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AN ABNORMAL EFFECT IN DIFFERENTIAL THERMAL ANALYSIS OF CLAY MINERALS

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ABSTRACT

If in differential thermal analysis the differential thermocouple is arranged radially through the center of an uncovered cylindrical sample holder, a spurious endothermic effect can be produced in the low-temperature region of curves of vermiculite (and of montmorillonite) when the amount of sample is reduced below a certain limit. No such peak occurs when the sample is covered with a lid or when the differential thermocouple is arranged along the axis of the sample holder with its bead at the center. The origin of the peak is investigated and it is shown how this depends on the experimental conditions and the clay mineral structure.

INTRODUCTION

In differential thermal curves of many samples of vermiculite examined at the Division of Building Research an extra low-temperature endotherm has been revealed. Such a peak has also been reported in the literature by Mielenz, Schieltz and King (1954). It occurs, in the experience of the authors, when the weight of vermiculite in the sample holder of the differential thermal equipment is reduced below a critical value (less than about half that required to fill the holder); it will frequently occur in samples of hydrobiotite that are naturally low in vermiculite. Since the extra endothermic peak has no counterpart in weight-loss curves (Mielenz, Schieltz and King 1954, and Cole, unpublished data) and can have no structural significance (Walker and Cole 1957), it has been of interest to discover why it occurs.

EXPERIMENTAL

The following materials were used in the investigation: a vermiculite from Valpy Claims, West Suk, South Africa; hydrobiotite from Libby, Montana; halloysite from Southern Indiana; sodium montmorillonite from Wyoming; gypsum from Kangaroo Island, South Australia.

Differential thermal analyses were made with the equipment described by Carthew and Cole (1953) in which the differential thermocouple is placed radially through the center of the cylindrical sample holder (Fig. 1A). The sample block is a metal cylinder (originally in stainless steel but now in nickel) $1\frac{5}{8}$ in. diameter and $\frac{15}{16}$ in. high. In it are drilled four flat-bottomed holes $\frac{3}{8}$ in. diameter and $\frac{5}{8}$ in. deep. Two of these holes, diametrically opposite each other, are used to hold the sample and reference material, respectively. The differential thermocouple wires are

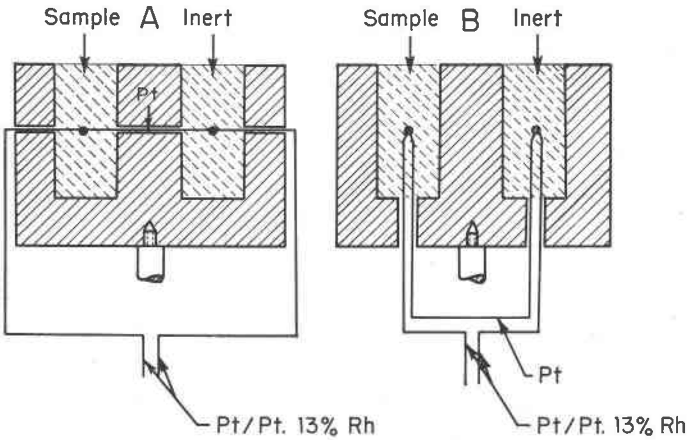

FIG. 1. A. Differential thermocouple arranged radially through the center of the cylindrical sample holder as in the equipment described by Carthew and Cole (1953).
B. Differential thermocouple arranged along the axis of the cylindrical sample holder with its bead at the center as in more conventional units (Mackenzie and Mitchell, 1957).

Pt/Pt.13%Rh of 0.5 mm. diameter. The sample holder contains about 0.8 gm. of material when lightly tamped and pressed finger tight. The heating rate is controlled at 10° C. per minute and the differential thermocouple voltage can, after amplification, be recorded at three levels; namely 100, 200 or 400 microvolts full scale deflection of the recording pen. Most of the present work was carried out on the 100 and 200 microvolt ranges. Analyses were also made with this equipment modified so that the differential thermocouple was placed along the axis of the cylindrical sample holder, with its bead at the center (Fig. 1B) as in more conventional units (Mackenzie and Mitchell, 1957). It should be noted that Carthew and Cole (1953) described their equipment as possessing a stainless steel lid to cover the block during analysis so as to screen the sample and reference material from direct radiation from the furnace tube at high temperatures. However, over the years the use of the lid has been discontinued. In this study it has been found that, at low furnace temperatures, the presence or absence of the lid is important for the effect to be described.

DILUTED SAMPLES

The effect investigated is illustrated in Fig. 2, which shows differential thermal curves produced by varying weights of vermiculite; the differential thermocouple being radially arranged and there being no covering lid to the sample holder. It is seen that when the weight of vermiculite is reduced to 25% of that required to fill the sample holder an inflection at

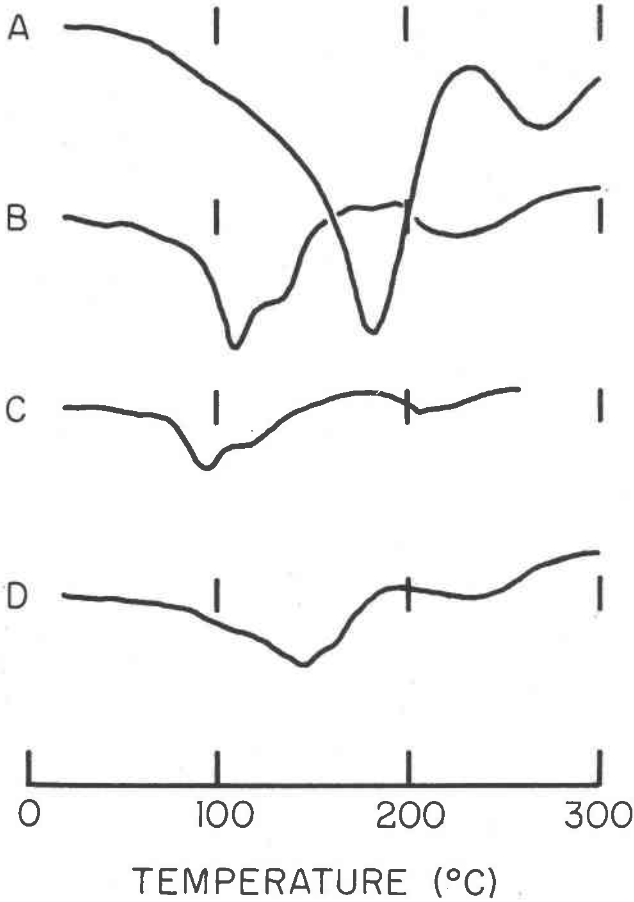

FIG. 2. Differential thermal curves of vermiculite and hydrobiotite produced by the equipment described by Carthew and Cole (1953) and run under the following conditions:
A. Vermiculite (0.8 g.) filling the whole of the sample holder.
B. Vermiculite (0.2 g.) mixed with alumina so as to fill the whole of the sample holder.
C. Vermiculite (0.1 g.) mixed with alumina so as to fill the whole of the sample holder.
D. Hydrobiotite (0.8 g.) filling the whole of the sample holder.

about 140° C. (B, Fig. 2) is apparent in the main low-temperature endotherm of the undiluted vermiculite (A, Fig. 2). Dilution to $12\frac{1}{2}\%$ accentuates the effect (C, Fig. 2). The differential thermal curve of a sample of hydrobiotite (D, Fig. 2) demonstrates a similar effect in a sample low in vermiculite (the vermiculite:biotite ratio of this sample is 1:3, Cole and Hosking, 1957). An extra endothermic peak can also be produced in the low-temperature region in samples of sodium montmorillonite (Wyoming bentonite) by similarly reducing the amount of the sample in the sample holder by dilution with inert material; the effect is thus not restricted to vermiculite.

The effect is *not observed* when differential thermal curves of diluted vermiculite are made with the *sample covered by a lid* or with equipment in which the differential thermocouple is arranged *along* the axis of the sample holder.

Sample Position and Thermocouple Arrangement

Since an extra endothermic peak can be induced by dilution of the sample for a particular arrangement of the differential thermocouple, it seems reasonable to expect that the disposition of the sample with respect to the thermocouple and the thermocouple arrangement must result in different thermal effects at the thermocouple bead. Consequently, a study was made of the influence on the differential thermal curve of placing samples of vermiculite, halloysite and gypsum in separate runs, above and below the differential thermocouple when this was arranged radially and along the axis of a cylindrical sample holder. The results in Fig. 3 show that:

(1) No matter how the thermocouple is arranged, the peak temperature is higher when the sample is below the thermocouple than when it is above; the difference is greater for a radial arrangement;

(2) When the thermocouple is arranged along the axis of the sample holder, the peak is sharpest and its area greatest when the sample is below the thermocouple; when the thermocouple is arranged radially the area of the peak is not greatly dependent upon the position of the sample but the peak is sharpest when the sample is placed above the thermocouple;

(3) When the differential thermal curves of vermiculite made with the sample below and above the thermocouple are compounded, an extra peak is introduced when the thermocouple is arranged radially (A, Fig. 3) but not when it is arranged along the axis of the sample holder (B, Fig. 3). The origin of distortions in the differential thermal curves of halloysite and gypsum, when these are made with the thermocouple arranged radially, also becomes apparent from the compounded curves.

Observations (1) and (2) have been verified in a further set of experiments in which the peak area and peak temperature have been measured for the two thermocouple arrangements for a small amount of vermiculite (~0.2 gm.) bounded by alumina and placed at various positions in the sample holder, between top and bottom. The results are plotted in Fig. 4. Observation (1) above follows from the plot of peak temperature against sample position. Observation (2) above follows from the plot of the peak area per unit weight against sample position. It is not clear why in Fig. 4 the results from position 3 are lower than those from positions 2 and 4. This anomaly does not affect the above observations.

Sample Lid

It has previously been stated that when the sample is covered by a lid the abnormal effect is eliminated. This is because, when a lid is used,

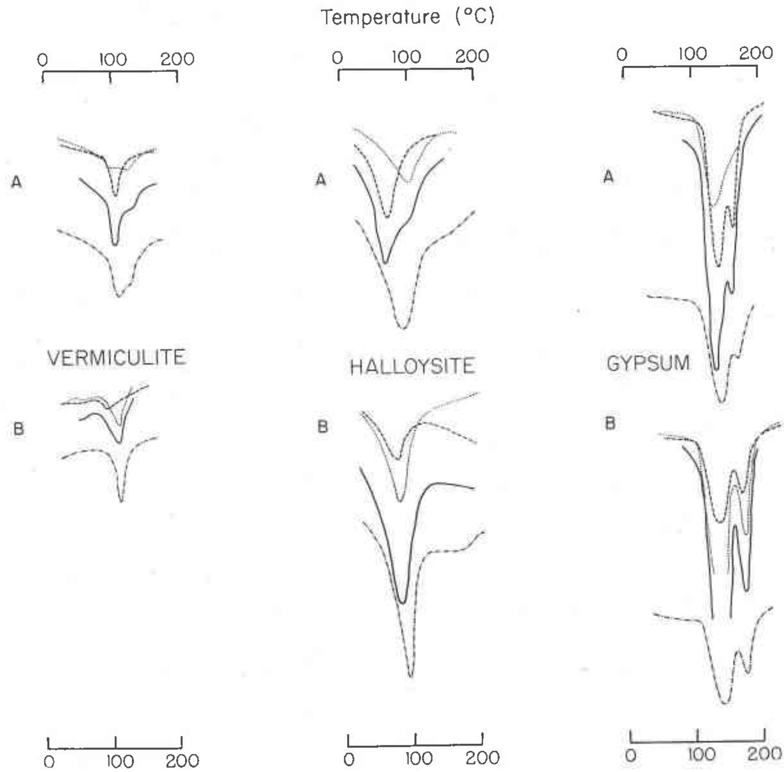

Fig. 3. Differential thermal curves of vermiculite, halloysite and gypsum as follows:

A. Differential thermocouple arranged radially through the center of the cylindrical sample holder as in Fig. 1A.

B. Differential thermocouple arranged along the axis of the cylindrical sample holder as in Fig. 1B.

- - - - Sample (about 0.2 g.) mixed with alumina to occupy fully the upper half of the sample holder (1).

...... Sample (about 0.2 g.) mixed with alumina to occupy fully the lower half of the sample holder (2).

——— Curve compounded from (1) and (2).

-·-·-· Sample (about 0.4 g.) mixed with alumina to occupy all the sample holder.

there is no longer a difference in temperature between the dehydrations of the sample from different parts of the block as was demonstrated to exist in Fig. 4 for an uncovered sample holder. This was verified in a separate experiment in which, for the radial thermocouple arrangement, the presence of a lid resulted in an increase by 30° C. in the temperature at which a 0.2 g. sample of vermiculite at the top of the sample holder (position 7, Fig. 4) dehydrated endothermically.

Remarks

When in differential thermal analysis the differential thermocouple is arranged radially across the center of an *uncovered* sample holder, an extra low-temperature endothermic effect can be produced from clay minerals if the weight of a sample component that is undergoing a low-temperature endothermic reaction becomes so low that the thermal effects from all parts of the sample do not even out at the thermocouple junction. Under such conditions, as the furnace temperature is raised the upper part of the sample dehydrates first, and this dehydration proceeds to completion before the sample in the lower part of the sample holder reaches the dehydration temperature. The differential thermocouple which has its bead and all its length common to the two halves of the sample thus tends to record two separate dehydration reactions. This is not the case when the differential thermocouple is arranged along the axis of the sample holder, for although the sample dehydrates as before, the arrangement of the thermocouple is such that the thermocouple records very little of the thermal reactions that take place in the upper half of the sample, its bead alone being in contact with this part of the sample. These observations imply that conduction of heat along the thermocouple wires is an important means of transferring the heat of reaction from the sample to the thermocouple bead. They also indicate that most of the thermal effect comes from the sample in the immediate vicinity of the thermocouple wires. These observations do not appear to have been considered in the theory of differential thermal analysis as yet, though the transfer of heat from the sample holder to sample (or vice versa) by conduction along the thermocouple wires, which results in a reduced peak area, has been discussed by Sewell (1955), Boersma (1955) and de Josselin de Jong (1957) for simplified geometrical arrangements. The observation that the upper half of the sample is largely wasted when the thermocouple is arranged vertically is in agreement with de Josselin de Jong's conclusion that "if the sample height surpasses a certain limit, the surplus of material does not influence the peak area, apparently being out of the influence zone of the thermocouple."

When the differential thermocouple is arranged radially across the

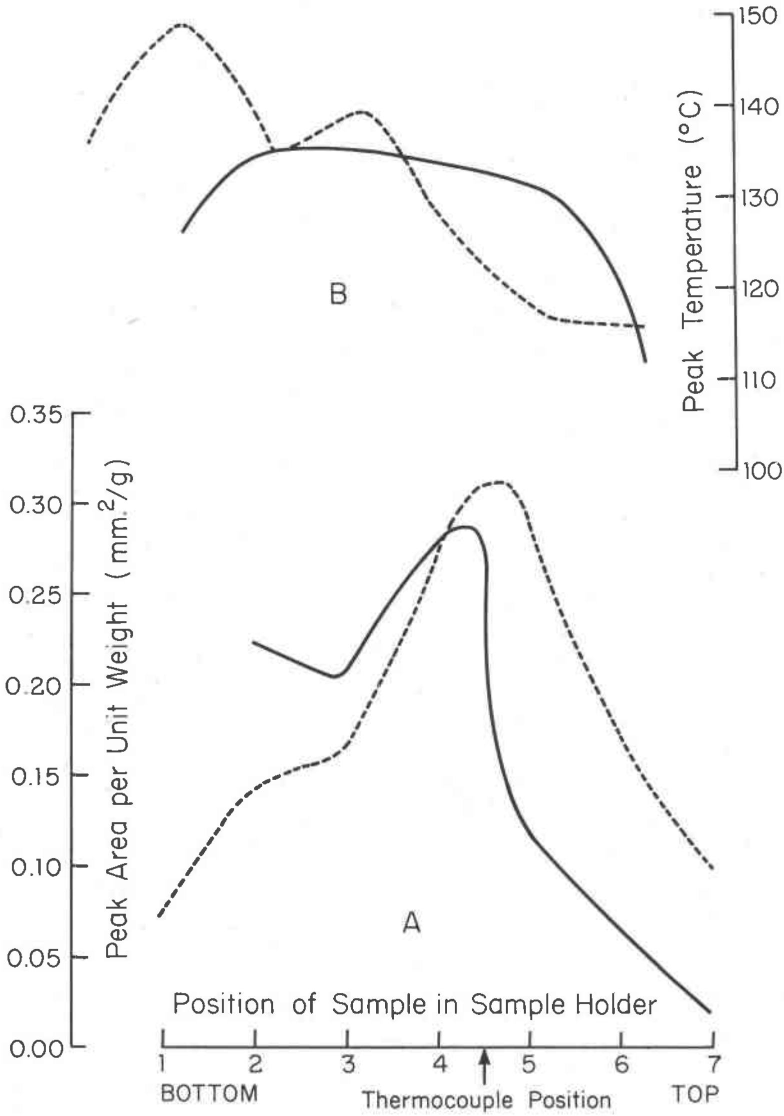

FIG. 4. Effect of the position of the sample in the sample holder on peak area (A) and peak temperature (B).

- - - - Differential thermocouple arranged radially through the center of the cylindrical sample holder as in Fig. 1A.

——— Differential thermocouple arranged along the axis of the cylindrical sample holder as in Fig. 1B.

center of a *covered* sample holder no extra low-temperature endothermic peak is introduced in the differential thermal curves of diluted samples of clay minerals, for the thermal effects from all parts of the sample reach the thermocouple junction at nearly the same time. The effect of the covering lid is to trap water vapor beneath it in the upper layers of the sample, so that a pressure of water vapor is generated which raises the dehydration temperature of the upper layers to a value which approaches that for the lower layers.

However, the fact that the effects described here have, for natural clay samples, been observed only with vermiculite indicates that it also must play a role. In the structure of this mineral the silicate layers are separated by the exchangeable cations which surround themselves by either a single or double sheet of water molecules, depending upon the relative humidity and temperature of the surrounding air (Walker and Cole 1957). Should water vapor concentrate within a sample of vermiculite it will be absorbed so as either to expand the structure from one possessing a single sheet to one possessing a double sheet of water molecules, or to increase the number of water molecules in the double sheet structure. When the differential thermocouple is arranged radially across the center of an uncovered sample holder, water vapor moves upwards to the atmosphere and downwards into the sample as the top layers dehydrate. That moving downwards cannot readily escape from the bottom half of the sample holder and produces a broad double endothermic peak (vermiculite sample A, Fig. 3) typical of a well-filled double layer structure. The peak from the upper half of the sample is much sharper and is typical of a partially-filled double layer or a single layer structure. When the differential thermocouple is arranged along the axis of the sample holder a sharp peak is produced from both halves of the sample since water vapor can readily escape from both regions. When the sample is covered by a lid the egress of water vapor is restricted to the thermocouple lead-ins, so that more uniform conditions are created within the sample holder and both top and bottom halves of the sample dehydrate under similar conditions and at similar temperatures. A true differential thermal record is then produced for vermiculite (and for montmorillonite too since it has a similar structure) with both types of differential thermocouple arrangements. Other examples of the importance of a lid in modifying differential thermal curves have been discussed by Kulp, Wright and Holmes (1949) for rhodochrosite and by Rowland and Jonas (1949) for siderite.

It should be noted that despite the limitations discussed here, which apply only to the low-temperature region, the radial arrangement of the differential thermocouple makes more economical use of the sample than the axially arranged one and should possess a higher sensitivity despite there being high conduction losses to the inert sample because of the short length of connecting wire used. The arrangement also has the advantage that the thermocouple beads can be more easily centered and this enables a better control of base-line drift. It becomes particularly valuable when small weights of sample only are available for the sample can (and should) be sandwich packed around the differential thermocouple leads so as to produce a maximum, but true, differential thermal effect.

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