

*Clay minerals and bauxitic minerals. A review and classification based on a statistical method.*

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### I. INTRODUCTION.

THE hydro-aluminous silicates form a well-defined natural group of minerals commonly known as clay minerals. According to their chemical composition they cover a wide range varying from substances rich in alumina, and thus approaching the bauxite group, to substances rich in silica. They vary greatly in their water content, and contain other constituents in addition to water, alumina, and silica—so-called impurities. Clay minerals always occur in the form of fine aggregates usually composed of minute crystals with a perfect basal cleavage, often ultra-microscopic in size (colloform and colloidal).

The absence of well-defined crystals of appreciable size makes the mineralogical and chemical investigations extremely difficult, since the separation of pure material is often impossible. The majority of published chemical analyses show a 'bulk' composition, i.e. composition of a mixture including the impurities. But the impurities cannot altogether be ignored, since they may throw some light on the nature of parent minerals or the composition of the intermediate products.

As to the nomenclature of these minerals, especially those belonging to the clay mineral group, we find ourselves in a maze of names, most of them quite obsolete and often applied to mixtures and not to definite stoichiometric compounds. Unfortunately the number of names seems to increase from year to year, thus introducing additional complications to the understanding of these minerals.

An attempt to classify clay minerals on a triangular diagram has been made by E. T. Wherry,<sup>1</sup> but only theoretical formulae of these minerals were used. As minerals of the clay and bauxite groups show such a great variation in composition and are difficult to study in a purified form, the present writer has decided to apply statistical methods to their study. The degree of accuracy and reliability of any statistical study depends on the following conditions: (1) the accuracy of the primary data, (2) the number of cases, and (3) the number of variables.

With the object of procuring as many cases as possible, it was decided to include all analyses in which the amount of clay constituents ( $H_2O$ ,  $Al_2O_3$ ,  $SiO_2$ ) was sufficiently high to guarantee that the greater part of the substance analysed was composed of hydrous aluminium silicate. To introduce a hypercritical attitude as to the quality of the material and the analysis would reduce the number of available analyses to a very small figure. Certainly the initial inaccuracy of the data is by no means removed by statistical computation, but provided that sufficient data are given, statistical methods may bring out, in the form of a significant distribution, many characters implicit in individual data. Persistent errors, if asymmetrical, can, in many cases, be traced by statistical methods, while distributive or symmetrical errors will only produce a wider deviation of distribution. Selection of primary data is even more dangerous than errors introduced through indiscriminate collection of them. For this reason a great number of analyses have been collected from all available sources, far too numerous to be quoted in this paper.

As already mentioned, the question of 'impurities' is rather important. The 'impurities' may be as follows: (1) mechanical admixtures of minerals other than the one presumed to have been isolated for analysis, (2) adsorbed substances, and (3) substances in chemical combination with a given mineral. As it is quite impossible to ascertain their nature and distribution, it has been decided to reject from the analyses all oxides, other than  $H_2O$ ,  $Al_2O_3$ , and  $SiO_2$ ,

<sup>1</sup> E. T. Wherry, *Amer. Min.*, 1925, vol. 10, p. 140.

and to recalculate these latter oxides to 100%. In order to find the true ratios of these oxides in the pure clay mineral, it is clear that one should also remove from the analysis any silica, alumina, and water which was in combination in the impurities. But there is no evidence which would enable one to do this; the correction would be small, and the errors introduced by its neglect would probably be of distributive nature.

All analyses showing less than 10% of impurities have been included. Analyses which showed a marked divergence from the total 100% were rejected. The calculated frequency curve for 'totals' shows a typical symmetrical modal distribution curve about 100%. The mean difference between the average total and the average sum of clay constituents, i.e. the average of impurities is about 5%. The total number of analyses included is as follows:

for $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system	. . .	689
for $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ system	. . .	320

All analyses, after being recalculated in terms of the principal variable constituents (calculated to 100%), have been plotted on triangular diagrams. As the variables have been thus reduced to a small number (three) it is easy to trace the relationships between different minerals. The plotting on the triangular diagrams show three characteristic forms of distribution: (1) clusters, (2) trend lines, and (3) disperse fields. These forms of distribution can easily be observed in the two triangular diagrams presented in this paper (figs. 1 and 7).

The molecular ratios between the three principal constituents were used in the construction of frequency curves. For a clay mineral we have the formula  $m\text{H}_2\text{O}.n\text{Al}_2\text{O}_3.p\text{SiO}_2$ , in which the three ratios are  $m:n$ ,  $p:n$ , and  $m:p$ . Taking  $m:n = h$  and  $p:n = s$ , we get  $h\text{H}_2\text{O}. \text{Al}_2\text{O}_3.s\text{SiO}_2$ . For the minerals of the bauxite group only one ratio  $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$  has been used.

## II. CLAY MINERALS.

The analyses of these minerals are plotted on the triangular diagram  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (fig. 1). The diagram representing lines of constant ratios and the position of minerals is shown in fig. 2, and the frequency diagrams in figs. 3, 5, and 6. Besides the clay minerals the triangular diagram includes a few minerals belonging to the group of opals and some hydrated products of sillimanite,

andalusite, &c. The ratio  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ( $s$ ) is used as a basis of classification and the minerals are classified in broad groups according to this ratio, while their precise position in the field is determined by the ratio  $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$  ( $h$ ).

1. *Fuller's earth group* ( $s$  from 4.5 to 9).

All members of this group are colloidal or colloform clay-like minerals of highly variable composition. This especially is shown in their water content, which in its greater part is colloiddally adsorbed water. Many of them also possess a high degree of adsorption for dyes and fats. When dry they adhere to the tongue.

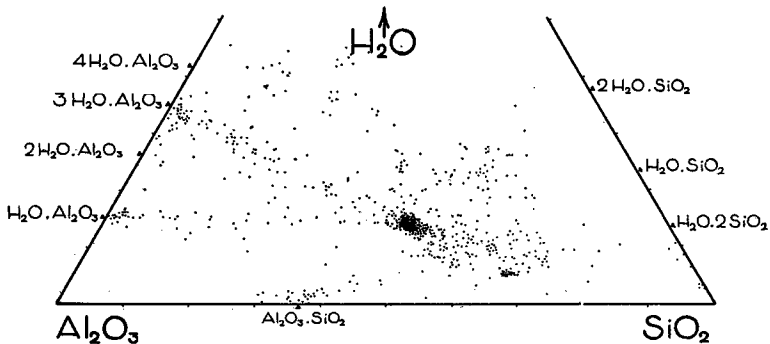


FIG. 1. The analyses of clay and bauxitic minerals plotted on the triangular diagram  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .

Besides the normal clay constituents, many of these minerals contain a certain proportion of alkalis and alkaline earths. These may be part of the mineral molecule or adsorbed material. In this respect they present an analogy to the zeolites. Owing to these loosely bound alkalis some of the fuller's earths (e.g. the so-called 'kil' in the Crimea) can be used as a substitute for soap.

Members of this group, containing considerable amounts of  $\text{R}_2\text{O}$  and  $\text{RO}$  oxides, cannot, strictly speaking, be classed with the clay minerals, if we define them as pure hydrous aluminium silicates. On the other hand, some 'bulk' analyses of bentonitic clays show the ratios  $s$  and  $h$  high enough ( $h = 9.9$ ,  $s = 7.25$ ) to place them in this division. Bentonites are also characterized by high adsorptive properties. Saponite is definitely excluded from this group. It belongs to the group of chlorites, although some saponites with a lower  $\text{MgO}$

content may form intermediate members connecting the chlorite group with that of fuller's earth.

Looking at the distribution of dots on the triangular diagram, one sees no evidence for the existence of any stoicheiometric compounds. Even if they do exist they are probably masked by the total effect of colloidal mixtures. The estimation of water is a difficult problem and very few analyses give a satisfactory answer as to its nature. Some minerals such as termierite were given formulae from the analysis of samples saturated with water ( $18\text{H}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ ).

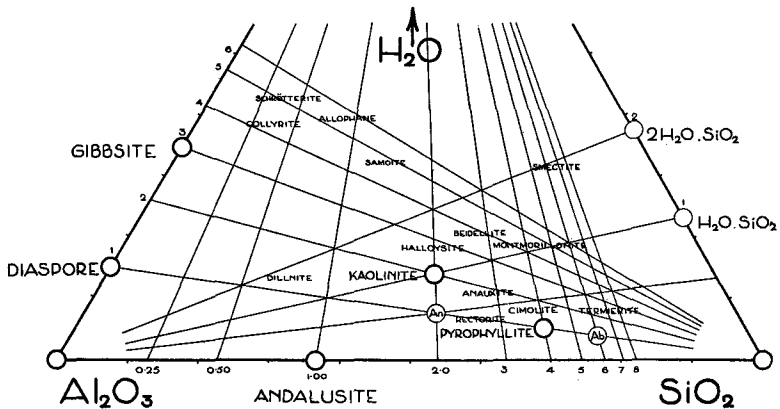


FIG. 2. The triangular diagram  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  with lines of equal ratios and mineral names. [An and Ab the aluminosilicic acids corresponding to anorthite and albite.]

By recalculating analyses in terms of three components we can represent them on the triangular diagram and draw a generalized scheme of their distribution; we must remember, however, that the names do not necessarily refer to definite chemical compounds, but more often to mixtures. According to the decreasing average ratio  $h$ , the minerals of this group can be arranged in the following way:

Malthacite	...	...	$h = 19$	(probably saturated sample)
Smectite	...	...	$h = 12$	
Ehrenbergite	...	...	$h = 6.5$	
Termierite	...	...	$h = 2.5$	(dried at $110^\circ\text{C}$ .)

It is quite possible that if these substances were analysed by uniform methods and the water given out at different temperatures accurately determined, their classification would be altogether different.

### 2. *Pyrophyllite group* ( $s$ from 3.5 to 4.5).

In this group we find a definite small cluster on the triangular diagram and significant modal peaks on frequency curves (figs. 1, 3, 5, 6), where we find  $h = 1$  (masked by the mode of diaspore) and  $s = 4$ . This, in conjunction with the mineralogical evidence, proves that the substance of composition  $H_2O \cdot Al_2O_3 \cdot 4SiO_2$  (pyrophyllite) is a definite crystalline compound.

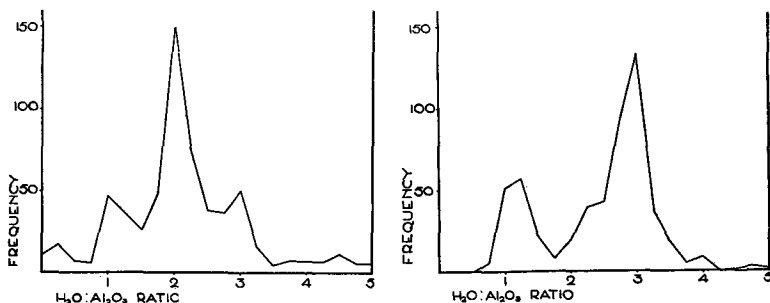


FIG. 3. The frequency diagram for  $H_2O : Al_2O_3$  ratio in clay minerals. Modes: 0.25 small, probably accidental; 1.00 medium, aluminium monohydrate and pyrophyllite superimposed; 2.00 kaolinite; 3.00 medium, aluminium trihydrate.

FIG. 4. The frequency diagram  $H_2O : Al_2O_3$  ratio in bauxitic minerals. Modes: 1.25 (1.00) aluminium monohydrate; 3.00 aluminium trihydrate.

Pyrophyllite was first described by R. Hermann<sup>1</sup> from the Ural Mts., but, as shown by F. Loewinson-Lessing,<sup>2</sup> the original analysis of Hermann was made, not of a pure sample of pyrophyllite, but of a mixture of pyrophyllite and the so-called pseudopyrophyllite ( $8H_2O \cdot 3RO \cdot 4Al_2O_3 \cdot 9SiO_2$ , where R is mainly Mg with a little Ca and Fe). According to Loewinson-Lessing pyrophyllite crystallizes in the orthorhombic system. It occurs as compact masses composed of minute flakes or fibres and also as a constituent mineral of shales and crystalline schists. It has a pearly lustre and white colour, but some varieties have a greenish tinge. Apparently it is widely distributed in nature. Several good analyses correspond closely to its theoretical formula. Pyrophyllite has been synthesized in an autoclave on several occasions.<sup>3</sup> A number of minerals described under

<sup>1</sup> R. Hermann, Ann. Phys. Chem. (Poggendorff), 1829, vol. 15, p. 592.

<sup>2</sup> F. Loewinson-Lessing, Journ. Russ. Min. Soc., 1895, vol. 33, p. 283.

<sup>3</sup> E. Baur, Zeits. Physikal. Chem., 1903, vol. 42, p. 567; and Zeits. Anorg. Chem., 1911, vol. 72, p. 119. M. Schlaepfer and P. Niggli, Zeits. Anorg. Chem., 1914, vol. 87, p. 52.

various names such as agalmatolite, pagodite, pyrauxite, gümbelite, westanite, biharite, neurolite, restormelite, &c., are substances more or less similar to pyrophyllite and apparently only differ in the state of aggregation and the presence of impurities.

Referring again to the triangular diagram, we see above the cluster of pyrophyllite an aureole of dots. They correspond to the analyses of various clay substances either amorphous or microcrystalline. The nearest region to pyrophyllite is occupied by the

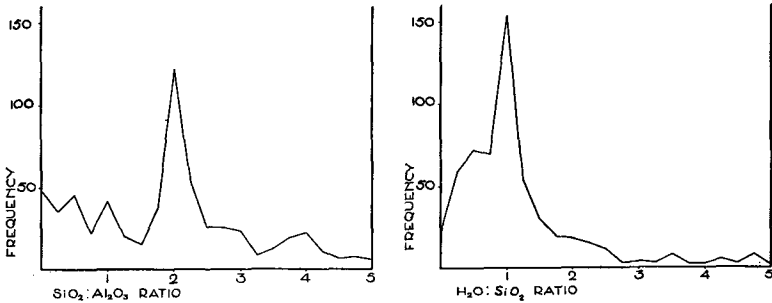


FIG. 5. The frequency diagram for SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio in clay minerals. Modes: 0.00 medium, bauxitic minerals; 0.50 medium, schrotterite, collyrite (?); 1.00 medium, allophane; 2.00 large, kaolinite; 2 to 3 slope, probably mixture of kaolinite and anauxite; 4.00 small, pyrophyllite.

FIG. 6. The frequency diagram for H<sub>2</sub>O:SiO<sub>2</sub> ratio for clay minerals. Modes: 1.00 large, kaolinite; the interval between 0.00 and 1.00 corresponds to a very dense disperse field of minerals of the region situated between pyrophyllite and kaolinite and the pyrophyllite ratio (0.25) is obscured; the mode of 0.50 is probably accidental; 1.00 to 3.00 slope, disperse field of minerals

mineral called cimolite (including pelicanite, hunterite, keffekil, sphragidite, &c.). The *s*-ratio for these substances varies round about 4, and the *h*-ratio between 1 and 4, so that some of them can be considered to represent either hydrated pyrophyllite or pyrophyllite aggregates with adsorbed water.

The cimolite field passes imperceptibly upwards into the field of montmorillonite. Substances named montmorillonite, as well as others named confolensite, delanouite, stolpenite, erinite, severite, &c., show a great variety of composition (*h*-ratio varies from 2.4 to 7.4, *s*-ratio from 2.8 to 5.6). Nearly all analyses, however, fail to differentiate water given above and below 105° C., and as these minerals usually occur in aggregates of fine flakes or colloform

masses, the amount of adsorbed water must be considerable (in analyses where this determination was carried out, water below 105°C is usually half of the total water). In addition many minerals of this group contain a certain amount of RO and R<sub>2</sub>O oxides. C. S. Ross and E. V. Shannon,<sup>1</sup> working on purified material derived from bentonitic clays, found the micaceous montmorillonite to approach in composition the theoretical formula 8H<sub>2</sub>O.(Mg,Ca)O.Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub>. As all the water of the analyses is included, this formula does not strictly speaking represent the composition of the crystalline phase. Excluding CaO and MgO, F. Heide<sup>2</sup> gave the theoretical formula of montmorillonite as 6H<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>. The same author found that montmorillonite has an X-ray spectrum similar to that of kaolinite. He suggested, therefore, that montmorillonite is not a distinct mineral, but a disperse system of silica hydrogels in a skeletal kaolinite lattice.

Considering the wide range of variation of analyses, the uncertain nature of constitutional water, and the absence of clusters on the triangular diagram, it is rather difficult to assign to montmorillonite a definite formula, but the following generalized formula may express its composition:  $h\text{H}_2\text{O}.r\text{RO}.Al_2\text{O}_3.s\text{SiO}_2.aq$ , where  $h$  varies from 2 to 4,  $r$  is usually about 1,  $s$  varies from 3 to 6 (higher values for  $s$  place the mineral in the group of fuller's earth, while values approaching 3 bring it into the field of beidellite).

So expressed, montmorillonite does not strictly speaking belong to the pure hydrous aluminium silicates. The dots on the triangular diagram are in this sense ambiguous, first because both constitutional and adsorbed water were included, secondly because of the presence of RO oxides in the analyses. A tetrahedral diagram constructed on our triangular diagram with RO + R<sub>2</sub>O occupying its apex would be more accurate for the representation of the analyses of these minerals.

### 3. *Anauxite group* ( $s$ from 2.5 to 3.5).

In this group we observe no definite clusters, but only a continuous disperse field. No definite stoichiometric compounds are therefore to be deduced from the diagram. Most of the minerals belonging to this group appear as 'amorphous' aggregates, but some are

<sup>1</sup> C. S. Ross and E. V. Shannon, Journ. Amer. Ceramic Soc., 1926, vol. 9, p. 77.

<sup>2</sup> F. Heide, Chemie der Erde, 1927, vol. 3, p. 91.



definitely crystalline (micaceous habit). The substances of the low index of hydration give the following average ratios :

		<i>h.</i>	<i>s.</i>
Agalmatolite	... ..	1.0	3.0
Neurolite (in part)	... ..	1.1	2.7
Rectorite (in part)	... ..	1.2	2.5
Gümbelilite	... ..	1.5	3.0

There is no evidence that any of these substances belong to a definite mineral species.

This field of low index hydration passes imperceptibly into the field occupied by a definite crystalline mineral anauxite (ionite), although there is no indication of a cluster on the diagram. The average formula of anauxite as given by V. T. Allen<sup>1</sup> is  $2.5\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , while C. S. Ross and P. F. Kerr<sup>2</sup> think that the formula  $11\text{H}_2\text{O} \cdot 0.5\text{Al}_2\text{O}_3 \cdot 14\text{SiO}_2$  corresponds to its average composition. My own recalculations of all published analyses of anauxite show a good approximation to both of these formulae, although the *h*-ratio is nearer to 2 than to 2.5. The average formula  $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$  ( $\text{H}_2\text{O}$  11.30,  $\text{Al}_2\text{O}_3$  32.05,  $\text{SiO}_2$  56.65%), in which  $\text{Al}_2\text{O}_3$  is sometimes replaced by  $\text{Fe}_2\text{O}_3$ , agrees well with the mean of the analyses of anauxite. According to C. S. Ross and W. F. Foshag<sup>3</sup> anauxite is monoclinic like kaolinite, while E. Dittler and J. E. Hibschi<sup>4</sup> are of the opinion that it is orthorhombic. But as shown by Ross and Kerr anauxite is similar to kaolinite in many respects—X-ray spectrum and optical properties, and it may be that anauxite is simply kaolinite with adsorbed silica, or it may be an intermediate product between kaolinite and pyrophyllite.

The next mineral above anauxite on the diagram (figs. 1 and 2) is beidellite, to which E. S. Larsen and E. T. Wherry<sup>5</sup> as well as C. S. Ross and E. V. Shannon<sup>6</sup> assign the formula  $h\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , where *h* is approximately 4, and  $\text{Al}_2\text{O}_3$  can be partly replaced by  $\text{Fe}_2\text{O}_3$ . It contains also a certain amount of CaO and MgO. The

<sup>1</sup> V. T. Allen, Amer. Min., 1925, vol. 13, p. 145. [Min. Abstr., vol. 3, p. 370.]

<sup>2</sup> C. S. Ross and P. F. Kerr, Prof. Paper, U.S. Geol. Survey, 1931, no. 165-E. [M.A. 5-359.]

<sup>3</sup> C. S. Ross and W. F. Foshag, Amer. Min., 1928, vol. 13, p. 153. [M.A. 3-488.]

<sup>4</sup> E. Dittler and J. E. Hibschi, Min. Petr. Mitt. (Tschermak), 1923, vol. 36, p. 85. [M.A. 2-306.]

<sup>5</sup> E. S. Larsen and E. T. Wherry, Journ. Washington Acad. Sci., 1925, vol. 15, p. 465. [M.A. 3-8.]

<sup>6</sup> C. S. Ross and E. V. Shannon, Journ. Washington Acad. Sci., 1925, vol. 15, p. 467. [M.A. 3-8.]

published analyses of beidellite show a variation of  $h$  from 3.0 to 5.5, and  $s$  from 1.8 to 3.9. As no definite clustering of dots is shown on the diagram, it is difficult to assign a definite formula to beidellite. According to E. S. Larsen beidellite is probably an orthorhombic mineral. It occurs in the form of minute micaceous flakes. Beidellite definitely belongs to the bentonite group and stands between the micaceous halloysite and montmorillonite.

#### 4. Kaolinite group ( $s$ from 1.5 to 2.5).

Of the low hydration forms belonging to this group we have only a few indefinite substances, represented by one or two analyses in each case. They are as follows:

	$h$ .	$s$ .
Talcosite ... ..	0.5 ...	2.0
Rectorite (in part) ...	1.0 ...	2.0
Batchelorite ... ..	1.0 ...	2.0

They are all scaly micaceous minerals. Some of them contain a small amount of alkalis and alkaline earths. The evidence afforded is not sufficient to assign them to any definite mineral species, as they may be low hydration forms of kaolinite or mixtures.

The principal mineral of this group is kaolinite. It gives the most prominent cluster of dots on the diagram, exactly corresponding to its theoretical formula  $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . This cluster is slightly elliptical in shape with its long axis stretched along the line connecting gibbsite with pyrophyllite. On all the frequency curves kaolinite gives the most prominent modal peaks. About 200 analyses enter into the composition of the kaolinitic cluster, but many dots are superimposed and cannot be seen. The great number of analyses of kaolinitic clays is mainly due to their commercial importance, but this, in itself, indicates their widespread occurrence in nature. The analyses entering into the composition of the kaolinitic cluster correspond not only to substances bearing the name kaolinite or kaolin, but also to many others described under the names of nacrite, myeline, steinmark, pholerite, tuesite, indianait, &c.

Kaolinite is a well-studied mineral and it is definitely established as a distinct mineral species. It occurs in the form of small monoclinic crystals with a perfect basal cleavage. As the recent work of C. S. Ross and P. F. Kerr<sup>1</sup> has shown, three distinct varieties of

<sup>1</sup> C. S. Ross and P. F. Kerr, Amer. Min., 1930, vol. 15, p. 34; and Journ. Sedimentary Petr., 1931, vol. 1, p. 55; loc. cit., 1931. [M.A. 4-247, 5-359.]

kaolin minerals must be distinguished, namely kaolinite, nacrite, and dickite. Their chemical composition and crystalline system are the same and they differ from one another in their optical properties and X-ray spectra. To these three varieties we may add, as suggested by J. W. Mellor,<sup>1</sup> a colloidal variety called clayite. It gives the same type of dehydration curve as kaolinite, namely a terrace at 500° C. and a hump at 900° C., not shown by any other clay mineral even halloysite. This suggests that clayite may be a colloid composed of crystalline molecules of kaolinite (disperse phase).

Above the kaolinitic cluster on the diagram there is a disperse field occupied by various colloform and microcrystalline substances. The principal mineral of this field is halloysite. Its average *s*-ratio is 2 the same as in kaolinite, but the *h*-ratio varies between 2 and 5. On heating, half of its water is given up at temperatures between 100° and 200° C., and one may suppose that this portion of its water is colloiddally adsorbed; and if it were not for the fact that its heating curve does not show any definite terrace at 500° C., one would suggest that halloysite is a colloform variety of kaolinite. Pure amorphous forms of halloysite may perhaps be considered analogous to clayite but with crystalline molecules of different structure. On the other hand, micaceous halloysite, containing a certain amount of RO and R<sub>2</sub>O oxides, is now grouped together with the minerals of bentonitic clays.

Other substances under the names of galapektite, gummite, lenzine, severite, indianaitite, samoite, &c., find their place in the same field as halloysite. All these names as applied to distinct mineral species are hardly justified. The mineral newtonite has no place among the clay minerals. The original analysis suggested the formula  $5\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , but a new analysis of the same substance by W. F. Foshag<sup>2</sup> has shown that it contains 34.92% of SO<sub>3</sub> and therefore is nearer to alunite in its composition. The mineral named kochite<sup>3</sup> has been described of the composition  $2 \cdot 5\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1 \cdot 5\text{SiO}_2$  and apparently crystallizing in the cubic system. As no clay mineral has up to the present ever been found to crystallize in the cubic system, the question as to the existence of kochite as a distinct

<sup>1</sup> J. W. Mellor, *Trans. Ceramic Soc.*, 1917, vol. 16, p. 73.

<sup>2</sup> W. F. Foshag, *Amer. Min.*, 1926, vol. 11, p. 33. [M.A. 3-351.]

<sup>3</sup> S. Kôzu, K. Seto, and K. Kinoshita, *Journ. Geol. Soc. Tokyo*, 1922, vol. 29, pp. 1, 148. [M.A. 2-51, 521.]

mineral species must be left open until it is confirmed by further research.

We have now before us the difficult question as to the position to be occupied by the mineral named leverrierite in our scheme and even if this name should be retained at all. Leverrierite was first described by P. Termier.<sup>1</sup> It occurs in the form of 'rouleaux' and hexagonal flakes similar to kaolinite. In the original analyses the *s*-ratio varies from 2.3 to 3.7 and the *h*-ratio from 1.3 to 4.5. In addition, some analyses show considerable amounts of MgO and CaO, and this fact is supported by recent work of E. S. Larsen and E. T. Wherry<sup>2</sup> and of E. V. Shannon.<sup>3</sup> Considering all the analyses published, leverrierite shows a great variability of composition. C. S. Corbett,<sup>4</sup> following Larsen and Wherry, placed leverrierite in the group embracing such various minerals as hatchelorite, rectorite, delanouite, and pyrophyllite, and gave the theoretical formula for the minerals of this group as  $2.5\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . This formula can apply to some of the analyses of leverrierite, but it certainly does not correspond to pyrophyllite, rectorite, &c. In a later paper Larsen and Wherry (*loc. cit.*, 1925) isolated some of the minerals previously described under the name of leverrierite and proposed a new name of beidellite for minerals of  $s = 3$ , restricting the name of leverrierite for minerals of  $s = 2$  ( $h = 4$ ). Analyses of purified samples of beidellite by Ross and Shannon (1925) show an approximation to the proposed formula and also emphasize the fact that there is always some MgO and CaO present. In certain samples  $\text{Fe}_2\text{O}_3$  partly replaces  $\text{Al}_2\text{O}_3$ , and it was suggested that beidellite represents an isomorphous mixture composed of  $n\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$  and  $n\text{H}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$ . Ross and Shannon (*loc. cit.*, 1926) and also Ross and Kerr (1930), in their review of the minerals of bentonitic clays, omit leverrierite altogether and place micaceous halloysite in the division corresponding to  $s = 2$ . C. S. Ross, in a private communication to the present author, suggests that the name 'leverrierite' should be dropped, since this mineral, as first described, is a member of the kaolinite family. This is no doubt true, if we consider the analyses poor in RO and  $\text{R}_2\text{O}$  oxides, but some of the

<sup>1</sup> P. Termier, *Compt. Rend. Acad. Sci. Paris*, 1889, vol. 108, p. 1071.

<sup>2</sup> E. S. Larsen and E. T. Wherry, *Journ. Washington Acad. Sci.*, 1917, vol. 7, p. 208. [M.A. 2-133.]

<sup>3</sup> E. V. Shannon, *Proc. U.S. Nat. Mus.*, 1922, vol. 62, art. 15. [M.A. 2-134.]

<sup>4</sup> C. S. Corbett, *Amer. Journ. Sci.*, 1925, ser. 5, vol. 10, p. 247. [M.A. 3-382.]

original analyses of leverrierite contain as much as 6-80% CaO, besides some MgO and K<sub>2</sub>O. This suggests that minerals of the composition  $n\text{H}_2\text{O}.m\text{RO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$  should find their place in the group of bentonitic clays and be given a distinctive name. Provisionally the name of micaceous halloysite may be accepted.

The group of bentonitic clays must therefore be considered as distinct from the group of pure clay minerals, although it is connected with the latter group by numerous intermediate members. The following generalized formula may be proposed as expressing the composition of all the members of the group of bentonitic clays:  $h\text{H}_2\text{O}.\text{RO}.\text{Al}_2\text{O}_3.s\text{SiO}_2$ ; and the individual members of this series are as follows:

- |    |                      |     |     |                 |
|----|----------------------|-----|-----|-----------------|
| 1. | Micaceous halloysite | ... | ... | $s = 2$         |
| 2. | Beidellite           | ... | ... | $s = 3$         |
| 3. | Montmorillonite      | ... | ... | $s$ from 4 to 6 |
| 4. | ?                    | ... | ... | $s$ from 6 to 9 |

It would be unwise to identify the last unnamed member of this series with saponite, for saponite, with its high percentage of RO oxides, is obviously a member of the group of chlorites.

The minerals of the bentonitic clays are not only related to pure clay minerals, but also to the group of micas. The generalized formula proposed for the group of bentonitic clays can apply with certain modifications also to the group of micas. To get an idea of the frequency distribution of the  $s$ -ratios in micas, I have calculated and plotted on a frequency diagram (not given here) this ratio for 479 analyses of muscovite, biotite, lepidolite, and zinnwaldite. The general variation curve shows a great amount of dispersion (from 1 to 8) and a marked asymmetry with a maximum density between 2 and 4, and a gradually decreasing density from 4 to 8. This curve, as regard dispersion and distribution of densities (excepting the modal peaks), corresponds to the frequency curve for clay minerals (from 2 upwards) (fig. 5). The main differences between the clay minerals, bentonitic minerals, and the micas are as follows:

Clay minerals	....	RO = 0	R <sub>2</sub> O = 0
Bentonitic minerals		H <sub>2</sub> O > RO	R <sub>2</sub> O small amount
Micas	... ..	H <sub>2</sub> O < RO	R <sub>2</sub> O considerable amount

(Signs < and > refer to weight percentages.)

Between the micas and the bentonitic group one can place the group of hydromicas, a group as yet only vaguely defined.

On the triangular diagram (figs. 1 and 2) the minerals of the bentonitic group are alined more or less parallel to and above the series of pure clay minerals (kaolinite, anauxite, pyrophyllite, termierite). Their actual position on the diagram is mainly due to the fact that on recalculating their analyses, in the majority of cases, the total amount of water had to be taken into account. Allowing 50% or even more of the total water to be adsorbed moisture, the whole group can be lowered down so as to coincide with the region of pure clay minerals.

It is also of interest to notice that if in the formulae of micas and feldspars the RO and R<sub>2</sub>O oxides be replaced by equivalent molecules of water, the resulting alumino-silicic acids when plotted on the triangular diagram occupy a region almost coinciding with that of the clay minerals.

#### 5. *Bauxitic clay group* (*s* from 0.0 to 1.5).

This group, embracing almost the whole of the left half of the triangular diagram, is mainly composed of two trend-lines of dots, stretching from the region of kaolinite towards gibbsite and diaspore respectively. As there is no reason to suppose that these minerals are capable of forming isomorphous mixtures, we must presume that the analyses represented by dots situated along these trend-lines belong to mixtures of kaolinite with the two bauxitic minerals. These mixtures are commonly known under the name of bauxitic clays. However, there are also dots situated outside the two trend-lines. Some of them refer to substances which were given distinct names, which are as follows:

	<i>s</i> (average).		<i>h</i> .	
Dillnite ...	...	0.75	...	0.2 - 1.7
Samoite ...	...	1.50	...	4.5 - 5.5
Allophane ...	...	1.00	...	4.0 - 10.0
Collyrite ...	...	0.50	...	4.0 - 6.0
Schrötterite ...	...	0.40	...	3.0 - 5.5

Only one of these minerals (dillnite) lies on the line connecting kaolinite and diaspore and probably represents one of the many possible mixtures of these two minerals. The remaining minerals are difficult to place. The frequency curve for the *s*-ratio (fig. 5) gives two small modes for the values of *s* = 0.5 and *s* = 1.0. If these two modes are not accidental (due to the magnitude of the selected interval for the lower values of *s*-ratio), they may refer to collyrite

and allophane respectively. In any case the number of analyses of these substances is not sufficient to draw any conclusions from the statistical data. All these minerals are found in colloidal or colloform state and only X-ray analysis can solve this problem. It may be, that some, if not all, of these minerals are hydrated mixtures of kaolinite and gibbsite. For example, a mixture of kaolinite and gibbsite in equal molecular proportions would give allophane, i.e.  $3\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 = 2(2 \cdot 5\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$ . Actual analyses of allophane show a higher proportion of water than indicated in the last formula, but this may be due to the fact that colloidal mixtures are apt to contain much adsorbed water.

### III. BAUXITIC MINERALS.

Pure alumina hydrates occur in nature only in exceptional cases. Usually they are found mixed with clay minerals and iron oxides (the two principal ingredients). The classification of bauxites are numerous. In a recent monograph on the bauxites of southern France, J. de Lapparent<sup>1</sup> gives a detailed chemical classification of bauxites, according to the prevalence of the two additional components  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , such as megaferric, ferric, microferric, megaluminic, aluminic, siliceous, and megasiliceous bauxites. On the other hand, A. Lacroix<sup>2</sup> and L. L. Fermor<sup>3</sup> accept the name of laterite as a generic term for all the rocks rich in alumina hydrates, with a further subdivision into silicic laterites, lateritic clays, &c. However, following a usage accepted by many writers, it seems advisable to apply the term bauxite to rocks mainly composed of alumina hydrates and restrict the term laterite to ferruginous bauxites. The following simplified scheme of classification is therefore proposed :

	Rocks.	Composition.
Clays	... ..	Clay minerals
Bauxites	Bauxitic clays (siliceous bauxites)	Mixture of clay and bauxitic minerals
	Pure bauxites ... ..	Bauxitic minerals
	Laterites (ferruginous bauxites)	Mixture of bauxitic and ferric minerals
Iron-ores	... ..	Ferric oxides and hydrates

<sup>1</sup> J. de Lapparent, Les bauxites de la France méridionale. Mém. Carte Géol. France, Paris, 1930.

<sup>2</sup> A. Lacroix, Minéralogie de Madagascar. Paris, 1923, vol. 3.

<sup>3</sup> L. L. Fermor, Geol. Mag., 1915. dec. 6, vol. 2, pp. 28, 77, 123.

It is obvious that there are no hard-and-fast demarcations between these divisions, as even ordinary clays, as shown by M. G. Edwards,<sup>1</sup> contain certain amounts of alumina hydrates, while the majority of bauxites contain clay minerals (the average of 16 analyses of French bauxites, as recalculated by J. de Lapparent, gives the following figures: boehmite and diaspore 54.05, gibbsite 16.35, kaolinite 29.60 %). The distribution of dots along the trend-lines on the two triangular diagrams (figs. 1 and 7) seem to support the idea of a perfect gradation between the clays, the bauxites, and the iron-ores.

In the present paper all the siliceous bauxites have been included in the triangular diagram  $H_2O - Al_2O_3 - SiO_2$  (fig. 1); while the ferruginous bauxites (to almost a pure iron-ore), to the total number of 320, have been included in the triangular diagram  $H_2O - Al_2O_3 - Fe_2O_3$  (fig. 7). Both diagrams show a distinct clustering of points at the positions of the mono- and trihydrates of alumina and two well-defined trend-lines stretching from these points towards kaolinite in one case, and towards  $Fe_2O_3$  and  $H_2O.Fe_2O_3$  in the other.

The frequency curve of the ratio  $H_2O : Al_2O_3$  in the clay minerals (fig. 3) already suggests the presence of substances of the ratio one and three. But as these two modes may have been produced by some of the clay minerals, the ratios  $H_2O : Al_2O_3$  for all bauxites (total 561) were calculated and plotted on a separate diagram (fig. 4). This frequency diagram brings out the existing relationship very clearly. Two prominent modes are present, namely ratio 1.25 and ratio 3. The ratio of 1.25 is probably a shifted mode of ratio 1, due to the fact that alumina monohydrate often occurs in a colloidal form and so is more apt to retain adsorbed water, or it may be due to the influence exercised by the presence of ferric monohydrate. The second mode corresponds exactly to alumina trihydrate.

The distribution about these modes is unsymmetrical, i.e. it has a greater density towards the minimum situated between them. The whole character of the frequency curve suggests that we are dealing here with a mixture of alumina monohydrate and alumina trihydrate; while the ratio of the ordinates of the two modes suggests that in the assemblage of analyses considered these two substances are present in the proportion of 1 to 2.3 respectively.

The ratio 2 falls near the minimum of the curve, and thus the statistical evidence suggests that the compound  $2H_2O.Al_2O_3$  has no real existence. Actually a compound of this composition has never

<sup>1</sup> M. G. Edwards, *Econ. Geol.*, 1914, vol. 9, p. 112.



been observed, either in nature or in laboratory. The original substance analysed by P. Berthier<sup>1</sup> in 1821, and later called 'bauxite' (A. Dufrenoy, 1847), is not a mineral but a rock, containing, in addition to alumina hydrates, over 27 % of  $\text{Fe}_2\text{O}_3$ , and the approximation of its ratio to 2 is purely a matter of accident. (In the frequency diagram, fig. 4, there are 20 analyses of bauxites, out of the total 561, in which this ratio is equal to two.) In rocks com-

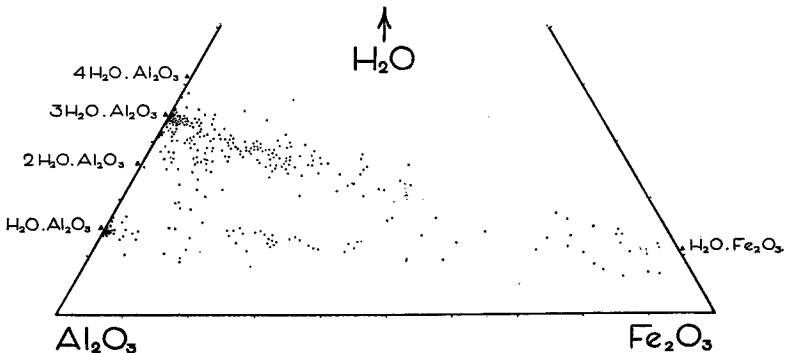


FIG. 7. The analyses of bauxites and laterites plotted on the triangular diagram  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ .

posed mainly of a mixture of alumina mono- and trihydrates, there is always a possibility of getting a mean proportion of the two. All works which attempt to prove the existence of a dihydrate of alumina from the consideration of a few individual analyses, such as a recent paper by T. V. M. Rao,<sup>2</sup> are based on this fallacy. To achieve the rank of a mineral species a given substance must be either capable of isolation in its pure crystalline (or amorphous) form, or of being produced in the laboratory. In the case of alumina dihydrate this proof of mineral status has never been achieved. The statistical evidence based on all available analyses, taken in conjunction with the negative evidence previously recorded by numerous observers, definitely points to the fact that alumina dihydrate, commonly called 'bauxite' ( $2\text{H}_2\text{O}.\text{Al}_2\text{O}_3$ ), does not exist as a mineral species. Therefore the name 'bauxite' as originally applied to the rock analysed by Berthier must be used as a generic term for rocks rich in alumina hydrates.

<sup>1</sup> P. Berthier, *Ann. des Mines*, 1821, vol. 6, p. 531.

<sup>2</sup> T. V. M. Rao, *Min. Mag.*, 1928, vol. 21, p. 407.

The frequency diagram (fig. 4) seems also to indicate that the gibbsitic bauxites are more abundant in nature than the diasporic bauxites. Apparently different regions have different proportions of these minerals in bauxites. Indian bauxites, for example, are mainly gibbsitic, while in the French bauxites, boehmite is the dominant constituent. Although only two hydrates of alumina are suggested by the present statistical study, there exist several polymorphous forms and isomers of each. The following is the list of bauxitic minerals drawn in accordance with the recent data :

Alumina monohydrate :

Diaspore	}	...	...	Orthorhombic isomers
Boehmite	}			
Kaysenite	}	...	...	Monoclinic isomers (?)
Tanatarite	}			
Sporogelite		...	...	Colloidal

Alumina trihydrate :

Gibbsite (hydrargillite)	}	...	...	Monoclinic isomers
Bayerite	}	...	...	

Alumina tetrahydrate :

Scaly variety <sup>1</sup>	...	...	Isotropic
Shanyavskite	...	...	Colloidal

The right-hand corner of the triangular diagram (fig. 7) is occupied by a few aluminous iron-ores. Apparently they indicate the presence of ferric monohydrate and ferric oxide. Ferric monohydrate occurs in two dimorphous forms, both crystallizing in the orthorhombic system, namely goethite and lepidocrocite (ruby-mica). J. Böhm<sup>2</sup> found that goethite gave an X-ray diffraction pattern similar to that of diaspore, while that of lepidocrocite was similar to that of boehmite. J. de Lapparent records the occurrence in bauxites of goethite and haematite only, with the addition of limonite as a product of weathering. These minerals, however, seldom occur as mineral grains, they are generally found closely mixed with alumina hydrates in a paste which de Lapparent calls 'gel alumino-ferrique'. The evidence derived from the study of the analyses plotted on the triangular diagram (fig. 7) points to the same conclusion. The laterites (ferruginous bauxites) are mechanical mixtures of alumina monohydrate, alumina trihydrate, ferric monohydrate, and ferric oxide. There is no indication of isomorphism between  $H_2O.Al_2O_3$

<sup>1</sup> P. Neogi and A. K. Mitra, Journ. Chem. Soc. London, 1927, part 1, p. 1222.

<sup>2</sup> J. Böhm, Zeits. Anorg. Chem., 1925, vol. 149, p. 311. [M.A. 3-430.]

and  $3\text{H}_2\text{O}.\text{Al}_2\text{O}_3$ , but a solid solution between  $\text{H}_2\text{O}.\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  is possible (turite?).

Bauxites, in addition to clay minerals and ferric hydroxides and oxides, contain minor constituents in varying amounts (manganese hydroxides, titanous hydroxides and oxides, zircon, tourmaline, &c.). Except for manganese hydroxides, which in certain bauxites attain considerable proportion, the other minor constituents play a very restricted role.

#### IV. SUMMARY.

A statistical study of clay and bauxitic minerals, which consisted of plotting all available analyses of these minerals on two triangular diagrams (figs. 1 and 7) and constructing frequency curves for the cardinal ratios, led to a classification of these minerals on a purely chemical basis. The suggestion is also made that among substances claimed to be minerals we can select only a few as belonging to definite mineral species, and that the others are probably mixtures of these selected minerals, or their hydration products, or colloidal hydrates of variable composition. The distinct crystalline mineral species thus singled out are as follows:

Pyrophyllite	...	...	...	$\text{H}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2$
Kaolinite and its isomers	...	...	...	$2\text{H}_2\text{O}.\text{Al}_2\text{O}_3.2\text{SiO}_2$
Diaspore	„	„	„	$\text{H}_2\text{O}.\text{Al}_2\text{O}_3$
Gibbsite	„	„	„	$3\text{H}_2\text{O}.\text{Al}_2\text{O}_3$

Besides these minerals, other substances, such as termierite, anauxite, allophane, &c., are suggested as probable species, without, however, any clear statistical evidence. The bentonitic minerals, not belonging strictly to the pure hydrous aluminium silicates, are placed in a separate group.

In conclusion, I should like to thank Dr. G. Hickling and Mr. G. S. Mockler for reading the MS. of this paper and for their valuable suggestions.

Calculated chemical composition of substances represented by certain cardinal points on the triangular diagram  $H_2O-Al_2O_3-SiO_2$  (fig. 2).

	$H_2O$ .	$Al_2O_3$ .	$SiO_2$ .	
$H_2O - 2SiO_2$ ...	13.00%	—	87.00%	... Di-silicic acid
$H_2O - SiO_2$ ...	23.05	—	76.95	... Meta-silicic acid
$2H_2O - SiO_2$ ...	37.46	—	62.54	... Ortho-silicic acid
$2H_2O \cdot Al_2O_3 \cdot 6SiO_2$ ...	7.22	20.46	72.32	... } (Termierite)
$8H_2O \cdot Al_2O_3 \cdot 6SiO_2$ ...	23.73	16.83	59.44	... }
$12H_2O \cdot Al_2O_3 \cdot 6SiO_2$ ...	31.82	15.03	53.15	... —
$H_2O \cdot Al_2O_3 \cdot 4SiO_2$ ...	4.99	28.29	66.72	... Pyrophyllite
$2H_2O \cdot Al_2O_3 \cdot 4SiO_2$ ...	9.52	26.92	63.56	... }
$3H_2O \cdot Al_2O_3 \cdot 4SiO_2$ ...	13.61	25.72	60.67	... } (Cimolite)
$H_2O \cdot Al_2O_3 \cdot 3SiO_2$ ...	5.99	33.92	60.09	... (Agalmatolite)
$2H_2O \cdot Al_2O_3 \cdot 3SiO_2$ ...	11.30	32.05	56.65	... Anauxite
$3H_2O \cdot Al_2O_3 \cdot 3SiO_2$ ...	16.07	30.31	53.62	... —
$H_2O \cdot Al_2O_3 \cdot 2SiO_2$ ...	7.48	42.42	50.10	... (Batchelorite)
$2H_2O \cdot Al_2O_3 \cdot 2SiO_2$ ...	13.93	39.48	46.59	... Kaolinite
$3H_2O \cdot Al_2O_3 \cdot 2SiO_2$ ...	19.54	36.92	43.54	... (Halloysite)
$H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	10.00	56.62	33.38	... —
$2H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	18.25	51.49	30.26	... —
$3H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	24.99	47.21	27.80	... —
$4H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	30.77	43.56	25.67	... }
$5H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	35.72	40.45	23.83	... } (Allophane)
$6H_2O \cdot Al_2O_3 \cdot SiO_2$ ...	39.99	37.80	22.21	... }
$8H_2O \cdot 2Al_2O_3 \cdot SiO_2$ ...	35.27	50.04	14.69	... (Collyrite)
$H_2O \cdot Al_2O_3$ — ...	15.00	85.00	—	... Diaspore
$2H_2O \cdot Al_2O_3$ — ...	26.11	73.89	—	... —
$3H_2O \cdot Al_2O_3$ — ...	34.63	65.37	—	... Gibbsite
$4H_2O \cdot Al_2O_3$ — ...	41.35	58.65	—	... —