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X-ray Study of Thermal Transformations in some Magnesian Chlorite Minerals

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The first stage of dehydration of magnesian chlorites is shown to involve the removal of water from the brucite layer only of the structure. Movement of the magnesium atoms from their original positions is indicated by the results of Fourier analysis. The second stage of dehydration is followed by the formation of olivine. The orientation of the olivine relative to the chlorite structure and the movements of the atoms in the transformation are discussed. These reactions proceed at somewhat higher temperatures as we go from penninite to clinochlore to sheridanite. Spinel and probably enstatite appear when the heating is continued to still higher temperatures. Curves obtained by the method of differential thermal analysis show endothermic peaks corresponding to the dehydration processes and an exothermic peak corresponding to the formation of olivine. They exhibit, however, a greater variety of results than the X-ray measurements, and the latter provide no immediate explanation of certain features of these curves.

1. Introduction

The thermal transformations of the chlorites give rise to a number of structural problems. Since they are essentially *hydrous* minerals, the first effect of heating is one of dehydration, the structural (OH) units being driven off as water. New minerals are produced which on further heating react together and give rise to further products. The dehydration process has been shown by Orcel (1927) and by Orcel & Renaud (1941) to take place in two well-defined stages, at both of which marked endothermic reactions occur. Considerable variation, however, exists in the curves obtained by the method of differential thermal analysis for different chlorites, and even for the same chlorite from different sources, the reasons for which are still not clear. The presence of iron probably has an important effect, and for this reason we have confined the present investigation to specimens which are essentially magnesian and contain little iron. X-ray powder studies (Orcel & Caillère, 1938) have established that the chlorite structure persists essentially until dehydration is complete. In a preliminary report (Ali & Brindley, 1949) we have shown that significant intensity changes occur in the chlorite powder diagram at the first stage of dehydration, although the diagram remains essentially of chlorite type.

The present paper extends the work previously reported in the following respects: (*a*) Fourier analysis has been applied to the detailed study of the structural change accompanying the first stage of dehydration. (*b*) The changes occurring at the second stage of dehydration, when the chlorites are converted to olivine, has been examined in more detail, and suggestions are made as to the probable atomic movements during the transition. (*c*) The work previously reported for penninite has been extended to clinochlore and sheridanite, and suggestions are made as to how the composition of the mineral influences the transitions.

The minerals employed in this work came from the following sources: Penninite from Binnental (Switzerland), a massive specimen containing a little fibrous asbestos, supplied by Dr F. A. Bannister, and a second specimen in powder form from Rimpfischwänge, Zermatt, supplied by Dr R. C. Mackenzie; these gave identical X-ray data. Specimens of clinochlore from West Chester, Pennsylvania, were supplied by Dr F. A. Bannister from the British Museum, in the form of flakes and fine powder (BM, 1940, 50) for X-ray work, and a massive specimen (BM, 26647) for thermal measurements. A massive specimen of sheridanite from St Colomban, Savoy, was supplied by Mlle S. Caillère, from the Museum d'Histoire Naturelle, Paris (no. 124, 257).

2. The chlorite structure—a résumé

The chlorites are mica-like layer-lattice silicates of varying chemical composition (see Orcel, 1927; Hallimond, 1939) built up on the same structural scheme. The fundamental unit consists of two layers, one similar to that found in talc or muscovite and of ideal composition $Mg_6(Si, Al)_8O_{20}(OH)_4$ per unit cell, and the other similar to that found in brucite and of composition $(Mg, Al)_6(OH)_{12}$ per unit cell. Mauguin (1928, 1930) first determined the unit-cell dimensions and discussed the composition of the mineral in terms of the content per unit cell. Pauling (1930) extended the work by finding the correct sequence of layers perpendicular to the basal (001) plane, and McMurchy (1934) attempted a more detailed analysis using X-ray powder analysis. Robinson & Brindley (1949) have commenced a detailed study of the polymorphism of the chlorites, using single-crystal methods. Their work confirms Pauling's layer structure but suggests modifications in McMurchy's structure; in particular, the arrangement of the layers in the structure described by McMurchy, which requires two layers per unit cell and therefore a basal spacing of about $2\times 14=28$ kX., is not confirmed. In the present paper it will be unnecessary to consider exactly how the layers are stacked relative to each other, since the X-ray evidence shows that for the crystalline material employed there exists a large measure of random displacement of the layers along the b axis by multiples of $\frac{1}{3}b_0$. It will be sufficient to regard the chlorite cell as being one layer thick and therefore having a basal spacing of about 14 kX.

3. Structural changes accompanying the dehydration of chlorites

These changes have been studied in detail for the mineral penninite, but other magnesian chlorites show similar changes. When powdered penninite is heated to about 600° C. for 2 hr. the intensities, especially of the basal reflexions, show marked changes, the (001) reflexion becoming many times more intense, (002) and (003) considerably weaker, and the higher orders also showing notable changes. The general distribution of the lines in the powder diagram, however, remains essentially the same, and the structure is still that of a chlorite; it will be referred to as the 'modified form' of the chlorite structure. Weight-loss measurements show that penninite in this form has lost about 50 % of the total removable water. The modified structure is quite stable, for after immersion in water for several weeks the X-ray powder diagram remains unchanged. Heating at somewhat higher temperatures up to 700° C. produced little or no further change, but when the temperature reached 760° C. most of the penninite lines disappeared, only a few of the stronger basal lines persisting as weak and diffuse lines. On heating to 800° C., these lines disappeared completely and lines corresponding to olivine appeared, faintly at first and then quite clearly after further heat treatment.

Similar changes are observed when rotation photographs of a small flake of penninite are taken, but in order to produce the modified structure and subsequently to convert this to olivine, higher temperatures and/or longer periods of heating are necessary. The transition to olivine especially takes place much more gradually than with a fine powder, and it is possible to observe simultaneously reflexions from both phases, so that their relative orientations can be studied.

4. The modified structure of chlorites; the first stage of dehydration

The intensities of the basal reflexions have been quantitatively determined up to (0,0,14) from measurements on a small flake of penninite before and after the first stage of dehydration. The intensities of the first five basal reflexions have also been measured by the powder method, and since good agreement was obtained with the flake measurements it is assumed that these were very little, if at all, affected by extinction. The experimentally determined structure factors, F_{00l}, are set out in Table 1. Values of F calculated from the Pauling layer structure for normal penninite are given in column (4) of Table 1. Their agreement with the measured values is good for the lower orders (confirming absence of large extinction effects), but for the higher orders the measured values fall progressively below the calculated ones. This is almost certainly due in large measure to distortions in the flake.

Table 1. *Structure factors of normal and modified penninite measured on powders and single flakes*

	Normal penninite			Modified penninite		
(1)	(2)	(3)	(4)	(5)	(6)	(7)
$00l$	Powder (obs.)	Flake (obs.)	(Calc.)	Powder (obs.)	Flake (obs.)	(Calc.)
001	29	24	−36	125	121	−83
002	61	67	+68	32	23	+24
003	91	81	+80	47	30	+52
004	*100*	*100*	*100*	*100*	*100*	*100*
005	75	67	−78	173	186	−159
006	—	0	− 2	—	100	−86
007	—	37	+47	—	58	+54
008	—	11	−14	—	0	−27
009	—	11	−12	—	43	−46
0010	—	37	+79	—	62	109
0011	—	0	−12	—	40	−25
0012	—	35	+105	—	—	—
0013	—	0	− 9	—	—	—
0014	—	27	+63	—	—	—

One-dimensional Fourier analysis was carried out to obtain the distribution of scattering matter perpendicular to the basal (001) plane for both forms of penninite. For the normal structure, the signs of F_{00l} were obtained from the calculations based on the Pauling layer structure and are given in column (4) of Table 1. For the modified structure, the signs were found as follows: The weight-loss measurements show that the modified structure has lost about $4\,H_2O$ per unit cell out of the total $8\,H_2O$ lost when the structure is fully dehydrated. This loss of water probably comes entirely from the brucite layer of the structure. In the first place, the talc layer of the structure contains insufficient water, only $2\,H_2O$ per unit cell, whereas the brucite layer contains $6\,H_2O$ per unit cell. Secondly, brucite itself dehydrates readily at about 400° C., while talc is resistant up to 900° C. or even higher temperatures. As a first approximation, the talc layer was assumed to remain intact while two-thirds of the brucite layer decomposed, liberating $4\,H_2O$ per unit cell. The remaining one-third of the brucite layer was considered to remain in its original position, thereby keeping the talc layers at about their original separation. This is the simplest suggestion which can be made to explain the very small changes in lattice parameters observed in this transition, as illustrated by the following data for penninite:

From 20° C. to 300° C. $a_0=5{\cdot}32, b_0=9{\cdot}22, c_0=14{\cdot}45$ kX., $\beta=97{\cdot}0°$.
At 600° C. $a_0=5{\cdot}36, b_0=9{\cdot}30, c_0=14{\cdot}22$ kX., $\beta=97{\cdot}6°$.
At 660° C. $a_0=5{\cdot}35, b_0=9{\cdot}31, c_0=14{\cdot}09$ kX., $\beta=97{\cdot}3°$.

Various suppositions were made regarding the positions of the Mg and O atoms in the decomposed portions of the brucite layers, and for each assumed arrangement values were calculated of F_{00l} for the modified structure. While the *numerical* values of F varied according to the model assumed, the *signs* were largely unaffected, certainly so far as the stronger reflexions were concerned, and they could therefore be used with reasonable confidence to carry out the Fourier analysis for the modified structure.

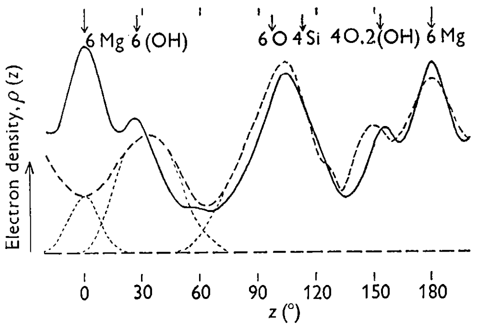


Fig. 1. One-dimensional Fourier analyses of the electron-density distribution in normal penninite (full line) and modified penninite, i.e. after first stage of dehydration (broken line). The distribution of atomic layers in normal penninite is indicated by arrows, and the composition of these layers is given. The light broken curves indicate how the electron-density curve for the modified penninite may be resolved into separate peaks in the region of the brucite layer.

The results of the Fourier analysis, shown in Fig. 1, confirm very well that the first stage of dehydration is essentially confined to the brucite layer. Since both curves are based on relative F values, the ordinates have been scaled so that the curves rise to about the same heights in the region of the talc layer. An outstanding feature of the transition is the very marked fall of the Mg peak at the centre of the brucite layer, $z=0$. If a base-line to the curves in Fig. 1 is tentatively drawn so that only a small electron density occurs in the region between the talc and brucite layers, then the amount of Mg remaining at $z=0$ is just about what would be expected from the amount of unchanged brucite, about one-third of the original amount. We conclude that in the first stage of dehydration the loss of water comes from the brucite layer and is accompanied by an outward movement of Mg towards the position indicated by the broad peak centred around $z=30°$, i.e. approximately the position previously occupied wholly by hydroxyls. Now two-thirds of these hydroxyls are lost in the dehydration, but, nevertheless, the peak at about $z=30°$ still contains about the same total scattering matter; this can only be supplied by the Mg atoms which have moved outwards from $z=0$. Each 'molecule' of $Mg(OH)_2$ which dehydrates liberates in the lattice one Mg atom, one O atom and creates one vacant site in the hydroxyl level of the structure. It appears that the Mg atoms move into or, at least, towards the vacant sites, thereby forming layers of composition MgO more or less coincident with the original hydroxyl layers.

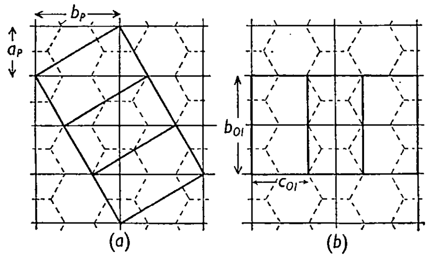
It is natural to compare these results with those found by Bussem & Köberich (1932) when brucite itself is dehydrated. Although dehydration occurs at about 400° C., the resulting MgO is very finely divided; recrystallization showing a well-orientated structure with the (111) planes of MgO parallel to the basal (0001) plane of brucite is obtained only after heating to 1150° C. The Fourier analysis provides no evidence for a similar orientation of MgO in penninite.

Similar conclusions are obtained from comparisons of observed and calculated F_{00l} values. Among the many arrangements of Mg and O atoms which were considered, the following may be mentioned: (*a*) Various arrangements in which the Mg atoms remained at or near $z=0$ and the liberated O atoms were displaced in various ways. (*b*) Arrangements in which some or all of the liberated Mg atoms occupied positions between the brucite layers and the talc layers at about $z=60°$. (*c*) Arrangements in which the liberated Mg and O atoms were in a semi-amorphous state, contributing little or nothing to the coherent reflexions. (*d*) Arrangements suggested by the Fourier analysis, in which the liberated Mg and O atoms were located in or near the original hydroxyl sheets. Arrangements of types (*a*), (*b*) and (*c*) failed to give satisfactory agreement between the observed and calculated F values, and only arrangements of type (*d*) produced calculated F values which varied in the observed manner with the order of reflexion. It was not possible to decide whether the liberated Mg and O atoms were located strictly in the hydroxyl sheets or only approximately in these levels. Calculated F values are given in Table 1 for a modified structure in which two-thirds of the brucite layer is decomposed and the liberated Mg and O atoms are in the hydroxyl sheets. The general agreement between the observed and calculated F's is seen to be about as good for this modified structure as it is for the normal chlorite structure.

The final conclusion is, therefore, that the first stage of dehydration consists of a loss of about half the removable water, accompanied by a migration of the liberated Mg atoms into or (at least) towards the hydroxyl sheets of the brucite layer.

5. Second stage of dehydration; the penninite–olivine transformation

Rotation photographs of single flakes taken at intervals during this transition have shown (Ali & Brindley, 1949) that olivine develops with a markedly preferential orientation, with the [013] and [011] directions of olivine along the *a* and *b* axes of penninite (see Fig. 2 (*a*)). From consideration of the hexagonal character of the chlorite layer, indicated by broken lines in Fig. 2, we see that the same relative orientation of the two structures is obtained with [010] and [001] of olivine along the *a* and *b* axes of penninite, as in Fig. 2(*b*). In all, there are three equivalent orientations at 120° to each other, but whether all three occur together when a single flake is converted to olivine cannot immediately be seen from rotations about the *a* and *b* axes of penninite, since the periodicity along [010] (10·21 kX.) is about half that along [013] (20·53 kX.), and similarly for [001] (5·98 kX.) and [011] (11·84 kX.). That all three orientations probably co-exist in a single flake is indicated by the fact that the *even*-order layer lines of olivine obtained by rotation about the *a* and *b* axes of penninite have many more spots than the *odd*-order layer lines. More positive proof is afforded by the fact that we cannot take a rotation photograph of a flake converted to olivine so as to reveal only the [010] or the [001] axis; the [013] or the [011] axis is always present.



(*a*) (*b*)

Fig. 2. Possible orientations of olivine structure (heavy lines) relative to basal plane of penninite (light lines). The Si–O network of penninite is indicated by broken lines. Orientation (*a*): [013] olivine parallel to *a* axis of penninite; [01$\bar{1}$] olivine parallel to *b* axis of penninite. Orientation (*b*): [010] olivine parallel to *a* axis of penninite; [001] olivine parallel to *b* axis of penninite.

The general character of the transition can be understood by considering (*a*) a combined projection on the basal plane of the chlorite and olivine structures, a simplified version of which is shown in Fig. 3, and (*b*) the vertical succession of atoms in the two structures shown side by side in Fig. 4. Fig. 2 shows that the areas $3b_{Ol}c_{Ol}$ for olivine and $4a_Pb_P$ for penninite are equivalent; the actual areas are not exactly equal because a small shrinkage occurs when olivine is formed. In view of this equivalence, the numbers of atoms in different layers listed in Fig. 4 correspond to three cells of olivine and four cells of penninite. We will now consider the probable changes which occur in penninite, layer by layer, when the transition occurs.

The shaded oxygen atoms of the Si–O hexagonal nets of penninite are retained wholly in corresponding layers of olivine with only minor movements in their own plane; certain groups of three O atoms rotate through ± 30° while other O atoms converge to build up new tetrahedra. The olivine tetrahedra are shown by broken lines in Fig. 3. The probable atomic movements are indicated by arrows.

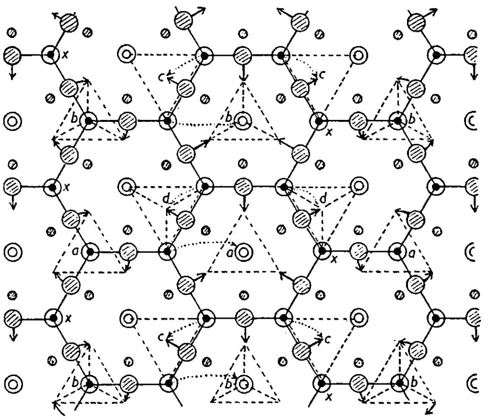


Fig. 3. Atomic movements during the penninite–olivine transformation. Full lines show Si–O network of penninite; atoms are represented with the same symbols as in Fig. 4. Continuous arrows show movements of O atoms, dotted arrows possible movements of silicon atoms. Letters *a*, *b*, *c* and *d* show the heights of the Si atoms in olivine, as indicated in Fig. 4, and *X* shows atoms which may be expelled from the structure. Triangles with broken lines indicate tetrahedra in olivine; silicons *b* and *d* lie in tetrahedra which point upwards, *a* and *c* in tetrahedra which point downwards.

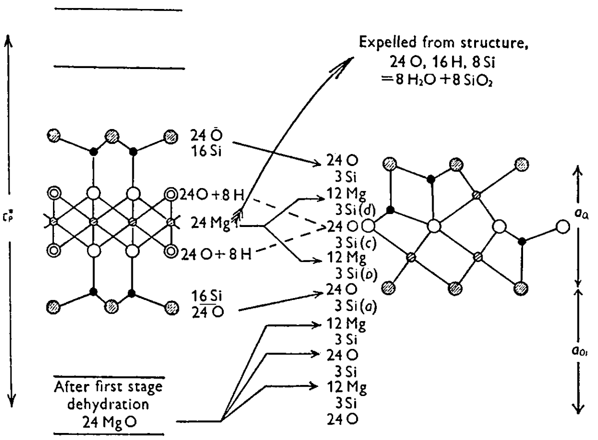


Fig. 4. Atomic movements in the penninite–olivine transformation; *a* axis of olivine is parallel to c^* axis of penninite. The numbers of atoms in different layers correspond to four cells of penninite and three cells of olivine. Note that out of 2 × 16 Si atoms in penninite, 8 × 3 atoms are accommodated in olivine, leaving 8 to be expelled from the structure.

The dehydration of the octahedral layer of the talc section of the penninite structure, the oxygen and (OH) atoms of which are shown by clear and double circles respectively, requires the expulsion of oxygen and hydrogen atoms from this layer. Altogether from a total of $(48\,\mathrm{O}+16\,\mathrm{H})$ atoms, 24 oxygen atoms go to furnish a layer of olivine and the residue, together with 8 excess silicon atoms (see later), are expelled as $(8\,\mathrm{H_2O}+8\,\mathrm{SiO_2})$. The chemical relationships are more involved if account is taken of the replacement of some Si by Al. Although one cannot say exactly which oxygen atoms are expelled, Fig. 3 shows that the remaining oxygen atoms are incorporated in olivine in exactly the same hexagonal arrangement as in penninite; observe in Fig. 3 that no displacement of the clear and double circles is indicated.

As regards the residue of the brucite layer, which is expressed as 24 MgO in Fig. 4, this furnishes one O and two Mg layers of olivine. This also is, to some extent, a simplification of the actual state of affairs, for in the first place the layer is not fully dehydrated when the first stage of dehydration is complete, and secondly, some of the Mg atoms will be replaced by Al.

The movement of the Si and Mg atoms need not be considered in detail. Fig. 3 shows by dotted arrows possible movements of the Si atoms parallel to the basal plane, and letters a, b, c and d show the levels of these atoms in the olivine structure (cf. Fig. 4). Since the tetrahedra in the chlorite structure are linked together in continuous sheets, but are separated in olivine, there is an excess of Si relative to oxygen which must be expelled during the transition. One-quarter of the Si atoms (and also any Al atoms acting as Si atoms in tetrahedral co-ordination) are expelled, and these are marked X in Fig. 3. The expelled atoms will presumably include all the 'tetrahedral' Al atoms. Provided the number of replacements of Si by Al does not exceed 1 in 4, which is roughly what occurs in penninite, then there will be sufficient Si atoms to build up layer by layer the olivine structure from the chlorite. But with other chlorites which contain more Al greater difficulties may arise in the transition.

As regards the Mg atoms, these move normal to the basal plane (see Fig. 4), no movements parallel to this plane being necessary.

This description of the transition process shows that the O atoms of the chlorite structure can pass, layer by layer, into olivine with only small movements in the basal plane. The movements of the Si and Mg atoms are also simple. The presence of Al replacing Si and Mg is the main complicating factor in the transition.

6. Comparison of transitions in penninite, clinochlore and sheridanite

In Orcel's classification of the chlorites, these minerals differ primarily according to the ratio $S=\mathrm{SiO_2}/R_2\mathrm{O_3}$, R being Al, Fe, Cr, ... and S having values about 4 for penninites, 3 for clinochlores and 2 for sheridanites. Since our materials were essentially *magnesian* chlorites, $R_2\mathrm{O_3}$ is mainly $\mathrm{Al_2O_3}$. Although in the absence of chemical analyses we cannot say exactly what is the ratio of Al to Si in tetrahedral positions in the minerals we have used, it is evident that in passing from penninite to sheridanite the proportion of these positions occupied by Al will increase, perhaps by as much as a factor of 2. It would be expected from the discussion of §5 that, as the proportion of Al increases, the transition to olivine would take place less readily.

The experimental results are summarized in Table 2. Essentially the same transitions occur with clinochlore and sheridanite as with penninite. The modified chlorite structure first appears at about 600° C. in all cases, but persists to higher temperatures at the sheridanite end of the series. The temperature at which olivine is first observed increases and the rate of its formation decreases in the order penninite, clinochlore, sheridanite. Transitions at higher temperatures have been examined in less detail, but the following have been noted: In the case of penninite the temperature must be raised 100–200° C. above that at which olivine first forms before spinel is clearly visible, but with clinochlore and sheridanite, especially the latter, spinel is clearly visible at the same temperature as that at which olivine first appears; evidently, with a larger percentage of $\mathrm{Al_2O_3}$, olivine formation is impeded but spinel formation is either unaffected or made easier.

Table 2. *Comparison of thermal changes in three chlorites*

	Penninite	Clinochlore	Sheridanite
Range of temperature in which modified chlorite structure occurs	600–700° C.	600–760° C.	600–800° C.
Temperature of disappearance of chlorite structure when powdered minerals are heated	760° C.	800° C.	850–900° C.
Temperature at which olivine is first clearly visible in X-ray diagram	800° C.	850° C.	950° C.

Observations at higher temperatures

Penninite. At 950° C., olivine + 3 additional lines, probably spinel.
At 1180° C., olivine + spinel + probably enstatite.
Clinochlore. At 850° C., olivine + spinel both clearly visible.
Sheridanite. At 1000° C., olivine + spinel + probably enstatite.

7. Comparison of X-ray and thermal data

Differential thermal analysis curves of these minerals, shown in Fig. 5, have been obtained by Dr R. W. Grimshaw and Dr A. Westerman, using the self-recording method developed by Grimshaw, Heaton & Roberts (1945). For penninite and sheridanite the same material was used as in the X-ray work; for clinochlore a different specimen was used but the material came from the same locality (West Chester, Penn.). When comparing the reaction temperatures indicated by Fig. 5 with those quoted in the earlier parts of this paper, it must be kept in mind that the thermal curves are obtained by a rapid rate of heating, about 10° C. min.$^{-1}$, whereas in the X-ray work the specimens were held for 2 hr. or more at any given temperature.

In view of the close similarity between the X-ray results for the three minerals, there is a surprising difference between the thermal curves. Their only approximately constant feature is the peak temperature of the first endothermic reaction, about 645° C. for penninite, and 630° C. for clinochlore and sheridanite. Penninite and clinochlore show exothermic reactions at 825 and 840° C. respectively, which correspond to the recrystallization of the dehydrated chlorites to form olivine, but with sheridanite any such reaction would be masked by the large endothermic effect at about the same temperature. It is difficult to suggest any explanation for the absence of a second endothermic peak for clinochlore. Examination of the thermal curves obtained by Orcel (1927) shows that in this respect clinochlores from different localities are variable; he examined three specimens, one of which (from Achmatovsk) showed two endothermic peaks, but the other two (of which one was from West Chester) showed only a single peak. Orcel (1927) considered that when a chlorite shows only one endothermic peak, the two stages of dehydration occurred too close to be resolved by the thermal method, but they could still be detected by his dehydration method of examination in which the vapour pressure of the liberated water is recorded. There is, however, nothing in the X-ray results to suggest that the two stages of dehydration are particularly close in the case of clinochlore (compare the data for the three minerals in Table 2).

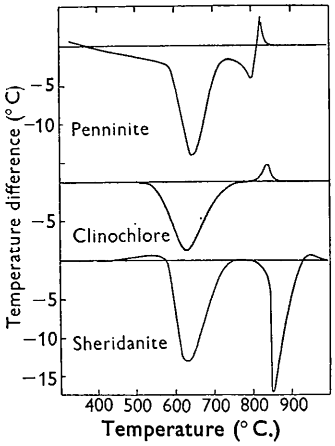


Fig. 5. Differential thermal curves of penninite, clinochlore and sheridanite; these curves were supplied by Dr R. Grimshaw and Dr A. Westerman.

Finally, we wish to record our great indebtedness to Dr F. A. Bannister, Mlle S. Caillère and Dr R. C. Mackenzie who supplied us with the chlorites used in this work. We thank also Prof. A. L. Roberts, of the Fuel Department of this University, in whose laboratories the thermal curves discussed in §6 were recorded by Dr R. W. Grimshaw and Dr A. Westerman. Thanks are also due to the Government Grant Committee of the Royal Society for grants with which essential apparatus has been purchased, and to the Government of India for the award of a research scholarship to one of us (S.Z.A.). Finally we desire to thank Prof. E. G. Cox for a critical discussion of the MS. of this paper.

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