

INTERPRETATION OF D.T.A. DIAGRAMS: THE LOW TEMPERATURE ENDOTHERMIC PEAK

BY R. GREENE-KELLY

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Introduction.—Differential thermal analysis has been used by Hendricks, Nelson and Alexander (1940) to study the sorption of water by montmorillonite. They measured the water uptake at a number of different relative humidities and then traced the low temperature endothermic peak of the resultant material on a differential thermal apparatus. They found that the resultant curves of Mg, Ca, Sr, Ba and Li-montmorillonite showed a division into two components at low relative humidities. Assuming that the area under the D.T.A. curve was proportional to the weight of water lost, a division of the total sorbed water was made between the two peaks. The authors found that for Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} the high temperature component represented approximately 5–6 water molecules per exchange ion, whilst for Li^+ it corresponded to 3.3 water molecules per exchange ion. It was concluded that these amounts of water correspond to that contiguous to the cations. In contrast, Na^+ , K^+ , Rb^+ and Cs^+ montmorillonite showed only a simple peak on dehydration under the same conditions, and it was suggested that the exchangeable cation was probably not hydrated in these cases.

Mackenzie (1950) has attempted to correlate the peak temperatures given by the above authors for different cations, with the hydration energies obtained from Bernal and Fowler (1933). The values given for the total hydration energy were corrected for the fact that an infinite dielectric was not present by subtracting the term $\frac{n-1}{2n} \frac{z^2 e^2}{R_z}$

where “ n ” is the dielectric constant of the dielectric outside the saturation sphere, “ R_z ” radius of the saturation sphere and “ ze ” charge of the ion. On plotting the resultant values against the corresponding peak temperatures of the high-temperature components of the endothermic peaks, an approximately straight line was obtained. Lithium diverged considerably from the straight line and was thought to be anomalous.

Mackenzie considered that a planar co-ordination of six water molecules about each monovalent cation would fill the interlamellar space entirely, thus leaving no room for water molecules not contiguous to the cations. The montmorillonite would then only give a single peak on D.T.A. No explanation of why Li-montmorillonite gives a double peak was offered.

It is not clear why monovalent cations should show six co-ordination in a planar configuration since Bernal and Fowler (1933) have considered that these ions are probably four-co-ordinated in solution.

A correlation of D.T.A. peak temperature and hydration energy must include the energy required to expand the silicate sheets. Thus water molecules require to do work before they can be sorbed on the interlamellar surface. If the work they require to do is greater than the free energy loss on sorption, no interlamellar sorption will take place. The work to be done per molecule must depend on the number of molecules sorbed per unit area, that is, the surface concentration. It follows therefore that there must be a minimum surface concentration which is compatible with any stable interlamellar distance and finally there will be a minimum surface concentration that is required to permit interlamellar sorption of any kind. During desorption, for example during D.T.A., the temperature at which water is evolved will depend on the critical surface concentrations and particularly the minimum critical concentration if the difference between exchange ions is being sought. The exchange ions will appear to be unhydrated if the lowest critical concentration is equal to or greater than the "hydration number" of the exchange cation.

During a recent study* of water sorption by montmorillonite it became evident that the minimum critical concentration for interlamellar sorption in Na-montmorillonite could be easily measured. That of K-montmorillonite was, however, found to be too high and of Li-montmorillonite too low for convenient measurement.

Results and Discussion.—It has so far been assumed that the "hydration number" as measured by D.T.A. is directly related to the equilibrium properties of the mineral. That is to say, the occurrence of double peaks is an indication of the occurrence of phase changes previously undetected by other methods. It is to be emphasised however that the D.T.A. method is a kinetic method of measuring water loss and therefore the complex peaks obtained may be indicative of differences of diffusion coefficient of the migrating water as well as phase changes in the mineral.

To settle which is responsible for the complex endothermic peaks obtained with montmorillonite it is necessary to compare the D.T.A. curves with detailed equilibrium isobaric dehydration curves obtained with the same material. Lithium saturated montmorillonite and hectorite were chosen for this work since they give well differentiated D.T.A. peaks. The samples were allowed to sorb water at 50% R.H. and 20°C and were subjected to isobaric dehydration and D.T.A. The former was carried out in an oven into which was passed a slow stream of air at a partial water pressure of 24 mm. The samples were placed in weighing bottles in the oven and left to reach equilibrium at every temperature, which in most cases took 1-3 days. The D.T.A. curves were obtained at a heating rate of 10°C per minute and were carried out by Mr W. A. Mitchell with a Kent type recorder and a ceramic sample block.

The results are shown in figs 1 and 2. Both the heating and cooling curves are shown in fig. 2. Hysteresis effects are present

*To be published shortly.

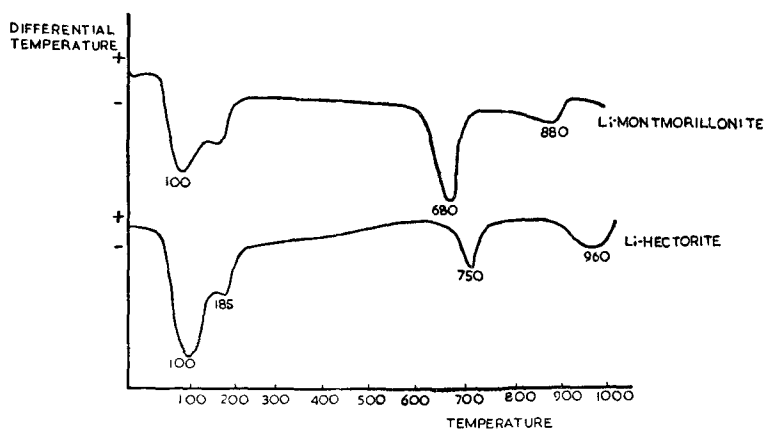
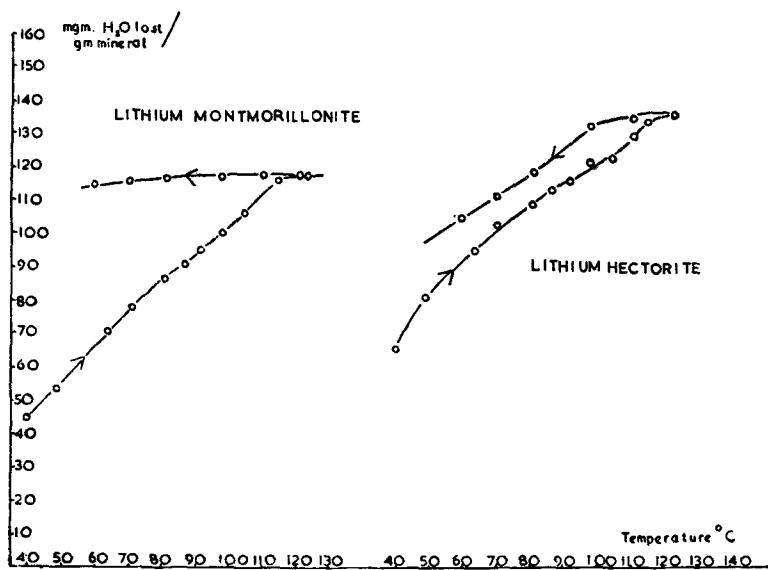


FIG. 1.

FIG. 2.—Isobaric dehydration-rehydration curves; $p = 24$ mm.

with both minerals, but are more marked in the case of Li-montmorillonite. This effect has already been discussed in previous papers (Greene-Kelly, 1952, 1953). The slight point of inflexion shown on the isobaric curves for these lithium saturated minerals is also a feature on the isobaric dehydration curves of materials that do not give complex endothermic peaks and it corresponds to about 0.5 water molecule per Li^+ which is much less than the 3-4 water molecules per Li^+ corresponding to the higher temperature component of the D.T.A. curve. It seems likely therefore that the D.T.A. curve is reproducing changes of diffusion coefficient, and the "hydration numbers" obtained by Hendricks, Nelson and Alexander would seem to have to be identified as the less mobile water. It is probable however, that this water is coordinated round the cations. The changes of activation energy detected by D.T.A. are in consequence not directly related to the hydration energy of the cation but also depend on other, rate-determining, factors.

The sorption measurements on Na-montmorillonite were carried out with a gravimetric high vacuum apparatus in conjunction with X-ray measurements on samples treated in the same way. By using a focussing monochromator, well defined (00/) reflections could be obtained over the entire range of water contents studied. It was possible in consequence to fix accurately the water contents where a rational series of reflections were obtained and the intermediate randomly interstratified systems were analysed by using the treatment given by Hendricks and Teller (1942). It was found that the mechanism of water uptake was different from that of loss but in both cases no interlamellar sorption took place when the surface concentration fell below 3-4 water molecules per sodium ion. It is apparent that this figure is equal to the amount of less mobile water in Li-montmorillonite as obtained from D.T.A. curves.

The explanation of why Na and K-montmorillonite only show simple peaks on D.T.A. would therefore be that in these substances the minimum surface concentration compatible with interlamellar sorption is above that which would, in a non-contracting mineral, show evidence of decreased mobility. In other words, the activation energy of the less mobile water is reduced by sheet collapse. Li-montmorillonite on the other hand is normal in this respect since its minimum surface concentration is low enough to allow these differences of mobility of the sorbed water to be developed.

This argument can be extended to vermiculite. Here the work required to expand the structure is presumably greater than in montmorillonite because of the greater charge density. If the free energy change on sorption is not increased at the same rate the critical concentration should increase, and hence some of the exchange cations which give double peaks on D.T.A. of the corresponding montmorillonite might give simple peaks on D.T.A. of the corresponding vermiculite. This effect is illustrated by some D.T.A. curves of a vermiculite saturated with different exchange cations.

published by Barshad (1948), where it is seen that although Li and Ba-montmorillonite give double peaks, the endothermic peaks of the vermiculite are single.

There is no reason therefore to consider either that in Na-montmorillonite the sodium ion is unhydrated, or that Li-montmorillonite is anomalous in some way. The behaviour observed on D.T.A. is merely a natural consequence of the fact that montmorillonite is an expanding mineral. It is to be expected that all expanding minerals will show this transition from single to double peaks.

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References.

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Discussion.

Dr R. C. Mackenzie.—The theory proposed by Dr Greene-Kelly was of very great interest to me, and in this connection I should like to make one or two remarks. My original suggestion regarding correlation of the hydration energy for close-packed sheaths and peak temperature was proposed not so much as a *complete* theory, but because it seemed to fit the evidence better than did the “hexagonal-net” theory, and it was felt at that time that it would be valuable as a starting-point, at least, for discussion. I shall look forward to seeing Dr Greene-Kelly’s paper in print, but his theory certainly sounds the most promising so far, and the fact that it can explain the Li^+ result without introducing any special postulate, is very much in its favour. Dr Greene-Kelly, I think, remarked that Li- and Ba-vermiculite showed only single low-temperature endothermic peaks. This does not agree with some experiments carried out a few years ago by us, where we found that not only did Li- and Ba-vermiculite give double low-temperature endothermic peaks, but so also did Na-vermiculite; in fact it was not till one used K^+ as the saturating ion that a single peak was observed. I wonder if he has any comments upon this?

Mr R. H. S. Robertson.—In view of the comparative stability of zincammine and cuprammine alginates, have ammines been studied by Dr Greene-Kelly?

Dr D. M. C. MacEwan.—Presumably the marked hysteresis of water sorptions visible from Dr Greene-Kelly's thermobalance curves for Li-montmorillonite is connected with the migration of Li^+ into octahedral positions, as postulated by Hofmann. Has Dr Greene-Kelly given any thought to the question of when exactly during the dehydration process, this migration of Li^+ occurs, or starts to occur? It also seemed peculiar to me that this migration of Li^+ gives rise to no visible thermal effect. Has Dr Greene-Kelly any ideas upon this subject?

Dr G. W. Brindley.—I am interested in Dr Greene-Kelly's suggestion that diffusion plays an important part in the process of formation of endothermic, dehydration d.t.a. peaks. Sabatier has shown very strikingly that the d.t.a. peaks and the dehydration characteristics of chlorites are very dependent upon crystal size—which is consistent with the view that diffusion plays a considerable part in the process. It is commonly argued that d.t.a. methods are not normally applied to powders of a coarse nature, but only to finely divided particles, such as clay materials. I am inclined to think, however, that even in the clay range of particle size, size may still be an important factor. For example, the lower temperature for the principal endothermic peak of *disordered* kaolin minerals as compared with those of *well-ordered* kaolinites may be due to the smaller particle size of the disordered kaolin. A well-ordered kaolinite of small particle size recently examined¹ has given an endothermic peak which, from the d.t.a. record alone, would have been interpreted as being due to a disordered form of the mineral!

Dr Mackenzie.—I should like to endorse the remarks of Dr Brindley regarding particle size and to emphasise that for all practical purposes, the fine-grained *well-ordered* kaolinite examined would have been classified, on d.t.a. evidence *alone*, as a type with *disordered* structure; not only was the peak temperature lower than that of kaolinite, but the asymmetry of the peak as measured by the "slope ratio"² was also in the range normally ascribed to the disordered material. In this connection, one wonders whether the decrease in peak temperature and increase in "slope ratio" from kaolinite to halloysite is not a function of absolute "crystal-size," *i.e.*, the size in which the layers exist in *regular* superposition. Thus the "crystal-size" of halloysite would be that of a single sheet since it is considered to be completely disordered; the "crystal-size" of disordered forms would be somewhat larger since there will be some regularity in superposition of the layers; and the "crystal-size" of kaolinite would be the actual size of the crystals, since the layers are regularly superposed. This is merely a suggestion, but seems to be borne out by present evidence.

¹ R. H. S. Robertson, G. W. Brindley and R. C. Mackenzie, *Amer. Miner.*, in press.

² L. Bramao, J. G. Cady, S. B. Hendricks and M. Swerdlow, *Soil Sci.*, 1952, **73** 273.

Dr R. Greene-Kelly.—In reply to Dr Mackenzie's point about the d.t.a. of vermiculite, I should say that an examination of the reasons for the differences between his results and those of Barshad would be worth while. Special attention might be paid to the differences of charge density between the minerals used for this work.

In reply to Mr Robertson, ammines involving pyridine, etc., are being studied at Rothamsted. The results, which would be too involved to discuss here, are to be published in due course. The d.t.a. of these complexes show some analogies to those of the water system.

In reply to Dr MacEwan, an investigation of the energies of activation associated with the release of the trapped lithium ions is in progress and may throw some light on the mechanism of the fixation. It is doubtful whether one could detect on d.t.a. a thermal effect, probably small, superimposed on the considerable heat changes involved in the loss of water.

MICA WEATHERING IN THREE SOILS IN CENTRAL NEW YORK, U.S.A.*

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Soil formation has been generally attributed to the interaction of five variables: parent material, vegetation, relief, time, and climate. This interaction may be considered as the impact of the latter four forces on the parent material and the resultant is a profile of weathering that varies with environment. The objective of this paper is to demonstrate how the mineralogical characteristics of soil profiles may be used to determine their genesis.

The two-square-mile area studied, Shackham Brook watershed, is located in central New York State, U.S.A. The steep to rolling topography reflects the influence of Pleistocene glaciation. The soils have developed on morainic material derived from Devonian graywacke shales and sandstones whose positions have been locally rearranged by glacial activity.

The three soils selected for this study all lie within the limits of the Brown Podzolic Great Soil Group. Each soil represents a different pedogenic expression of the same graywacke parent material. Shackham Soil #6 is the modal soil of the watershed, representing

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