study of phosphorus in some Nebraska soil profiles. *Soil Sci. Soc. Amer. Proc.* **24,** 450–452.

SOREM, R. K. (1961) X-ray diffraction technique for small samples. Norelco Reporter **8,** 39.

TOMAN, F. A. (1962) A simple technique for mounting minute samples for x-ray diffraction analysis. *Norelco Reporter* **9,** 47.

WILCOX, R. E. (1959) Use of spindle stage for determining refractive indices of crystal fragments. *Amer. Mineral.* **44,** 1272–1293.

DIFFERENTIAL THERMAL ANALYSIS OF BIOTITIC VERMICULITE TO DETERMINE VERMICULITE CONTENT

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INTRODUCTION

Differential thermal analysis was used to determine the vermiculite component of biotitic vermiculite by G. F. Walker in 1951. This was accomplished by measuring the area associated with the endotherms below 350°C and then comparing this area to that of a high purity vermiculite. Essentially identical thermograms were obtained by Walker from a biotitic vermiculite (or hydrobiotite: Gruner, 1934) sample and from a mixture of vermiculite with a suitable amount of inert material.

A rapid method of ascertaining the approximate vermiculite content of biotitic vermiculite is presented here. The methods avoids some of the difficulties of determining a true base-line and of attaining equilibrium at constant humidity. The data show that in at least one instance by any reasonable criterion a mechanical mixture of minerals is an inadequate substitute for a natural mixed-layer sample. Some observations on the structure of the low temperature peaks are also presented.

METHOD

Table 1 lists the samples used. These samples, obtained as large flakes up to 5 g, were vigorously washed and prepared for DTA by slicing them (with a razor) into pieces that passed through a 250 μ sieve but not through a 150 μ sieve. Slicing rather than grinding was used to preserve the layered nature of the samples. The samples were stored at constant humidity. Where ion exchange was used, the methods of Barshad (1948) were employed.

The vermiculite contents of the samples were gratefully received from

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TABLE 1. DESCRIPTION OF SAMPLES

Natural state	Locality	Source
Mg—vermiculite	Kenya, Africa	G. F. Walker
Na—vermiculite	Young River, W. Australia	G. F. Walker
Mg—hydrobiotite	South Africa	G. F. Walker
Ca—, Mg—hydrobiotite	Libby, Montana	M. L. Jackson

G. F. Walker and from M. L. Jackson. The methods of analysis for Kenya vermiculite (Mathieson and Walker, 1954) and for Montana hydrobiotite (Alexiades and Jackson, 1965) have been published.

The Dupont 900 Differential Thermal Analyzer was used with a single aluminum heating block containing the sample, reference and control thermocouples (copper-constantan) in 2 mm capillary tubes. Dried alumina was the reference for the samples, which weighed 5 mg. The samples were heated at $18.5°C/min$ from $30°C$ to $400°C$.
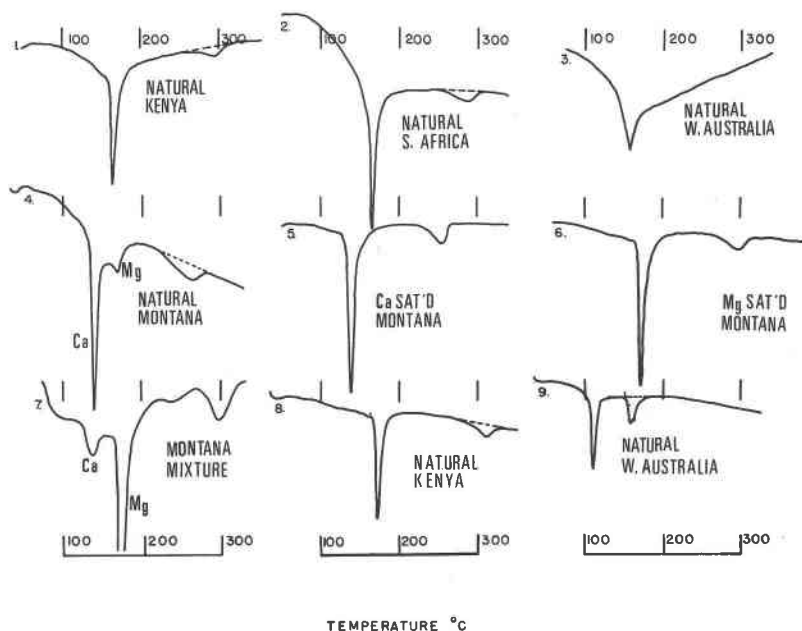

TEMPERATURE °C

FIG. 1. Differential thermal curves. 1. Kenya vermiculite, 50% relative humidity; 2. So. Africa hydrobiotite, 50% r.h.; 3. W. Australia vermiculite, 50% r.h.; 4. Montana vermiculite, 50% r.h.; 5. Montana Ca saturated, 50% r.h.; 6. Montana Mg saurated, 50% r.h.; 7. Mixture of 5., 6., and inert material, 50% r.h.; 8. Kenya vermiculite, 100% r.h.; 9. W. Australia vermiculite, 100% r.h.

RESULTS

The thermograms are presented in Figure 1. The dotted lines represent the "base" lines used when areas were measured.

The areas of the endotherms enclosed by the dotted lines in Figure 1 were measured on successive weeks until both equilibrium and reproducibility were assured. The percentage of vermiculite was determined as the ratio of the area measured to the area of the reference sample, Kenya vermiculite, equilibrated at the same humidity, as summarized in Table 2. The established percentages in the table are those reported by Walker or by Jackson.

DISCUSSION

Though the vermiculite content of a biotitic vermiculite can be determined from the area of its low temperature endotherms (Walker, 1951),

TABLE 2. RESULT OF CALCULATIONS

Sample studied	Relative humidity	Vermiculite content	
		Calculated percentage	Established percentage
Kenya (reference)	50%, 100%	—	99+
Montana	50%	44	48
South Africa	50%	43	50
West Australia	50%	—	~95
West Australia	100%	93	~95

this approach is limited by, and very sensitive to, the accuracy of the base-line. A further problem is the extreme sensitivity of the lowest temperature endotherm to humidity (Walker and Cole, 1957), For these reasons we chose to measure the "third" endotherms (see Fig. 1), resulting from that portion of the water of hydration which has not already escaped as the "unbound" water (Walker and Cole, 1957; Barshad, 1948). The "third" endotherm does not severely overlap the others, and the overlap can be minimized by the choice of heating rate. However, the measurement is still difficult because the base-line must be established. The choice of baseline indicated in the illustrations is based on the assumption that the "third" endotherm is overlapped only slightly and that this overlap is small and will be proportional to the vermiculite content in thermograms of the same general peak structure. The results do not contradict these assumptions.

A Na-vermiculite has not been previously shown to exhibit the "third" endotherm demonstrated by sample 3 of Figure 1, stored at 50 percent

relative humidity. However, sample 9 exhibited this peak after four months storage at 100 percent relative humidity. The total area of the endotherms below 300°C and the area of the "third" endotherm both give a vermiculite content of 93 percent. This assumes that for the "third" endotherm the water of hydration left for Na ions is the same as for Ca and Mg ions.

The Libby, Montana sample (Bassett, 1959) has a more detailed peak structure than has been reported (Barshad, 1948). A chemical analysis was performed. The results (1.3 percent Ca, 19.90 percent MgO, 5.46 percent K_2O) show that there is indeed no more than 2.4 percent Ca vermiculite present. Ca- and Mg-saturated Libby, Montana samples were prepared for comparison. These samples (Nos. 5 and 6) identify the peak structure in the natural material. The sharp peak at 138°C is due to the Ca, and the broad peak at 168°C is due to Mg. However, a mechanical mixture of Ca- saturated Montana vermiculite, Mg-saturated Montana vermiculite and inert material, as shown by sample 7, is not equivalent to the natural material.

Conclusions

The modified area of the "third" endotherm of biotitic vermiculite can be used to estimate rapidly the vermiculite content.[1] Care must be taken to use a heating rate and a reference that will make the results valid. The sensitivity of our apparatus, particularly because it can be used on micro samples, was a great asset in this study.

A method was not found for using the DTA data to measure the relative Ca and Mg content of the Libby, Montana vermiculite. A mechanical mixture failed to reproduce the mineral. The resulting peaks do not have the same shape, and two "third" endotherms are seen. This is probably partly due to a different activation energy for water release from a homoionic Ca layer and from a heteroionic Ca, Mg layer.

The appearance in Na vermiculite (W. Australia, thermogram no. 9) of a "third" endotherm and of a total area comparable to that of Kenya vermiculite indicates that a double sheet of water 14.5 Å thick (Walker and Cole, 1957; Barshad, 1950) was present. Also, this indicates that under certain conditions not all of the water of hydration is lost as the "unbound" water. Indeed, the water of hydration left is comparable to that left for Mg and Ca samples.

[1] I wish to thank the referee for noting that this method is valuable because it is closely related to the relative number of each kind of ion present rather than to the basal spacing.

References

ALEXIADES, C. A. AND M. L. JACKSON (1965) Quantitative determination of vermiculite in soils. *Soil Sci. Soc. Am. Proc.* **29,** 522–527.

BARSHAD, ISAAC (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analysis, differential thermal curves, and water content. *Amer. Mineral.* **33,** 141–143.

——— (1950) The effect of interlayer cations on the expansion of the mica type of crystal lattice. *Amer. Mineral.* **35,** 225–238.

BASSETT, W. A. (1959) The origin of the vermiculite deposit at Libby, Montana. *Amer. Mineral.* **44,** 282–299.

GRUNER, J. W. (1934) The structure of vermiculites and their collapse by dehydration. *Amer. Mineral.* **19,** 557–574.

MATHIESON, A. McL. AND G. F. WALKER (1954) Crystal structure of magnesium vermiculite. *Amer. Mineral.* **39,** 231–255.

WALKER, G. F. AND W. F. COLE (1957) The vermiculite minerals. In *The Differential Thermal Investigation of Clays*, Ed. R. C. Mackenzie, Mineral. Soc., London, 191–206.