THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 24 SEPTEMBER, 1939 No. 9

RANDOM STRUCTURES OF LAYER MINERALS AS ILLUSTRATED BY CRONSTEDITE ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$). POSSIBLE IRON CONTENT OF KAOLIN

STERLING B. HENDRICKS,
Bureau of Chemistry and Soils, Washington, D. C.

Lack of replacement of aluminium in kaolin minerals by magnesium or iron is an extremely important factor in the formation of soil. Aluminium in muscovite can be replaced by magnesium and iron forming phlogopite and biotite. The iron present in micas and other ferro-magnesian minerals is expelled as oxides or hydrous oxides when weathering to kaolin takes place. Montmorillonite, nontronite and related minerals, on the other hand, which are more closely similar to micas than are the kaolin minerals, can retain iron as weathering proceeds.

The maximum amount of iron in the fourteen samples of kaolinite and anauxite described by Ross and Kerr[1] is 2.00 per cent Fe_2O_3 and only two of the samples, both of which were anauxites, contained more than 1.5 per cent Fe_2O_3. This corresponds to a maximum substitution of 4 per cent of Al^{+++} by Fe^{+++}. Thirteen analyses of halloysite,[2] six of dickite, and three of nacrite showed a maximum of 0.64 per cent Fe_2O_3 which corresponds to replacement of 1.00 per cent of Al^{+++} by Fe^{+++}. The magnesium content of these samples is also very low, not exceeding 0.35 per cent in unquestionable material.

Pauling[3] has shown that the structures of the kaolin minerals and chlorites are closely related to those of the micas. The four kaolin minerals, kaolinite, halloysite, nacrite and dickite, represent alternative methods of stacking aluminium-silicate layers having the composition $(OH)_4Al_2Si_2O_5$. Factors contributing to the polymorphism of these minerals have been discussed elsewhere.[4] Pauling stated, "The non-existence of a magnesium analog of kaolinite is accounted for by the large value

---

[1] Ross, C. S., and Kerr, P. F., The kaolin minerals: *Prof. Paper* **165E**, *U. S. Geological Survey* (1930).

[2] Ross, C. S., and Kerr, P. F., Halloysite and allophane: *Prof. Paper* **185G**, *U. S. Geological Survey* (1934–35).

[3] Pauling, L., *Proc. Nat. Acad. Sci.*, **16**, 578 (1930).

[4] Hendricks, S. B., *Zeits. Krist.* (In press).

of the fundamental translations in the brucite layer, which would cause the kaolin layer to curve." This statement would also be expected to hold for an iron analog of kaolinite.

Both the iron-bearing minerals, cronstedite and faratsihite, have been considered as related to the kaolins. The following work is a further study of these minerals, the former of which is particularly interesting because of the continuous scattering of *x*-radiation from some crystal zones.

THE CRYSTAL STRUCTURE OF CRONSTEDITE

Cronstedite is usually classified as a chlorite and is variously described as monoclinic or trigonal pyramidal. Commonly developed forms are: {00.1}, {10.2}, {20.1}, and {30.1}, referred to hexagonal axes.[5] Gossner[6] has studied the crystal structure of cronstedite from Kisbanya, Hungary. The analysis and succession of atomic layers parallel to the perfect cleavage, according to Gossner, are:

			Succession of layers
SiO_2	16.42%	2.00 mols.	6, O
Al_2O_3	0.90	0.06	2, Si and 2, Fe'''
Fe_2O_3	29.72	1.36	4, O and 2, OH
FeO	41.86	4.26	2, Fe''' and 4, Fe''
CaO	1.32	0.17	6, OH
H_2O	10.17	4.12	

The structure as given by Gossner is isomorphous with point group C_s-m, and is related to that of kaolin. Dimensions of the unit of structure are $a_0=5.48$Å, $b_0=9.49$Å, $c_0=7.09$Å, and $\beta=90°$. Gossner's conclusion that iron is present in tetrahedral coordination is verified, but other details of the structure require revision.

EXPERIMENTAL RESULTS

Work was greatly facilitated by use of splendid crystals of cronstedite from the Roebling and Canfield collections made available by Dr. W. F. Foshag of the U. S. National Museum. These included a specimen, number R 7807, from Kisbanya, that was closely similar to the one described by Gossner. Crystals more suited for *x*-ray work were obtained from specimen R 4550, Kuttenberg, Bohemia, and C 3733, Cornwall. The former contained thin trigonal plates similar to those from Kisbanya, but much less distorted. Crystals from the Cornwall specimen were elongated parallel to the *c* axis and were suitable for photographs taken with rotation about that axis.

Laue photographs taken with the *x*-ray beam normal to {00.1} of crystals from Kuttenberg had the symmetry of the point group $D_{3d}-\bar{3}m$.

---

[5] Dana, E. S., *A System of Mineralogy*, New York 656 (**1914**).

[6] Gossner, B., *Centralblatt. Mineral.*, 195 (**1935A**).

A number of continuous radial streaks were present in addition to a pattern of intense normal reflections. Gossner has stated that a Laue photograph of a crystal from Kisbanya showed monoclinic symmetry, but was badly distorted. Crystals from specimen R 7807 gave photographs that were too distorted to permit determination of symmetry.

Rotating crystal and equatorial and layer line x-ray goniometer photographs of cronstedite were taken with FeK and MoK radiation with rotation about the c axis and the normals to $\{10.0\}$ and $\{01.0\}$. All the photographs agreed with apparent trigonal symmetry, the $\{10.0\}$ normals being equivalent. Lattice dimensions obtained from these photographs and from measurements of the cleavage spacing against β Al_2O_3 as reference are:

$$a_0 = 5.48\text{Å} \qquad c_0 = 21.25\text{Å}$$

The corresponding monoclinic or orthohexagonal unit of structure has $a_0 = 5.48\text{Å}$, $b_0 = 9.49\text{Å}$, $c_0 = 21.25\text{Å}$, and $\beta = 90°$, c_0 being three times as great as Gossner's value.

STRUCTURE DETERMINATION

The Kisbanya material according to Gossner's analysis corresponds rather closely to

$$(Fe''', Al''')_{.84}(Fe'', Ca'')_{4.43}(Fe_2'''Si_2'''')O_{6.4}(OH)_{11.6}$$

the amount of water being somewhat high. This can be idealized for structural purposes as

$$(Fe''', Fe'', Al''', Ca'')_{4-6}(Fe_2'''Si_2'''')O_8(OH)_{10}$$

which is comparable with the composition of a layer in the unit of structure of a kaolin mineral, $Al_4Si_4O_{10}(OH)_8$, and a hypothetical kaolin mineral, $Fe_6Si_4O_{10}(OH)_8$. Moreover, the calculated molecular weight in a layer of the monoclinic unit of structure is 740, which, in view of the complexity of the mineral, is in agreement with 770, the value determined from the density (3.445, Gossner) and lattice dimensions.

The probable atomic arrangement in a layer of the cronstedite lattice is shown in Fig. 2 as a projection on (001) of Gossner's monoclinic unit of structure. Ferric iron is hardly to be considered as merely replacing silicon in tetrahedral coordination but only does so with accompanying separation of surrounding oxygen ions as is shown by the increase in a_0 and b_0. It is further improbable that silicon and iron randomly fill a set of positions with tetrahedral coordination; rather ferric ions fill just half of the positions. The hydroxyl content can be increased above that of kaolin if each oxygen ion of a tetrahedron about ferric iron that is not shared between two tetrahedra is changed to hydroxyl in cronstedite.

Relative intensities for $\{00l\}$ reflections were calculated for a kaolin-like structure of cronstedite with parameter values as shown in Fig. 2. These are compared with the observed values in Table 1 and it is perhaps evident that the agreement is very satisfactory.

Table 1. Observed and Calculated Relative Intensities for Some Reflections from Cronstedite—MoKα Radiation, Pseudo-hexagonal Indices ($a_0=3.18$Å, $c_0=21.25$Å) of the Rhombohedral Lattice

$\{00.l\}$		$\{30.l\}$ $\{\bar{3}0.l\}$	$\{10.l\}$		$\{\bar{2}0.l\}$	$\{40.l\}$	$\{\bar{1}0.l\}$		$\{20.l\}$	$\{50.l\}$
l			l				l			
0		ms 80	2	vw 10	vw 8	vw 1	1	s 190	ms 110	vw 6
3	vs 820	mw 13	5	s 260	m 40	w 16	4	vs 510	s 130	w− 9
6	vs 670	mw 20	8	ms 60	vw 3	vw 2	7	vs 210	ms 60	vw 3
9	s 100	w+ 13	11	s 170	m 40	w 13	10	vs 350	s 100	w− 10
12	m 30	vw 3	14	s 150	mw 30	w 14	13	m 19	mw 9	
15	s 100	mw 30	17	mw 24	w 8	vw 4	16	m 60	mw+ 20	
18	m 60	w 13	20	m 50	w+ 18	vw 7	19	mw 22	mw 17	
21	m 45	mw− 17	23	a 0			22	vw 6	vw 2	
24	m 40	w 9	26	w 20			25	m 50	mw 27	
27	a 3		29	w 12			28	w 7	w 10	
30	w 15		32	a 9						
33	a 7		35	vw 12						
36	a 4									
39	w 14									

The diffraction patterns of cronstedite can be referred to an ortho-hexagonal unit of structure (O.H) having $a_0=5.48$Å, $b_0=\sqrt{3a_0}$, and $c_0=3\times 7.083=21.25$Å. Continuous scattering is present along lines connecting $\{h_ak_bl\}$, $k\neq n\times 3$, reflections. Thus on the photograph reproduced in Fig. 1 the $\{11l\}$, $\{15l\}$, and $\{17l\}$ reflections are very weak (note Table V) and are connected within a group by continuous scattering. The $\{13l\}$ and $\{19l\}$ reflections are very intense and are not accompanied by general scattering.

Reflections for which the k index is a multiple of three, although varying in intensity, are very strong on the average. They can all be referred to a rhombohedral lattice having $a_0 = 3.16$Å and $c_0 = 21.25$Å as hexagonal translations (H). The transformations from orthohexagonal (O.H) to hexagonal (H) indices are

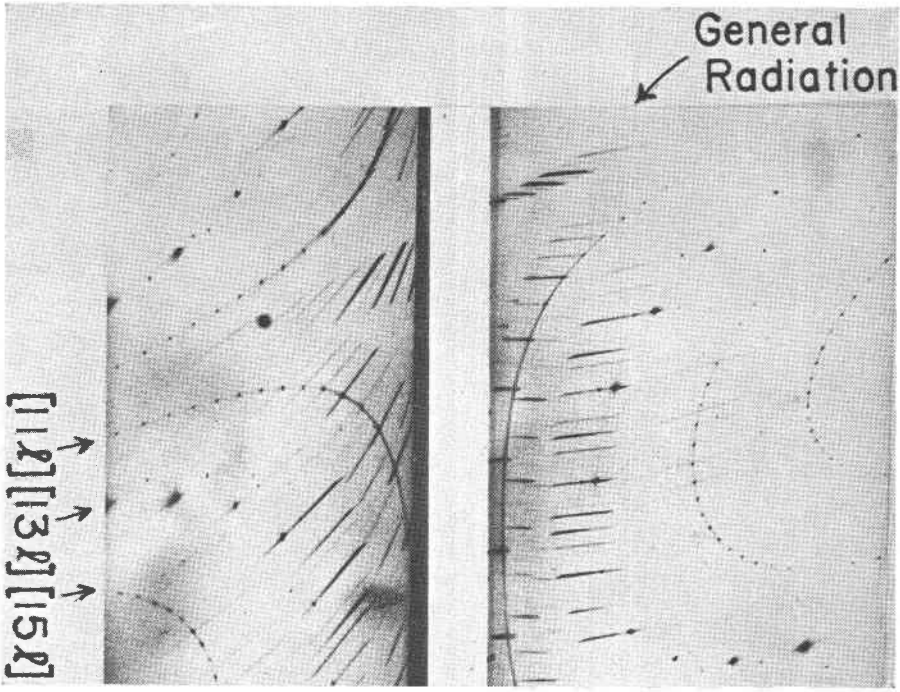

FIG. 1. Weissenberg x-ray goniometer photograph of the first layer line with rotation about the orthohexagonal a axis of cronstedite. Continuous streaks crossing lines connecting $\{h_a k_a l\}$ reflections are due to general radiation present with FeKα.

$$H = \frac{h-k}{2}(\text{O.H}) \quad L = l(\text{O.H}) \quad K = k(\text{O.H}).$$

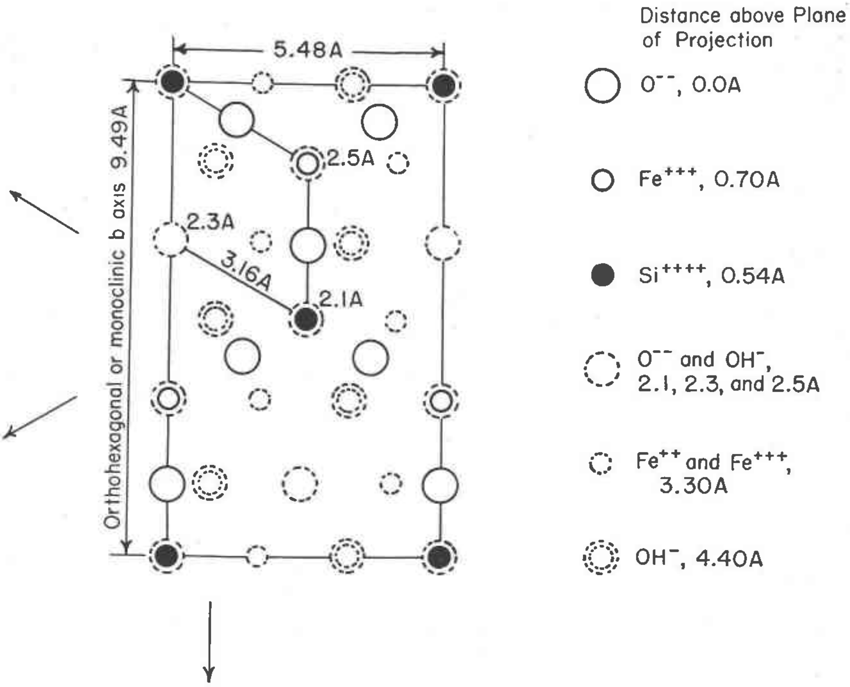

FIG. 2. The atomic arrangement in cronstedite shown in projection on {001}. The three arrows indicate the directions of the random translation in the lattice.

The cell is shown on the projection in Fig. 2. Observed intensities as listed in Table 1 are in close agreement with values calculated according to the following average arrangement given by space group C_3^4-R3:

Number	Atom	x	y	z
3	$\frac{Si+Fe}{3}$	0	0	.03
3	.9 Fe	0	0	.83
3	$\frac{O+2OH}{3}$	0	0	.11
3	OH	0	0	.54
9	$\frac{O}{6}$	½	0	0
9	$\frac{O}{6}$	0	½	0

Similarly good agreement between calculated and observed intensities was obtained for {13*l*}, {19*l*}, and {06*l*} (O.H) reflections.

TABLE 2. OBSERVED INTENSITIES OF $\{0kl\}_{\text{O.H.}}$ REFLECTIONS OF CRONSTEDITE—FeKα RADIATION

l/k	0	2	4	6	8
0	over exposed	w+	w	over exposed	present but very weak
1		−			
2		+			
3		+			
4		−	+		
5		+	−		
6		+	+		
7		−	+		
8		+	−		
9		+	+		
10		−	+		
11		−	−		
12		−	+		
13		−	+		
14		+	+		
15		−	+		

NOTE: In order to bring out $\{0kl\}$ with k not a multiple of 6, it was necessary to strongly over expose $\{0kl\}$, $k=n\times 6$.

It would seem, therefore, that the structure is correctly represented by the averaged arrangement. Nevertheless it is still probable that the atomic positions in any one layer are those leading to the structure shown in Fig. 2. The averaged structure apparently results from a random shift of $nb_{\text{O.H}}1/3$ along the b axis of one layer with respect to another, the layers otherwise being stacked with trigonal symmetry. These random shifts correspond to the separation of the hydroxyl groups within a layer and are without effect on the relative positions of the hydroxyl groups in the top of one layer and the oxygen ions in the bottom of the adjacent layer.

Increased lattice dimensions as compared with the kaolin minerals which result from the presence of ferric iron with tetrahedral coordination permits almost complete filling of octahedral coordination positions by Fe^{+++}, Fe^{++}, Ca^{++}, Al^{+++}. Since practically all of these positions are filled, the coordination figures become more closely equivalent and the entire structure becomes more symmetrical. As a result of this regularity the layers can be stacked in a less ordered manner than is the case for nacrite where the individual layers are somewhat distorted from the ideal arrangement. The same condition is beautifully shown in the polymorphism of the micas.[7]

---

[7] Hendricks, S. B., *Nature*, **143**, 800 (1939).

Diffuse scattering in cronstedite is restricted to those zones having constant h and k indices with variable l index, the k index not being a multiple of three. There is thus an immediate and necessary connection with the random structure that leads to the pseudo unit of structure. Unordered translations of various layers by $nb_0/3$ would not alter the atomic arrangements relative to planes having $k=n\times 3$. Such reflections, therefore, should be sharp as they are observed to be. In other zones, however, the indefinite sequence of layers would give an indefinite sequence of atomic positions which would necessarily lead to diffuse scattering in those zones. In a crude way this is equivalent to variation in the length of the c axis by integral multiples of a fundamental spacing.

While scattering along lines connecting $\{h_ak_al\}k_a\neq n\times 3$, reflections is continuous from cronstedite crystals, normal narrow reflections are present which, though very weak in comparison with $\{h_ak_al\}k=n\times 3$ reflections as a class, are more intense than the neighboring continuous scattering. Pseudo-rhombohedral indices cannot be assigned to these reflections. They indicate that the structure is not entirely random throughout but is regular in a very small fraction of a crystal.

Dickite,[8] pyrophyllite,[9] and talc[9] all have random structures similar in type to that of cronstedite but their crystals show little or none of the diffuse scattering along lines connecting $\{h_ak_al\}$, $k_a\neq n\times 3$, reflections. A partial explanation for this is that the several structures vary in randomness. Dickite, pyrophyllite and talc crystals probably have large regions of order in which the sequence of layers is that required by a monoclinic space group, separated by not necessarily more than a single layer with some other shift of $nb_0/3$. This type of structure would prevent calculation of intensities for $\{hkl\}k\neq n\times 3$ reflections, but would not lead to observable continuous scattering. As the number of random layers increases the intensity of the diffuse scattering should increase in the neighborhood of the normal reflections and should depend in intensity upon them. Cronstedite thus is an extreme case.

Similar diffuse scattering has been observed for micas, vermiculites, chlorites and stilpnomelanes in all of which random structures are developed to various extents.

THE NATURE OF FARATSIHITE AND POSSIBLE IRON CONTENT OF KAOLINS

Lacroix,[10] who originally described faratsihite, considered it to be a kaolin in which part of the aluminum had been replaced by iron. The

---

[8] Hendricks, S. B., *Am. Mineral.*, **23**, 295 (1938).

[9] Hendricks, S. B., *Zeits. Krist.*, **76**, 211 (1930).

[10] Lacroix, M. A., *Bull. Soc. France de Mineral*, **37**, 231 (1914).

mineral has recently been studied by Gruner[11] and he has decided that it is strictly a nontronite; that is, a single layer in the lattice is formed of two $(Si_2O_5)_n^{--}$ sheets jointed by octahedral coordination about iron.

A number of *x*-ray and electron diffraction patterns were made from a sample of Lacroix's original faratsihite obtained from Dr. C. S. Ross of the U. S. Geological Survey. Ordinary *x*-ray powder diffraction data were essentially in agreement with those listed by Gruner. The important features of these data for present arguments are:

Spacing of reflection	Intensity
13.9Å	6
7.1	indistinct
4.87	0.5
4.44	3
3.54	2
1.519	2
1.481	2

Samples of faratsihite oriented by settling from suspensions in water and examined after the method of Bradley, Grim and Clark[12] showed greatly enhanced intensities of reflections for the 13.9, 7.1, 4.87, and 3.54Å lines. In particular the 4.87Å reflection in such photographs was more intense than the one at 4.44Å. It would seem, therefore, that these four lines must be $\{00l\}$ reflections of micaceous minerals. However, at least two minerals must be present since the lines do not form a regular sequence of orders.

Gruner really had considerable evidence that both faratsihite and nontronite from White Oak Creek near Bakersville, N. C., were mixtures of two minerals, one related to montmorillonite, the other to kaolinite. Thus the 13.9Å reflection of faratsihite disappeared upon heating to 300° while that at 7.1Å was unaffected. Moreover, the 1.481Å reflection is in the position required for one of the strongest lines of the kaolin pattern, and while it is present for the above two minerals, it is absent for a number of other nontronites that also failed to give reflections near 7.0Å. The reflection at 13+Å for these other nontronites was shifted to 9.5–10Å upon heating to 300°.

Differential heating curves as reproduced in Fig. 3 also clearly indicate that faratsihite is a mixture containing a large amount of a kaolin mineral. The essential feature of the nontronite curve shown by faratsihite is an absorption of heat, influenced by the relative humidity, in the region 150–200°. The prominent heat absorption near 600° is a characteristic feature of kaolins, accompanying their loss of water of composition.

---

[11] Gruner, J. W., *Am. Mineral.*, **20**, 475 (1935).

[12] Clark, G. L., Grim, R. E., and Bradley, W. F., *Zeits. Krist.*, **93**, 307 (1938).

Absence of the same type of exothermic reaction in faratsihite, as shown by kaolinite above 900° and a kaolinite-nontronite mixture, is not unexpected, since the recrystallization of the amorphous Al_2O_3 is greatly influenced by other components of an intimate mixture. The small endothermic reaction near 300° is in the region in which goethite loses water. However, treatment with nascent H_2S after the method of Truog and his associates, which was kindly carried out by Dr. L. T. Alexander of the Bureau of Plant Industry, indicated that no free oxides or hydrous oxides of iron were present.

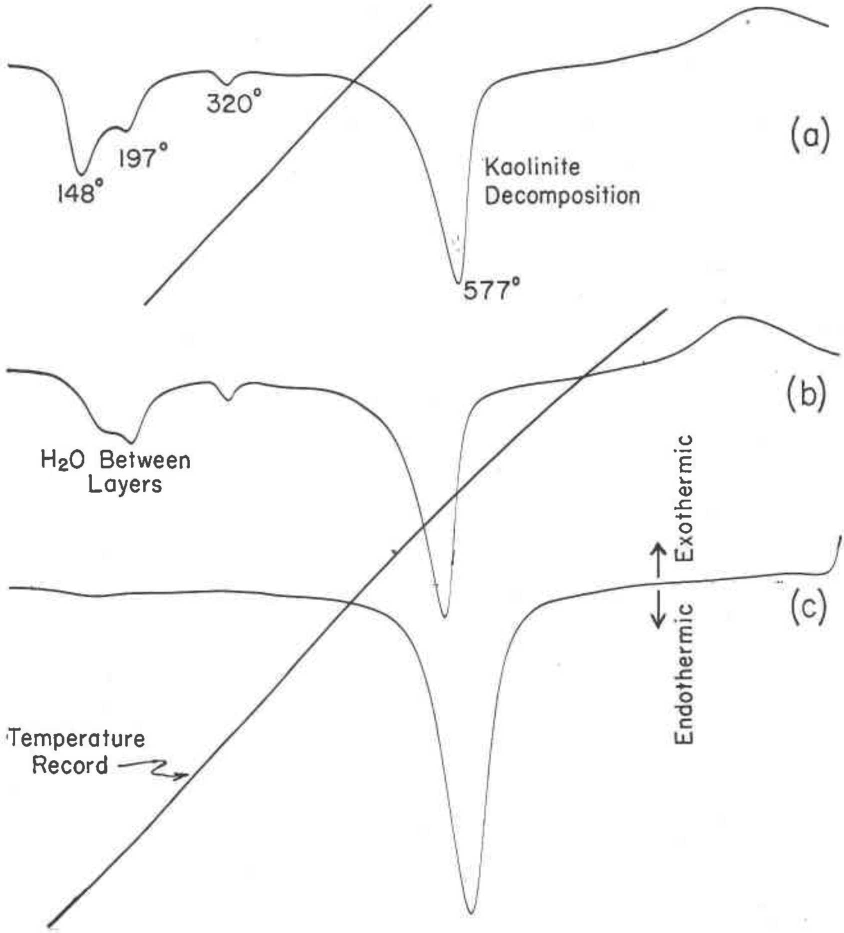

FIG. 3. Differential heating curves of (*a*) faratsihite, 75% relative humidity, sample weight 0.50 g. (*b*) faratsihite, 50% relative humidity, sample weight 0.44 g. (*c*) kaolinite, 50% relative humidity, sample weight 0.36 g.

Despite this confusing situation, it does not seem probable that the kaolin mineral in the mixture contains any appreciable amount of iron. The chief evidence for this is that diffraction patterns of faratsihite have reflections in the expected positions for ordinary kaolinite.

RAOUL'S ANALYSIS OF LACROIX'S MATERIAL[10]:

SiO_2	41.60%	0.692 mols.
Al_2O_3	22.68	.222
Fe_2O_3	15.22	.095
FeO	0.54	.007
MgO	0.11	.003
CaO	0.60	.011
Na_2O	0.16	.002
K_2O	0.22	.002
TiO_2	0.13	
P_2O_5	0.21	
H_2O at 150°	5.71	
H_2O at red heat	13.02	

The amount of water lost above 150° considerably exceeds that expected for nontronite and approaches that required for kaolin. If the $Al_2O_3:SiO_2$ ratio of the kaolin present is assumed to be 1.7:1 then the ratio $(Fe_2O_3 + \frac{2}{3}FeO):SiO_2$ is 3.14:1, which is well within the possible range of nontronite. The sample would contain about 60 per cent kaolin and this is in approximate agreement with the heating curves which suggest 50 per cent.

Since the kaolin and nontronite present in the mineral faratsihite apparently grew together from solution, it would seem that conditions might have been favorable for formation of an iron-bearing kaolin. Its absence thus would suggest that such a compound is quite unstable as also is indicated by the particular structure of cronstedite.

SUMMARY

The mineral cronstedite ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$) is formed of kaolin-like layers containing ferric ions with tetrahedral and octahedral coordination of surrounding oxygen and hydroxyl ions. These layers are superimposed with a random mixing of three possible structures which results in diffuse reflections along lines connecting $\{h_a k_a l\}$ reflections for which k_a is not a multiple of three. Although cronstedite is related to kaolinite ($Al_2O_3 \cdot SiO_2 \cdot 2H_2O$) in structure it is improbable that the kaolinite lattice will accommodate appreciable amounts of iron in solid solution. The mineral faratsihite is shown to be a mixture of nontronite and an ordinary kaolin mineral.

✓