOSS
DETERMINATION FOR A VERMICULITE SAMPLE

| | SAMPLE 1 | SAMPLE 2 | SAMPLE 3 |
|--|-------------|-------------|-------------|
| Heating to 220 °C | | | |
| Weight (gms) of: | | | |
| sample + bottle + cap | 22.4917 | 22.5665 | 22.3141 |
| bottle + cap | 21.0845 | 21.0042 | 20.8623 |
| air-dry sample | 1.4072 | 1.5623 | 1.4518 |
| sample + bottle + cap | 22.4917 | 22.5665 | 22.3141 |
| oven-dried sample + bottle + cap | 22.3182 | 22.3767 | 22.1365 |
| Weight loss (gms) | 0.1735 | 0.1898 | 0.1776 |
| Percent weight loss | 12.33 | 12.15 | 12.23 |
| Average weight loss = $12.24 \pm 0.09\%$ = H ₂ O- | | | |
| Heating to 1,000 °C | | | |
| Weight (gms) of: | | | |
| sample + crucible | 6.8224 | 6.6372 | 6.8004 |
| crucible | 5.2792 | 5.1445 | 5.1849 |
| sample | 1.5432 | 1.4927 | 1.6155 |
| sample + crucible | 6.8224 | 6.6372 | 6.8004 |
| fired sample + crucible | 6.5395 | 6.3585 | 6.5017 |
| Weight loss (gms) | 0.2829 | 0.2787 | 0.2987 |
| Percent total weight loss | 18.33 | 18.67 | 18.49 |
| Average total weight loss = $18.50 \pm 0.17\%$ | | | |
| Weight percent H ₂ O ⁺ = | | | |
| Percent total weight loss - Weight percent H ₂ O ⁻ = | | | |
| $6.26 \pm 0.26\%$ | | | |

as 9.4 percent instead of the more accurate value of 6.0 percent, which is closer to expected values for mica-type lattices.

A thorough knowledge of the non-clay mineral composition of the sample, such as the presence of carbonates, sulfates, sulfides, or organic matter, which might contribute to total weight loss values, is also necessary for accurate estimations of the weight loss on firing. The H₂O⁺ value depends not only on the accurate determination of the total weight loss on firing, but also on the accurate and realistic determination of the H₂O⁻ content.

With a thorough knowledge of the material and careful experimental technique, weight-loss determinations can provide meaningful information to clay-mineral investigations.

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Board on Geographic Names Decision

The name Mount Oklahoma has been approved by the U. S. Board on Geographic Names for a 13,845-foot-high peak in the Sawatch Range, Lake and Pitkin Counties, Colorado. At latitude 39°10'44" N, longitude 106°30'24" W, Mt. Oklahoma is on the Continental Divide, 12 miles southwest of Leadville and 1.5 miles northeast of Deer Mountain.

OKLAHOMA GEOLOGY NOTES

Volume 27

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Number 8

IN THIS ISSUE

| | <i>Page</i> |
|--|-------------|
| <i>Clay-Mineral Dehydration</i> | |
| RAYMOND L. KERNS, JR. | 155 |
| Devil's Canyon | 154 |
| Board on Geographic Names Decision | 164 |