

The nomenclature of the halloysite minerals.

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THE name 'halloysite', first used in 1826 by Berthier (1), is derived from that of Omalius d'Halloy, who found the mineral in Angleur, Liège, Belgium. In 1935, Mehmel (2) discovered that there were two distinct substances included under the name halloysite, one of which contains loosely bound water and shows a 10 Å. basal reflection on an X-ray diagram, the other none and shows a reflection at about 7 Å. Mehmel preserved the name halloysite for the hydrous mineral, and for the product of its dehydration he proposed the name 'metahalloysite'. Both substances may occur naturally (though this may not have been known to Mehmel at the time). Previous to this work it had been suggested by Hofmann, Endell, and Wilm (3) that the 10 Å. material on dehydration at a low temperature gave kaolinite. Mehmel showed that this was wrong; and that the error was due to the similarity of the X-ray diagrams of kaolinite and metahalloysite. Hofmann and co-workers, and Mehmel, all tacitly assumed that the name halloysite was correctly applied to the 10 Å. material rather than the 7 Å. material.

In the United States, the practice introduced by Hendricks (4) of using 'halloysite' for the *non*-hydrated material and 'hydrated halloysite' for the hydrated material has usually been followed in recent years. This practice never became universal; and in fact all three terms continued in use, with 'halloysite' used in both senses. Recently in America yet another revision of the nomenclature has been proposed, in an attempt to clear up the confusion. This consists in the introduction of a new name 'endellite' (5) for the hydrated mineral, the name 'halloysite' being retained for the dehydrated mineral. This nomenclature has been adopted in another recent American paper (6). In the present note I wish to point out that this suggestion has found little favour among workers on clay minerals in this country; to present the arguments against it; and to suggest a convenient nomenclature which takes account of recently discovered properties of the halloysite minerals.

The introduction of the name 'endellite' would mean adding to the already overloaded mineralogical terminology. The name has no obvious connexion with halloysite, so that, in effect, if it were adopted, three separate acts of memory would be required of students (i.e. the two names for the hydrated and non-hydrated forms, and the fact of their—undoubtedly—close connexion in nature) instead of one (or one and a fraction). The new name might be justified if it stood for a completely distinct substance. But does it? I wish to suggest that recent research has shown that halloysite and metahalloysite (hydrated halloysite and halloysite; or endellite and halloysite) are so closely connected that they are more conveniently regarded as two aspects of a single substance than as entirely separate substances.

The picture of the halloysite structure which emerges from recent work is this (5–8). The hydrated form of the mineral consists of kaolinite sheets interspersed with monomolecular sheets of water molecules. There is no regularity detectable by X-rays in the packing of the sheets, apart from the constant distance between them, measured in a perpendicular direction. In conformity with this idea of a structure of very high energy, the structure is a very labile one, and the water layer may readily be replaced by a layer of other polar molecules, e.g. ethylene glycol, glycerol, methanol, &c. On dehydrating halloysite at low temperatures, the water sheets are lost, but the kaolinite sheets remain intact, and come into contact with each other, becoming linked by O–H–O bonds. The energy of this inter-sheet linkage depends on the exact treatment of the specimen, and though some specimens of metahalloysite will give the glycol compound on treatment with glycol, others will not. Thus the following points are clear:

(a) The hydrated form of halloysite ('endellite') is only one of a number of possible complexes in which the large kaolinite sheets are interspersed with monomolecular layers of polar molecules.

(b) Metahalloysite is a substance of doubtful uniformity and may show various degrees of energy of binding of the structural sheets.

In addition, it may be mentioned that:

(c) Naturally occurring halloysite minerals may be intermediate between the hydrated halloysite ('endellite') and the non-hydrated halloysite ('metahalloysite') (this fact is supported by published analyses, mentioned below, and also by X-ray diagrams which I have made of natural halloysites).

These facts make it clear that the two halloysite minerals are only two members of a series of substances which includes various intermediate

forms, as well as forms in which water of hydration is replaced by other molecules. The situation is very similar to that arising in connexion with the mineral montmorillonite. Like halloysite, this has a highly irregular structure, with mobile inter-sheet molecules. The hydrated forms of montmorillonite may be irreversibly dehydrated by heating (to 200° as against 50° for halloysite), though according to Bradley (9) it may then still be rehydrated via the glycol compound (cf. similar behaviour of halloysite (7)).

In describing this mineral the usual practice (seldom explicitly stated) has been to use one name 'montmorillonite' to cover all its possible forms, with various quantities of water or other molecules. The name 'montmorillonite' is thus regarded as a general name covering various particular forms; these have been more precisely designated as hydrated montmorillonite, glycerol-montmorillonite, &c. This seems the only reasonable procedure with such a reactive substance.

My suggestion is that the same procedure be adopted in the case of halloysite. Thus the name 'halloysite' would be taken to cover all the naturally occurring halloysite minerals (hydrated, non-hydrated, and intermediate) as well as artificially produced complexes; and for particular forms the precise terms 'hydrated halloysite', 'glycerol-halloysite', &c. would be used (whether these were obtained starting from the hydrated or the non-hydrated form). The convenient term 'metahalloysite' would be retained for the non-hydrated form (with the understanding that it is only an approximative term, and that the material thus described may not be uniform). It is contended that this suggestion provides a logical, coherent nomenclature for all the manifestations of the halloysite minerals, particularly for the organic complexes. The 'endellite-halloysite' system of nomenclature breaks down rather badly when dealing with these. The glycerol complex, for instance, is generally obtained starting with 'endellite'. Is it therefore to be called 'glycerol-endellite'? This seems wrong because the term endellite suggests the presence of water molecules, which do not occur in the glycerol complex. If the term 'glycerol-halloysite' is to be used, then the case for 'hydrated halloysite', and thus for the whole system of nomenclature proposed here, seems to be admitted ('hydrated halloysite' is misleading if 'halloysite' is taken to mean metahalloysite, for metahalloysite cannot generally be hydrated (10); but correct if halloysite is understood as a general term).

It is perhaps desirable to discuss briefly here how the usage suggested above fits in with the historical use of the name 'halloysite', since there

seems to have been as much confusion over this as over the other aspects of the nomenclature. When Hendricks proposed his first system of nomenclature (4) (i.e. 'halloysite' in the sense of metahalloysite, and 'hydrated halloysite') he stated that 'as a rule, Mehmel's metahalloysite is the usual halloysite of others'. No references were cited to support this statement. In a later summarizing paper on the clay minerals, Grim (11) went still farther, and stated that 'Hendricks has suggested the names "hydrated halloysite" and "halloysite", respectively, for these minerals [i.e. hydrated and metahalloysites], thus retaining the name "halloysite" for material of the composition to which it was first applied'. Alexander and others, in the introduction of their paper (5), implicitly support the idea that the original usage of the term 'halloysite' was identical with that of Hendricks's.

I believe that, in fact, Hendricks's original statement is very doubtful, and Grim's definitely incorrect. The accompanying table gives a list of analysed samples of halloysite, derived from papers published before 1934 (the date of the Ross and Kerr paper mentioned below), together with the total number of molecules of water in the formula for the air-dry or lightly dried material, as quoted by the authors or deduced from their data (based on one Al_2O_3 group per formula: but analyses were rejected for which the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio differed markedly from 2). This number should be 2 for meta-, and 4 for hydrated halloysite: a glance at the table shows that in most cases it is nearer to the latter than the former, though practically the whole intermediate range is covered. Le Chatelier (19) in particular analysed a large number of halloysite specimens, and distinguished between water lost above and below 250°C . His results correspond to formulae varying from $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \frac{1}{2}\text{H}_2\text{O}$ to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\frac{1}{2}\text{H}_2\text{O}$, the second group of water molecules representing the more loosely bound water. It was perhaps this paper, with its emphasis on the method of differential thermal analysis, introduced by Le Chatelier, which resulted in a widening of the connotation of the term 'halloysite' to include various minerals which gave essentially the same type of differential thermal diagram. In the earlier literature, there were a number of different names for material which was probably essentially halloysite, and a few of these are given in the table. It shows incidentally that the name 'lenzinite' really has priority, for it was used by J. F. John (12, 13) in 1816 to describe a material essentially the same in composition as the hydrated variety of halloysite. However, the name 'lenzinite' got applied to a number of ill-defined materials of widely varying composition, so its demise is understandable.

Table of water-content data from halloysite analyses.

This table lists halloysite analyses made before 1934; although not claimed to be exhaustive, it probably gives a fair sample, and should include all the important ones. The total number of molecules of water in the air-dry or lightly dried material is given in each case, together with the locality of origin, the analyst (not necessarily the same as the author of the paper), and the name under which the mineral was described if different from 'halloysite'.

	Mols. H ₂ O.
'Lenzinite argileuse' (John, 1816) (12)	4.0
'Lenzinite', Eifel, Germany (John, 1816) (13)	3.8
Angleur, Belgium (Berthier, 1826) (1)	4.4
Lavoulte, France (Dufrénoy, 1833) (14)	4.2
Thiviers, France " " "	3.9
Miechowitz, Silesia (Oswald, 1837) (15)	3.9
'Glossecollite', Dade Co., Georgia (Pisani, 1861) (16)	3.2
'Indianaite', Indiana (Pemberton, 1878) (17)	3.7
Drenkova, Banat (Helmhacker, 1880) (18)	3.5
" " " " "	4.5
Brandberg, Germany " " "	4.5
Eifel, Germany (Le Chatelier, 1887) (19)	2.4
Laumède, France " " "	2.6
Huelgoat, France " " "	2.6
Miglos, France " " "	3.1
Russia " " "	3.2
Angleur, Belgium " " "	3.6
Breteil, France " " "	4.2
'Indianaite', Indiana (Noyes, 1904) (20)	2.2
(cf. Pemberton's analysis, above)	
Kolyvansky mine, Altai (Pilipenko, 1915) (21)	2.5
Wagon Wheel Gap, Colorado (Larsen and Wherry, 1917) (22)	3.8
Radzionkow, Silesia (Šplíchal, 1919) (23)	2.7
Angleur, Belgium " "	3.7
Worm's Heath, Surrey (Edge, 1919) (24)	3.4
Djebel Debar, Algeria (Granger and Brémont, 1922) (25)	4.0
Kedabek, Elizavetpol (Chirvinsky, 1929) (26)	4.1
Elbingerode (Erdmannsdörffer, 1930) (27)	4.9

Statements abound in the earlier literature to show that the analysts were well aware of the existence of additional loosely bound water in the samples they examined. As an example, Helmhacker's important paper (18) may be cited. He points out that at 100° C. the formula of halloysite approaches that of kaolinite, but shows considerably more water at lower temperatures. The formula given by Rammelsberg in his 'Mineralchemie' (28) shows four molecules of water, though he wrongly suggests that three of these are more loosely combined than the other one. Larsen and Wherry in their paper (22) put forward the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{aq}$. It is true that in the more recent series of analyses of halloysites mostly of American origin, quoted by

Ross and Kerr (29), the amount of water found in excess of the theoretical value for metahalloysite is always small, and it may be on the authority of this important paper that the American practice of using 'halloysite' for metahalloysite has arisen. Ross and Kerr, however, were not aware of the nature of the hydrated form of halloysite, and cannot therefore have known of the importance of guarding against the loss of the inter-sheet water. The pre-treatment used on their samples was not specified, but may have resulted in this water being driven off. In this connexion, Hendricks's statement (4) is interesting, that this water was lost (as shown by X-ray photographs) on exposure to the laboratory air for one week. This is not true of the perhaps relatively under-heated laboratories in this country according to my experience (confirmed by others).

In the original paper of Berthier (1), the 'analysis of halloysite' which he quotes would lead to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4 \cdot 4\text{H}_2\text{O}$. There can be no doubt therefore that the type material was hydrated halloysite. Šplíchal's (23) and Le Chatelier's (19) analyses of material from the same locality also correspond to hydrated halloysite (3.7 and 3.6 H_2O respectively). The adoption of the 'endellite' nomenclature would thus mean giving a new name to material identical with Berthier's original 'halloysite'. It is true that Berthier states that the 'true composition' of halloysite is probably ' $2\text{AlS}^2 + \text{AlAq}^2$ '; or, in modern symbols, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. This formula, however, is based on the supposition that the water lost below 100°C . is not to be regarded as part of the structure. Berthier makes it clear that this supposition is only tentative, by referring specifically to the difficulty of deciding what part of the water is to be regarded as definitely bound. In choosing a 'theoretical' formula he may also have been influenced by a now-defunct theory of 'chemical types'; the analyses furnish no justification for splitting the alumina into two parts. The difficulty of classifying the low-temperature water is one which has persisted until to-day, for it occupies a peculiar intermediate position between 'adsorbed' and 'combined' water. As regards energy and type of binding it resembles the former; but the series of adsorption complexes, of which hydrated halloysite is one, have a more clearly defined individuality than most. The proposed nomenclature takes account of this fact by giving them separate, but not unconnected, names.

Hofmann and co-workers, and Mehmel, were historically correct in assuming that the hydrated halloysite was the true halloysite, so that Mehmel's nomenclature is better justified than Hendricks's, or the 'endellite' nomenclature. I believe, however, that the system I have

suggested is really the best historically as well as from the point of view of modern knowledge. Its adoption would mean that everything which has been called 'halloysite' in the earlier literature (obvious errors excepted) could still be called halloysite; the qualifying prefixes 'hydrated', 'partly hydrated', or 'meta' being added only if required. In soil work the proposed nomenclature will be valuable, for it will enable a measure of vagueness to be introduced into descriptions where it is unavoidable, and precision, devoid of cumbrous terminology, where it is justified. Ideally, of course, soil-clay mineralogists should be able to say of any sample whether it is hydrated halloysite ('endellite'), metahalloysite, or something intermediate. In practice, however, there may often be doubt whether the pre-treatments used on the clay may not have resulted in hydrated halloysite being altered to metahalloysite. The term 'halloysite', covering both minerals, may then be used; as has in fact often been done in the past, though not always explicitly stated. Dr. L. J. Spencer (*Min. Mag.*, vol. 26, p. 336) agrees with my criticisms of Hendricks's nomenclature, and the 'endellite' nomenclature, but would prefer the term 'halloysite' to be confined to the fully hydrated variety. As a soil-clay worker, I think that such a specific use of 'halloysite' would be difficult to observe consistently in practice.

The possibility must be considered that there exist minerals which are intermediate between (meta) halloysite and kaolinite, i.e. less regular than kaolinite, but not so irregular as halloysite (30). Such minerals, in their relation to halloysite, might be similar to certain hydrous micas (6) in relation to montmorillonite. The nomenclature proposed here does not take account of them; obviously more data on their nature and variation must be accumulated before a satisfactory nomenclature is arrived at. The material from Saglik for which Bel-yankin and Ivanova have used the name 'hydrokaolin' (31) may be of this type; it contains rather more water than normal kaolinite and is birefringent.

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