

*Ferrous chamosite and ferric chamosite.*

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1. *Introduction.*

IN a previous paper (Brindley, 1951) chamosites from a number of localities were examined, and their structure was shown to be of kaolin-type. Furthermore, it was shown that many of the variations in X-ray powder diagrams of chamosites can be accounted for by the existence of two kaolin-type structures, one hexagonal and one monoclinic, with simply related cell dimensions.

Previous work (Brindley and Ali, 1950; Brindley and Robinson, 1951) had shown that chlorite minerals produce a modified form on heat-treatment at about 600° C., characterized by a large increase in intensity of the 14 kX basal reflection. In general, however, kaolin-minerals did not show any such phenomenon, and accordingly, thermal examination has been used in conjunction with X-ray powder diagrams in cases where a mixture of chlorite and kaolin minerals was suspected (Brindley, Oughton, and Youell, 1951).

During the course of an investigation on the Frodingham and Northampton sedimentary ironstones, a modified structure was observed after heat-treatment of an exceptionally good chamosite specimen, and although this structure was clearly still of kaolin-type, it was largely dehydrated and oxidized. The new structure is accordingly termed *ferric chamosite* to distinguish it from the common *ferrous chamosite*. Taylor (1949) describing the preparation of rock sections from chamosite oolites and mudstones says: 'Any excessive heat treatment in this operation causes a flaky recrystallization of the chamosite and, at a higher temperature, converts it to a mass of brown and yellow-brown material. Slides indistinguishable from those of weathered chamositic oolites and mudstones may, in this way, be produced from fresh material.' It is probable that this product was similar to the ferric chamosite described here. A detailed thermal and X-ray study of the two types of chamosite was carried out, and forms the subject of this paper.

The X-ray powder technique employed was identical with that used previously (Brindley, 1951) and need not therefore be described in detail. Methods of heat-treatment were in the main conventional, although the technique used for reducing the ferric chamosite will be described in a later section.

## 2. X-ray data for ferrous and ferric chamosites.

The chamosite specimen used came from location A3, Stanion Lane pit, Corby, Northamptonshire, and was supplied by Dr. W. Davies of

TABLE I. X-ray powder data for ferrous and ferric forms of chamosite, Stanion Lane pit, Corby, Northamptonshire.

| Ferrous chamosite. |         |           |                | Ferric chamosite. |         |           |
|--------------------|---------|-----------|----------------|-------------------|---------|-----------|
| <i>d.</i> (kX)     |         | <i>I.</i> | <i>(hkl)</i> . | <i>d.</i> (kX)    |         | <i>I.</i> |
| obs.               | calc.   | obs.      |                | obs.              | calc.   | obs.      |
| 7.105              | 7.100   | vs        | 001            | 7.05              | 7.048   | s         |
| 4.67               | 4.680   | m-        | 02*            | 4.535             | 4.540   | m-        |
| 4.295              | —       | w-        | —              | —                 | —       | —         |
| 3.927              | 3.899   | w         | 021            | —                 | —       | —         |
| 3.546              | 3.550   | vs        | 002            | 3.520             | 3.524   | s         |
| 3.060              | —       | w-        | —              | —                 | —       | —         |
| 2.704              | 2.702   | m-        | 200            | 2.622             | 2.622   | m         |
| 2.520              | 2.524   | vs        | 201            | 2.460             | 2.458   | ms        |
| 2.147              | 2.146   | ms        | 202            | 2.103             | 2.103   | m-        |
| 1.775              | {1.776} | m         | {203}          | 1.749             | 1.749   | w+        |
|                    | {1.769} |           |                | {240}             | —       | —         |
| 1.560              | 1.560   | ms        | 060            | 1.514             | 1.513   | m         |
| 1.523              | 1.524   | m-        | 061            | 1.483             | 1.479   | w         |
| 1.478              | 1.478   | m         | 204            | 1.462             | 1.462   | w         |
| 1.429              | 1.427   | w+        | 062            | 1.395             | {1.391} | w         |
| 1.413              | {1.420} | vw        | {005}          |                   | {1.409} |           |
|                    | {1.410} |           |                |                   | {044}   |           |
| 1.324              | 1.327   | w+        | 401            | —                 | —       | —         |

\* This denotes the head of a 2-dimensional diffraction band rather than a 3-dimensional reflection.

### Lattice parameters.

|          |     | Ferrous form. | Ferric form. | % contraction. |
|----------|-----|---------------|--------------|----------------|
| <i>a</i> | ... | 5.404 kX      | 5.244 kX     | 3.00           |
| <i>b</i> | ... | 9.360         | 9.080        |                |
| <i>c</i> | ... | 7.100         | 7.048        | 0.75           |

the United Steel Cos. Ltd., Rotherham. The hand-specimen was a clear green colour with no obvious sign of oxidation or weathering. Dr. Davies's petrological description is 'mixed ooliths of dark green chamosite, and of limonite and siderite surrounded by chamosite, in a matrix of siderite'. X-ray diagrams showed that it contained about

equal quantities of chalybite and chamosite, with traces of quartz and gypsum. The chamosite was fine-grained, and after crushing, a simple sedimentation in distilled water followed by drying on a steam-bath produced a fine fraction containing about 94 % chamosite, chalybite forming most of the remainder. It is unusual to have so pure a specimen available in quantity.

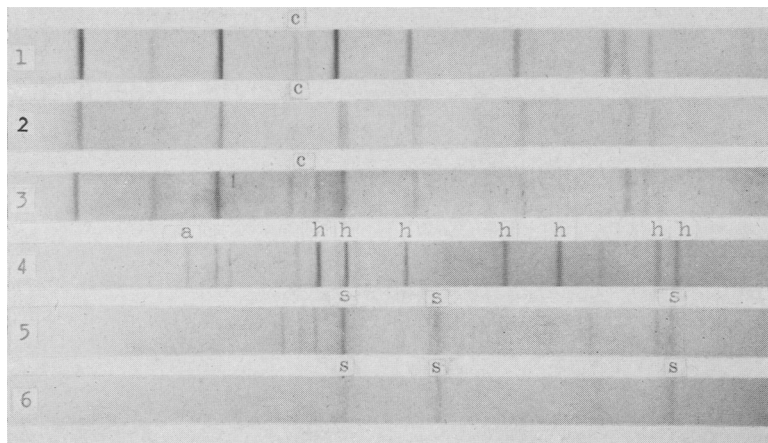


Fig. 1. X-ray powder diagrams. Marked lines: c = chalybite; a = anhydrous calcium sulphate; h = haematite; s = spinels.

1. Ferrous chamosite, Corby, Northamptonshire.
2. Partial conversion to ferric chamosite by heating at 300° C.
3. Ferric chamosite, after heating at 400° C.
4. Formation of haematite by heating in air at 900° C.
5. Formation of spinel and ferrous aluminate by heating ferrous chamosite in steam at 800° C.
6. Formation of ferrous aluminate by reducing ferric chamosite in H<sub>2</sub>/H<sub>2</sub>O mixture at 650° C.

The ferric chamosite was formed on heating the sample in air to 400° C. for two hours. Further heating at this temperature did not produce any apparent further change. Heating at 300° C., however, produced a mixture of the ferrous and ferric types. The colour of the mineral changed progressively from green through yellow to brown.

X-ray powder diagrams were obtained with a 20-cm. diameter semi-focusing camera, employing filtered Co-K $\alpha$  radiation. The specimens were set 9° to the incident beam. The spacings for the two forms are shown in table I, and the photographs in fig. 1, numbers 1 and 3. The strongest line of chalybite appeared on the diagrams but is omitted from

the table. The ferrous chamosite diagram is virtually identical with the ortho-hexagonal form found in the Ayrshire chamosite described previously (Brindley, 1951). The unit cell,  $a$  5.40 $\mu$ ,  $b$  9.36,  $c$  7.10 kX, is slightly larger than that of the Ayrshire material, but small differences in composition easily account for the discrepancy. The most noteworthy feature is that there is no trace of the monoclinic form which was present to extents varying from 10 to 55 % in the previous chamosites examined. The specimen is clearly a nearly pure ortho-hexagonal form, with no contaminant apart from the chalybite.

A direct comparison of the ferrous and ferric diagrams shows that oxidation is accompanied by an overall displacement of the lines corresponding to a shrinkage of the lattice. There was also a progressive diminution in intensity of the (20 $l$ ) reflections as  $l$  increased. The (200) reflection is about equally strong in the two forms, the (201) is appreciably diminished, the (202) markedly diminished in the ferric form, and so on. Another easily noticeable feature of the photographs, and one which is very useful for diagnostic purposes, is the conversion of the medium strong line at 1.560 to a medium strength line at 1.514 kX, and the virtual disappearance of the 1.523 and 1.478 lines.

The values of the spacings calculated for the ferric form assuming it to retain the ortho-hexagonal structure are also included in table I, and they agree closely with the observed values. A comparison of the parameters for the two forms shows that the  $a$  and  $b$  parameters have contracted by 3 % and the  $c$  parameter by 0.75 %. The change in parameters arises largely from the change in the ionic radius of iron, namely, 0.83 Å. for ferrous and 0.67 Å. for ferric ions. The difference in percentage contraction of the  $a$  and  $b$  parameters on the one hand and the  $c$  parameter on the other may be explained by considering the positions of the iron atoms in the kaolin-type structure of chamosite (Brindley, 1951). The iron atoms, being in the octahedral layer of the unit cell, can be regarded as influencing only a portion of the structure in the  $c$  direction, about one-third, but the whole structure in the  $ab$  plane.

### 3. *Chemical analyses and structural formulae.*

As regards the general chemical properties of the two forms of hexagonal chamosite, the ferrous form is the less stable and therefore is the more reactive. In particular it dissolves more readily in acids and even in the absence of air it decomposes at a lower temperature than the ferric form.

The chemical analysis of the ferrous chamosite (table II, column 1)

indicated that the only appreciable impurities were chalybite and calcium sulphate. In correcting the analytical results for these impurities, all the  $\text{SO}_3$  with the appropriate amount of  $\text{CaO}$  was taken to form  $\text{CaSO}_4$ . The remaining  $\text{CaO}$  and the  $\text{MnO}$  were taken with

TABLE II. Chemical analyses of ferrous and ferric chamosites.

|                                         | Ferrous chamosite. |       |        | Ferric chamosite. |       |        |
|-----------------------------------------|--------------------|-------|--------|-------------------|-------|--------|
|                                         | 1.                 | 1a.   | 1b.    | 2.                | 2a.   | 2b.    |
| $\text{SiO}_2$ ...                      | 22.47              | 22.47 | 23.81  | 23.48             | 23.48 | 24.69  |
| $\text{Al}_2\text{O}_3$ ...             | 21.82              | 21.82 | 23.12  | 22.45             | 22.45 | 23.61  |
| $\text{Fe}_2\text{O}_3$ ...             | 0.22               | 0.22  | 0.23   | 45.15             | 43.37 | 45.61  |
| $\text{FeO}$ ...                        | 39.79              | 37.24 | 39.45  | 1.51              | 0.45  | 0.47   |
| $\text{MgO}$ ...                        | 2.82               | 2.57  | 2.72   | 2.83              | 2.60  | 2.74   |
| $\text{CaO}$ ...                        | 0.38               | —     | —      | 0.36              | —     | —      |
| $\text{MnO}$ ...                        | 0.03               | —     | —      | 0.03              | —     | —      |
| $\text{TiO}_2$ ...                      | trace              | —     | —      | trace             | —     | —      |
| $\text{P}_2\text{O}_5$ ...              | nil                | —     | —      | nil               | —     | —      |
| $\text{SO}_3$ ...                       | 0.11               | —     | —      | 0.12              | —     | —      |
| $\text{S}$ ...                          | trace              | —     | —      | trace             | —     | —      |
| $\text{V}_2\text{O}_3$ ...              | nil                | —     | —      | nil               | —     | —      |
| $\text{Cr}_2\text{O}_3$ ...             | nil                | —     | —      | nil               | —     | —      |
| $\text{CO}_2$ ...                       | 2.04               | —     | —      | 1.14              | —     | —      |
| Loss on ignition to constant weight ... | (7.72)             | —     | —      | (3.72)            | —     | —      |
| $\text{H}_2\text{O} \dagger^*$ ...      | 10.07              | 10.07 | 10.67  | 2.74              | 2.74  | 2.88   |
|                                         | 99.75              | 94.39 | 100.00 | 99.81             | 95.09 | 100.00 |

\*  $\text{H}_2\text{O} -$  = loss on ignition less  $\text{CO}_2$  plus  $(\text{FeO}) \times 8/72$ . Loss in weight in preparing ferric chamosite, 4.05 %.

1. Ferrous chamosite, Stanion Lane pit, Corby, Northamptonshire, Analyst, R. F. Youell, on 1.5 grams dried at  $105^\circ\text{C}$ .

1a. After correction for  $\text{FeCO}_3$  4.11,  $\text{CaCO}_3$  0.54,  $\text{MgCO}_3$  0.47,  $\text{MnCO}_3$  0.05,  $\text{CaSO}_4$  0.19 %.

1b. Scaled to 100 %.

2. Ferric chamosite, prepared from the same sample of material by heating in air at  $400^\circ\text{C}$ . for two hours.

2a. After correction for  $\text{FeCO}_3$  1.70,  $\text{CaCO}_3$  0.49,  $\text{MgCO}_3$  0.49,  $\text{MnCO}_3$  0.05,  $\text{CaSO}_4$  0.21,  $\text{Fe}_2\text{O}_3$  1.78 %.

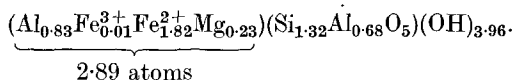
2b. Scaled to 100 %.

$\text{CO}_2$  to give carbonates. In considering the correction for the remaining  $\text{CO}_2$ , an analysis was made of a sample of chalybite from the Northamptonshire field which showed that it contained iron, calcium, and magnesium carbonates in molecular proportions very nearly 7:1:1. This agrees with published analyses by Harvey (Taylor, 1949, pp. 48-49) of chalybite specimens which included one from Stanion Lane pit. Although the amount of chalybite in our purified chamosite ore and

the resulting corrections were small, it was considered preferable to divide the remaining  $\text{CO}_2$  in the ratio 7:1 between iron and magnesium carbonates. On taking the resulting figures with the  $\text{CaCO}_3$ , the molecular ratio was  $\text{Fe}:\text{Mg}:\text{Ca} = 7:1:1.08$  which is in satisfactory agreement with the known composition of chalybite. The water content was calculated from the loss on ignition with allowance for the  $\text{CO}_2$  and  $\text{FeO}$  contents. No correction was made for any possible dehydration of a hydrated calcium sulphate in view of the very small amount present. The corrected chamosite analysis is given in column 1a of table II, and in column 1b the corresponding ratios after scaling the total to 100 %.

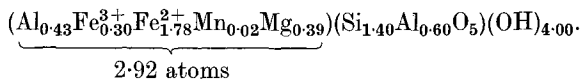
The ferric chamosite was prepared from the same sample as that used for the ferrous analysis. Correction of the result was complicated by the partial decomposition of the chalybite at  $400^\circ \text{C}$ . An analysis of chalybite heated under identical conditions showed that  $\text{CaCO}_3$  and  $\text{MgCO}_3$  remained, while about 60 % of the  $\text{FeCO}_3$  had decomposed to give  $\text{CO}_2$  and  $\text{Fe}_2\text{O}_3$  by oxidation. Calcium sulphate, calcium carbonate, and manganese carbonate were corrected as before. From the weight loss in preparing the ferric form, the  $\text{MgCO}_3$  and  $\text{FeCO}_3$  contents before partial decomposition were calculated. The  $\text{CO}_2$  remaining after allowing for calcium, magnesium, and manganese carbonates was attributed to  $\text{FeCO}_3$  and the difference between original and actual  $\text{FeCO}_3$  was allowed for as  $\text{Fe}_2\text{O}_3$ . The decomposed fraction amounted to 61% of the total  $\text{FeCO}_3$ , in good agreement with the independent results. Column 2a gives the corrected analysis and column 2b the chamosite figures scaled to 100 %. Subsequent direct determination of water gave 10.00 % for the ferrous and 2.66 % for the ferric chamosite as compared with the values calculated from ignition weight losses of 10.07 and 2.74 % respectively.

If the previous conclusion (Brindley, 1951) is accepted that chamosite is a kaolin-type structure with a formula of the type  $X_n(\text{Si}_2\text{O}_5)(\text{OH})_4$ , where  $X$  represents the 'octahedral' atoms and  $n$  varies between 2 and 3, being ideally 2 when  $X$  is wholly trivalent and 3 when  $X$  is divalent, then the formula for ferrous chamosite may be evaluated on the basis of five oxygen atoms per formula weight. The following result is obtained:

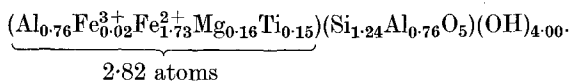


It is particularly satisfactory to find that the amount of (OH) agrees almost exactly with the ideal value of 4.

This formula may be compared with two others: A Frodingham chamosite analysed by Harvey and described by Hallimond (1939) gives:

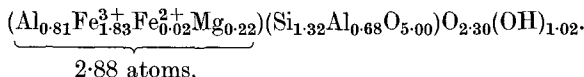


An Ayrshire chamosite analysed by Dixon and quoted by Brindley (1951) gives:



The analysis of the Corby material in the ferrous state is therefore in agreement with these previous analyses.

The calculation of the structural formula of the ferric chamosite raises a difficult and fundamental problem. In any mineral containing structural water, as (OH), there is always a possibility of loss of water before the sample is analysed, and the tendency of actual analyses to fall short of the idealized (OH) figure is clearly due to this cause. The deviation is, however, usually a small percentage of the total water content. In the case of ferric chamosite the chemical analysis (table II) shows a marked decrease in the percentage of H<sub>2</sub>O and without a detailed knowledge of the structure there is no justification for proceeding on the basis of five oxygen atoms in the formula and indeed this leads to an unconvincing result. The only reasonable approach is to keep the number of Si and Al atoms constant. Proceeding on this basis, we obtain for the structural formula of ferric chamosite the following expression:



This formula retains the original number of cations in the octahedral positions, which would be expected since oxidation does not alter this figure. Furthermore, the fact that we now find only one (OH) in the formula in place of the original (OH)<sub>4</sub> also admits of a simple structural interpretation. In fig. 2 is shown diagrammatically the distribution of atoms in layers in ferrous chamosite and the probable distribution in ferric chamosite. In the first place there is the same number of cations in both tetrahedral and octahedral positions. These layers are therefore probably closely similar in the two structures. Secondly, one (OH) per formula weight is needed, together with two oxygen atoms, to complete

the middle layer of two O and one (OH) atoms. It seems reasonable to suppose that the single (OH) is used to complete the middle layer. This is probable not only on numerical grounds, but also because it occupies a central position in the layer and therefore may be less easily dehydrated than the outermost hydroxyls. (The OH groups in analogous

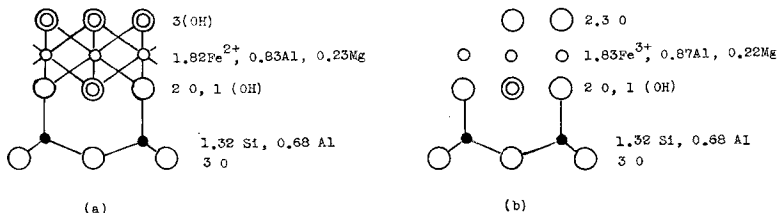
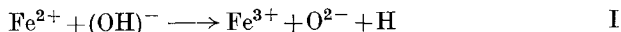


FIG. 2. Diagrammatic representation of layer structures of: (a) ferrous chamosite; (b) ferric chamosite. The positions of the 2·3 oxygen atoms in (b) are uncertain.

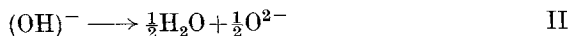
positions in the mica structure, for example, are not removed below about 800° C.) The oxygen atoms in excess of five in ferric chamosite, namely 2·30, must presumably replace the 3(OH) layer in ferrous chamosite.

The combined process involving oxidation and dehydration may be considered as follows: Each ferrous ion on oxidation gives a ferric ion and an electron. The electron reacts with a hydroxyl group to give an oxygen ion and a hydrogen atom.

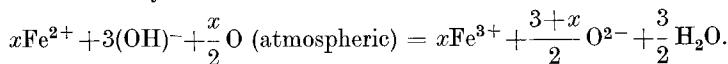


The  $\text{O}^{2-}$  ions remain in the lattice, and the H atoms are removed as water by aerial oxidation. In the absence of oxygen for this removal of H as water, the reaction does not take place, as we have shown experimentally. This process accounts for a part only of the loss of (OH) ions from the lattice, namely, a diminution of (OH)'s equal in number to the ferrous ions.

It appears that a second reaction, involving dehydration only, occurs of the form:



For a lattice containing  $x$  octahedral ferrous ions the combined oxidation-dehydration process is obtained by adding together  $x$  (reaction I) +  $(3-x)$  (reaction II). Taking account also of the atmospheric oxidation we obtain finally:





In the present case  $x = 1.82$ . We therefore expect  $\frac{3+1.82}{2}$  or 2.41 oxygens replacing 3(OH). This is in good agreement with the analytical results.

#### 4. Reduction of ferric to ferrous chamosite.

If ferric chamosite differs from ferrous chamosite only by the removal of H and H<sub>2</sub>O from the lattice, then a suitable treatment based on the thermodynamic properties of the system FeO-Fe<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>-H<sub>2</sub>O may bring about the reverse process. The heat of formation of hydrous silicates from oxides is low and therefore the free energies of ferrous and ferric hydrous layer silicates should not differ greatly from those of ferrous and ferric iron oxides. A 'mixed' silicate structure analogous to the oxide Fe<sub>3</sub>O<sub>4</sub> is conceivable, but no definite intermediate products have been observed during the laboratory oxidation. Since continuous replacement of divalent by trivalent iron in the lattice is possible, the existence of a ferroso-ferric chamosite is largely an artificial consideration. Intermediate states of oxidation, not corresponding to any simple ratio ferrous/ferric have been identified in naturally occurring chamosites, and will be described in a later paper.

The equilibrium diagram of iron and its oxides in relation to temperature and H<sub>2</sub>/H<sub>2</sub>O ratio has been studied by many investigators (Glassstone, 1948; Mellor 1929). The essential features of the system are shown in fig. 3.

The reaction  $\text{Fe}_2\text{O}_3 + \text{H}_2 \rightleftharpoons 2\text{FeO} + \text{H}_2\text{O}$  is reversible and the ratio  $K = p(\text{H}_2)/p(\text{H}_2\text{O})$  determines the relative stability of ferrous and ferric iron.

By passing hydrogen several times through water in a saturator, an equilibrium mixture of hydrogen and water vapour, of known composition, was obtained. With suitable arrangements to prevent premature condensation, the mixture was passed over the ferric chamosite in a tubular electric furnace. By altering the temperature of the saturator

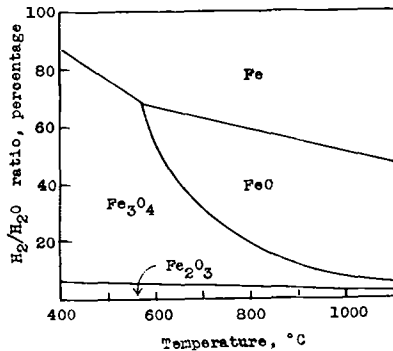


FIG. 3. Equilibrium diagram of iron-iron oxides system in relation to temperature, and H<sub>2</sub>/H<sub>2</sub>O ratio.

the  $H_2/H_2O$  ratio was adjusted to be below the Fe-stable region but above the  $Fe_2O_3$ -stable region. The reaction was rather slow, and the temperature conditions were critical. The optimum temperature was  $460^\circ C.$ , at which temperature ferrous chamosite was present after six hours, together with some lines on the X-ray diagram due to impurities and a heavier background, both presumably due to decomposition by side reactions. The specimen was a light greenish-brown colour, showing that although the original ferrous chamosite was not completely restored, the change had proceeded to a considerable degree.

At lower temperatures little or no reaction occurred, while at higher temperatures the chamosite structure disintegrated and the product corresponded to ferrous aluminate. This indicates both reduction and lattice breakdown either concurrently or consecutively. The same spinel, as will be shown later, occurs when ferrous chamosite is heated in absence of air. The product was greenish in colour, confirming the reduction process.

#### 5. *Thermal decomposition of chamosites.*

In order to obtain a more complete picture of the properties of ferrous and ferric chamosities, they were examined after heating at  $100^\circ C.$  intervals (a) in air or oxygen, (b) in a vacuum, (c) in steam. X-ray photographs were taken at critical temperatures to detect any line in the 14 kX region which is diagnostic of a chlorite structure (Brindley and Ali, 1950), but the bulk of the photographs were taken with the camera set to record reflections from 9 kX downwards. No chlorite structure was observed at any stage, confirming the previous finding of one of us (Brindley, 1951).

Generally any observable reaction was complete in about 2 hours at any particular temperature. The reactions proceeded rapidly during this time and photographs taken after  $\frac{1}{4}$ ,  $\frac{1}{2}$ , and 1 hour showed incomplete reactions, whereas prolonged heating did not produce a substantial difference from the 2-hour heating. At low temperatures, however, 2-hour heating did not always produce complete change. For example, at  $300^\circ C.$ , ferrous chamosite was converted to the ferric form only partially in 2 hours, but prolonged heating caused more reaction to take place.

The original chamosite, roughly purified by sedimentation, and ferric chamosite prepared from it at  $400^\circ C.$  were used for the experiments. The results obtained are represented diagrammatically in fig. 4.

*Heating in air.* -The chamosites pass from or through the ferric stage

to an amorphous state without further change of colour at 450–500° C. Little is visible on the X-ray diagram at this stage except general background scattering, which is to be expected from an amorphous or largely amorphous material.

Recrystallization commences at about 550° C., when some haematite lines appear, together with a small quantity of anhydrous CaSO<sub>4</sub> impurity. The sedimentation processes were carried out in distilled water, showing that the CaSO<sub>4</sub> is a natural trace-mineral and not introduced in

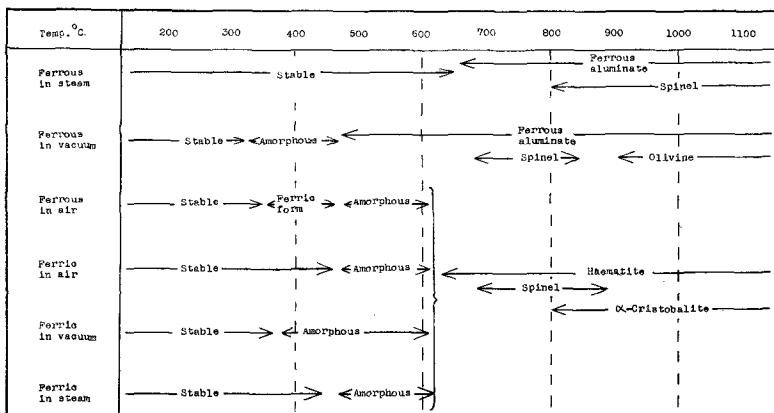
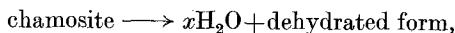


FIG. 4. Heat-treatment of chamosite.

manipulation. The haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) improves in crystallinity up to 1000° C., at which temperature it gives all the expected lines with sharpness. Spinel appears at 800° C. and is present in quantity at 900° C. but no longer at 1100° C. The lines from this spinel correspond to true spinel  $\text{MgAl}_2\text{O}_4$  and not to the spinel-type  $\text{FeAl}_2\text{O}_4$  found in non-oxidizing conditions.

$\alpha$ -Cristobalite appears at 900° C. and is present in quantity at 1100° C. Weak lines visible at 1000° and 1100° C. are probably due to enstatite and mullite.

*Ferrous chamosite in steam and in a vacuum.*—When heated in absence of air, the ferrous form does not oxidize to ferric chamosite. If we consider that the dehydration of layer silicates is, to some extent at least, reversible, then it is to be expected that in a reaction, such as



raising the partial vapour pressure of water surrounding the mineral, should delay the change, while reducing it should accelerate dehydration. This is confirmed by experimental results. The ferrous form is stable up

to 650° C. in steam at 1 atm. pressure, but only to 350° C. in a vacuum. Recrystallization occurs in steam at 675° C., without any amorphous phase intervening, to ferrous aluminate of quite well-developed form (fig. 1, no. 5). Ordinary spinel appears transiently at 800° C., but as the various spinel forms  $\text{MgAl}_2\text{O}_4$  and  $\text{FeAl}_2\text{O}_4$  are capable of solid solution no pure type is likely. The occurrence of lines in the regions 1.42–1.48, 2.00–2.04, and 2.40–2.48 kX is, however, characteristic of all spinels and all materials examined after treatment at these temperatures give lines or bands in these positions.

In a vacuum, ferrous chamosite gives an amorphous product before recrystallization, and the spinel product is less well developed than in steam. Some olivine lines appear at 900–1000° C. after vacuum treatment. The products are all dark green to black in colour.

*Ferric chamosite in steam and vacuum.*—Little difference is observed between the thermal transformations in air, vacuum, and steam. This is to be expected since the ferric form contains only a small amount of water. In vacuum, the amorphous form appears at a rather lower temperature than in air, but the decomposition is not appreciably retarded in steam. Haematite and minor constituents appear as in the treatment in air.

*Heat-treatment of monoclinic chamosite.*—An Ayrshire chamosite found by one of us (Brindley, 1951) to contain 55 % of a monoclinic form of chamosite, the remainder being ortho-hexagonal, was subjected to heat-treatment. At 400° C. a well-crystallized ferric form appeared, identical with that from the ortho-hexagonal ferrous chamosite. The line at 2.40 kX, previously shown to be a good indicator of the monoclinic form, disappeared and additional weak lines at 1.68, 1.88, and 3.28 kX appeared. Possible interpretations are: (i) the bulk of the monoclinic ferrous form passes to the ortho-hexagonal ferric form and the additional lines are impurities due to side-reactions, (ii) the monoclinic form breaks down to a poorly crystallized form yielding only a few weak lines.

#### 6. *Significance of ferrous and ferric forms in chamosite identification.*

The principal findings of sections 1–5 are as follows: (1) Substantially pure ortho-hexagonal chamosite can be obtained free from the monoclinic form. (2) A stable oxidized, largely dehydrated form can be obtained with somewhat smaller unit-cell dimensions but an essentially similar structure. (3) This process implies a 2-stage thermal decomposition not previously observed in a kaolin-type structure. (4) The ferrous-ferric change is to a considerable extent reversible. (5) The breakdown

of ferrous chamosite depends largely on the water-vapour pressure surrounding it as well as on the temperature. (6) A variety of decomposition products can be obtained from the various forms of chamosite. (7) The absence of a chlorite-type chamosite conforms with the previous conclusion.

These findings, combined with those of the previous paper (Brindley, 1951), shed considerable light on many problems arising in connexion with chamosite. Not only can the X-ray diagrams vary with composition and the unit-cell type, but also with the state of oxidation of the mineral. Position and intensity of the lines vary between those of the ferrous and ferric forms, and this provides a further reason for the diversity of X-ray diagrams reported for chamosite. Moreover, the fact that a sample contains little structural water need not rule out the possibility of its being a kaolin-type mineral in the structural sense. This also has a bearing on identification of chamosite by differential thermal analysis. The endothermic peak depends on loss of water from the structure, and this depends in chamosite on the availability of atmospheric oxygen without which the ferric dehydrated form does not occur. Moreover, the ferric form would not be expected to give a prominent endothermic peak, since it is already largely dehydrated. The results obtainable by thermal analysis of chamosite minerals are therefore likely to vary with the design of the apparatus and the particular variety of chamosite which is being tested.

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