NEW DATA ON THE COMPOSITION AND IDENTIFICATION OF CHLORITES

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ABSTRACT

A series of clay minerals with a 7A series of reflections has been shown to exist in the MgO-Al₂O₃-SiO₂-H₂O system. It has been demonstrated both on synthetic and natural samples that these minerals are polymorphous with the 14A-series chlorite minerals. Widespread occurrence of these minerals in nature is expected. The polymorphic relationship found clarifies the whole picture of the isomorphism of the chlorites. The problem of nomenclature of these 7A series minerals is examined and the term "septechlorites" hesitantly proposed.

On the basis of some experimental work it is shown that the currently adopted procedure for the identification of chlorites is not generally valid, and that the factors of time, temperature, composition and particle size are of crucial importance in such procedures.

INTRODUCTION

Recent recognition of the fact that chlorite minerals occur widely in clay materials has re-emphasized the fundamental problems of chlorite genesis and constitution. At the same time new reliance has been placed rather generally on old and insufficiently tested techniques for the identification of chloritic constituents of clay mineral mixtures. This paper summarizes the results of experimental investigations that bear, we feel, significantly on the problems of identification and genesis of chlorites, particularly those that may occur in clay materials.

Many attempts have been made to relate the wide variations in chemical composition to a general picture of chlorite constitution. Among these was Tschermak's (1891) suggestion that the variations in chemical composition of the magnesian chlorites could be accounted for by assuming complete solid solution between serpentine, Mg₃Si₂O₅(OH)₄, and amesite, Mg₂Al₂SiO₅(OH)₄. Later Winchell (1926) extended this idea by suggesting that the compositions of the iron-bearing chlorites could be explained by assuming solid solution between the ferrous iron analogues of serpentine and amesite (Fig. 1). Recent structural studies have shown that many variations in chemical composition can also be accounted for by ionic substitutions in a chlorite crystal lattice characterized by a 14 A series of basal x-ray reflections. However, certain "chlorites," including serpentine, greenalite, amesite, and chamosite, possess structures giving a 7 A series
of basal reflections in their x-ray diagrams. Solid solution between these different structural types in harmony with the Tschermak-Winchell concept is difficult to imagine. Furthermore, chamosites from different localities may give either a 14 A series or a 7 A series of reflections; similarly certain single crystals of amesite appear to show only the 7 A series, whereas most powdered samples of this mineral give in addition a 14 A series with the odd orders very weak. This confusing state of affairs has led Brindley and Robinson (1951, p. 177) to divorce from the chlorite group all the above minerals that give a 7 A series of basal x-ray reflections. Our experimental work was undertaken to determine whether mineral synthesis experiments could resolve some of the problems raised by these observations on natural materials.

ISOMORPHISM AND POLYMORPHISM OF THE CHLORITES

Figure 1 shows Tschermak's classification of the magnesian chlorites plotted on a square diagram. Our synthesis experiments followed up earlier work (Roy and Roy, 1952) on phase equilibrium in the system MgO-Al₂O₃-SiO₂-H₂O in which solid solution between chrysotile and clinochlore had been demonstrated and its further extension suspected. These experiments involved chemical compositions equivalent to pure magnesian

![Chemical classification of the chlorites modified after Tschermak and Winchell.](image)

**Figure 1.**—Chemical classification of the chlorites modified after Tschermak and Winchell. Two separate isomorphous series, one with a 7A series of reflections ("septechlorites") and the other with a 14A series exist, bearing a polymorphic relationship to each other. The 14A series does not appear to extend completely over to the left-hand edge, a certain minimum of R₂O₃ apparently being essential to its formation.
chlorites which would plot along the base of the diagram at short intervals between serpentine and amesite. All of the chlorites between penninite and amesite were synthesized and gave a 14 A series of basal reflections in their x-ray diagrams; the normal chlorite pattern. At low temperatures, however, these same synthetic compositions formed single phases that gave a 7 A series of basal reflections, the same as for natural chamosites, serpentines and aluminous serpentines. At higher temperatures all of the synthetic 7 A phases for compositions between penninite and amesite transformed (at a very slow rate) into single phases that gave a 14 A series of basal reflections. In addition to these synthesis experiments antigorite from Antigorio Valley and a chrome amesite from the Urals (both 7 A structures) were converted into chlorites giving a 14 A series of basal reflections in their x-ray diagrams. The fundamental result of these experiments is that there is a polymorphic relation between 7 A chlorites and 14 A chlorites. It appears, therefore, that two series of chlorite minerals must exist. One is the normal chlorite series characterized by a 14 A sequence of basal x-ray reflections, and these minerals range in composition from penninite to amesite. The other chlorite series ranges in composition from serpentine to amesite and typically gives a 7 A sequence of basal x-ray reflections. Complete solid solution exists within each one of these series, and 7 A chlorites of appropriate compositions that are polymorphs of normal chlorites may be converted into normal chlorites under proper conditions.

These data make it possible to understand why different structural types of chlorites may be found in nature. The two different structural types are formed as a result of different environmental conditions during sedimentation. The 7 A chlorites formed during sedimentation may be converted into 14 A chlorites in one case or remain as 7 A chlorites in another as a result of different post depositional histories of the sediments that contain them.

CRITICISM OF IDENTIFICATION PROCEDURES FOR CHLORITIC MATERIAL

Whereas the synthesis data seem to clarify our concept of chlorite constitution they raise new problems in identification of chlorites. Figure 2 shows, for example, that the range of basal x-ray spacings of the 7 A chlorites overlaps the range of basal reflections of the kaolin minerals. Recognition of this problem led us to perform some dry heating experiments with chloritic materials in the hope that changes in the intensities

1 The details of these synthesis experiments and their bearing on phase equilibria and the genesis of chlorites in natural clay materials will be reported in another place (Nelson and Roy, 1953).

2 Reflections from the 7 A chlorites are conveniently indexed on the basis of a 14 A unit cell in accord with the structural determinations of unit cells for chrysotile and amesite.
of the basal reflections after calcining might provide a convenient method for differentiating the kaolin minerals, the 7 A chlorites, and the normal 14 A chlorites. Results of these experiments are summarized below.

In Figure 3 the changes induced in the x-ray diagrams by calcining clinochlore for two hours and chamosite for one-half hour at 590°C are summarized diagrammatically. The first-order clinochlore reflection increases remarkably in relative intensity, whereas chamosite achieves an "amorphous to x-rays" state as a result of the heat treatment. The x-ray diagrams for kaolinite show the same characteristics as those of chamosite. A combined thermal and x-ray method has recently come to be generally accepted as a method for distinguishing clay minerals with 7 A structures from normal 14 A chlorites and was based on results similar to those illustrated in Figure 3. Similarly the observation of an enhanced 14 A reflection after heating is generally used to identify normal chlorites in mixed clay materials.

In the course of heat treatments on other chloritic materials we have observed effects that are not consistent with the results just described. Figure 4 illustrates the changes in the x-ray diagrams of a chrome amesite produced by calcining at 590°C for various periods of time. The diagram obtained from the normal chlorite produced by hydrothermal treatment of the original 7 A material at 600°C for twenty-six days is also shown. The essential features of these diagrams are: 1) persistence of an intense series of 7 A reflections even after prolonged heat treatment (up to twenty-four hours in some cases); 2) appearance of a broad line at 13.2 A (unaccompanied by the lower odd orders of the 14 A series) after nine hours calcining; 3) a complete sequence of odd and even orders for the
normal chlorite produced by hydrothermal treatment. Results analogous to these have been observed for all of the 7 A chlorite minerals thus far examined. The length of time required to cause the appearance of the line at 13.2 to 13.6 Å varies with the individual specimen and must be a function of both composition and particle size. Synthetic 7 A chlorites, which are extremely fine grained, achieve an "amorphous to x-rays" condition after just one-half hour of calcining. In the coarser grained natural materials increasing alumina content requires a longer heating period to achieve the new line in the diagrams. The type antigorite from Antigorio Valley requires nearly thirty hours to form the new line. A fibrous chrysotile (tubular under the electron microscope) from Globe, Arizona, gives a new line at 13.6 Å when calcined at 590°C for just one hour, as Figure 5 shows. The effect of composition may be seen also in the behavior of chamosite, but since synthetic magnesian 7 Å chlorites become "amorphous to x-rays" after just one-half hour of calcining, too, the result obtained for chamosite may be assigned at least partly to particle size.

Experiments with some 14 Å chlorites suggest that certain of these may become "amorphous to x-rays" after prolonged heat treatment at 590°C. The amesite from Chester, Massachusetts, appears to be a mixture of the polymorphous 7 Å and 14 Å chlorite types. The results of heat treatment of this material are shown in Figure 6. The lines for the 7 Å component

FIGURE 3.—Highly schematic diagrams illustrating the changes of intensity in the basal reflections of clinochlore and chamosite as a function of heat treatment (Temp. 590 ± 5°C; clinochlore ground, —325 mesh, chamosite —325 mesh, but may be much finer originally).
remain strong after calcining for one-half hour, but gradually decrease in intensity with continued application of heat until the 7 A component becomes "amorphous to x-rays" after twenty-four hours. The first order basal reflection for the 14 A component shows the characteristic increase in intensity after the first calcining. Thereafter the 14 A line grows in intensity as the lines for the 7 A component decrease. After twelve hours all the lines in the pattern begin to decrease in intensity until finally the whole material becomes "amorphous to x-rays". The behavior of the 7 A component can be understood by reference to Figure 7, which shows the changes in the x-ray diagram produced by calcining Chester amesite freed of the 14 A component according to the procedure of Brindley, Oughton, and Youell (1951, p. 557). The diagram obtained after one-half hour's heating indicates that all of the normal chloritic component had been removed, as reference to Figure 6 will show. After twenty-four hours this material becomes almost completely "amorphous to x-rays".

CONCLUSIONS ON IDENTIFICATION METHODS

The results of these experiments raise grave doubts in our minds as to the advisability of relying indiscriminately on the combined thermal and x-ray examinations currently recommended for identifying chlorites in
natural clay materials. These experiments show: 1) that many 7 A chlorite type structures do not decompose to an “amorphous to x-rays” state after short periods of heating at nearly 600°C; 2) the 7 A “chlorites” themselves develop a reflection in the vicinity of 14 A after only a moderate amount of heat treatment; 3) materials of both the 7 A and 14 A type may become “amorphous to x-rays” after heat treatments for different lengths of time. We conclude, therefore, that although combined thermal and x-ray examinations of clay materials may be of value in differentiating mineral species in specific instances, the following variables must always be specifically considered: a) heating temperature (± 10°C); b) length of the heating period; c) chemical composition of the individual minerals; d) particle size and degree of crystallinity of the material. These variables determine whether or not a given mineral will achieve the “amorphous to x-rays” condition.

DIFFERENTIAL THERMAL ANALYSIS METHODS

The results of differential thermal analysis of several natural chloritic minerals are summarized in Figure 8. The differential thermal curve obtained for penninite is typical of all the normal 14 A chlorites examined.
FIGURE 6.—Effect of heat treatment on Chester amesite (Temp. 590° C ± 5° C; ground, —325 mesh).

FIGURE 7.—Effect of heat treatment on Chester amesite "purified" according to the method of Brindley. Note the development of a 14A reflection in material which is originally presumed to have contained only 7A series material (Temp. 590° C; ground, —325 mesh).
The antigorite curve is similar to those obtained from other 7 A chlorites. The curve obtained from the Chester amesite indicates that that material is a mixture of the two chlorite polymorphs. These curves indicate that differential thermal analysis may be a very valuable qualitative tool in distinguishing individual types as well as mixtures of types of 7 A chlorites, 14 A chlorites, and kaolin minerals. Typical curves for the kaolin minerals differ from those obtained from 7 A chlorites by the lower temperature of the endothermic reaction and the fact that the final exothermic reaction is delayed. In 7 A chlorites the final exotherm follows im-

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3 The 14 A chlorite component is not an admixed impurity, because the chemical analysis of the bulk material (Shannon, 1920) results in a formula for the whole that plots at the extreme limit of the chlorite solid solution series (Fig. 1).
mediately the endotherm due to dehydration. It is essential to recognize, however, that fine grained and poorly crystallized minerals do not necessarily give the same results as those obtained in these differential thermal runs with well crystallized minerals: the above results apply only to coarsely crystalline material.

NOMENCLATURE OF THE CHLORITES

Finally there is a problem of chlorite nomenclature to be discussed. With reference to the existence of both 7 A and 14 A chamosites, Brindley (1951, p. 65) says,

If agreement can be obtained among workers on the 'chamosite problem', it will obviously be necessary to choose names for the kaolin-type and chlorite-type minerals present in materials now labeled 'chamosite'.

Since our work on chlorite synthesis reveals the fundamental relation between 7 A and 14 A chlorites, we suggest that the chlorites characterized by a 7 A series of basal x-ray reflections be referred to as "septechlorites". This is a term that need only be used when a chloritic material has been studied in the laboratory and found to give a 7 A series of basal reflections. This name has the added advantages of indicating the compositional and structural similarity to chlorites. In this way the names used to describe chlorites in the field or as the result of optical study may be retained. It would be unfair to suggest to the field worker or the petrographer that he adopt a new name for a material that he is unable to distinguish with the tools at his command. These workers will continue to refer to all chamosites as "chamosites", for example. But if a chamosite is examined by x-ray methods and found to be a 7 A mineral, it may be characterized easily by the term "septechamosite". If, on the other hand, the mineral is a normal 14 A chlorite, the name "chamosite" suffices.

It will perhaps be argued that the 7 A chlorites resemble the kaolin group of minerals very closely, and from gross structural considerations, of course, they do. It should, however, be noted that there are characteristic differences even in the x-ray diagrams. In the kaolin minerals the third and fourth order basal reflections are always quite strong with the third stronger than the fourth. The corresponding sixth and eighth order basal reflections of the septechlorites, on the other hand, are markedly weak and sometimes absent with the sixth order weaker than the eighth. Perhaps this is a result of the crystallochemical differences between septechlorites and kaolin minerals. The septechlorites are trioctahedral structures which allow a great variety of ionic substitutions. The kaolin minerals are dioctahedral and no natural or synthetic replacements of silicon or aluminum by other ions are known. The differential thermal curves of septechlorites and kaolin minerals are similar in possessing but

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4 We are indebted to W. F. Bradley for pointing out these differences which are easily verifiable (see, for example, Brindley, 1951, p. 71-73).
5 See paper by R. Roy in this volume.
a single endothermic peak, but as has already been pointed out the exothermic reaction in septimechlorites follows immediately the endothermic peak whereas it is delayed in kaolin type minerals. The fundamental difference between kaolin minerals and septimechlorites, however, is the septimechlorite-chlorite polymorphism and the possible transition from the one to the other. This relationship has been demonstrated for both natural minerals and synthetic phases. The kaolin minerals are, of course, unique entities. We feel that the structural, chemical, thermal, and mineralogical character of septimechlorites and kaolin minerals are so fundamentally different that the two should be distinguished by different names. The changes produced in the x-ray diagrams as a consequence of heat treatment in the case of amesite (Figs. 6 and 7) are misleading if described in terms of chlorite and "kaolin type" minerals. However, there is no mistaking what is meant when one refers to the chlorite from Chester as a mixture of septimeamesite and amesite. We hope mineralogists will agree that the term "septimechlorite" is a happy solution to this problem, although it is of course not so important what terms are used so long as the fundamental relations between the two types of chlorites are recognized, and are described in an unequivocal manner.

Another suggestion for the naming of these minerals is to use the prefix 7 A — or 14 A. The chief objection to this, apart from the phonetic difficulty, is the fact that in point of fact the so-called 7 A "series" really has also a 14 A unit cell. And while the reflection-series is indeed a 7 A series, a most difficult situation would arise if a series of minerals with a true 7 A unit cell and 7 A series were to be found. The nonspecific nature of the prefix "septe" therefore may serve a further useful purpose, since while it provides sufficient connotation to indicate a 7 A series of reflections, it is not specific enough to be outmoded by later work.

REFERENCES CITED


DISCUSSION

G. W. Brindley.—The results described by these authors showing the transformation of 7 A-type layers to 14 A-type layers by low temperature, hydrothermal treatments, constitute one of the most important advances of recent years in our knowledge of hydrous layer-silicate minerals.

The geometry of the transformation is less difficult to visualize than it may at first sight appear to be. It is necessary only for Si atoms to move from what may be called ‘cis’ to ‘trans’ positions in order that two kaolin type layers may change into a hydroxide layer plus a mica-type layer, i.e., a chlorite-type layer. The paper by Brindley and Gillery in this Conference discusses a relationship of this type and the co-existence within individual single crystals of both 7 A and 14 A sequences.

The energy of the transformation is a matter for separate consideration. Simple geometrical relations do not necessarily imply an easy passage from the one to the other form. The height of the potential barrier may be and probably is considerable, so that long periods at a sufficiently high but not too high temperature are required for the process.

I have only one adverse comment to make and this concerns the description of 7 A minerals which can be converted to 14 A chlorite-type minerals as “septechlorites.” The characteristic sequence of layers in true chlorites has been established for 25 years and is widely known and understood. To apply the term “chlorite,” prefixed in any manner whatsoever, to a mineral with a different sequence of layers can only lead to most serious confusion. A further objection arises from the similarity of the term to “heptaphyllitite,” but heptaphyllites are dioctahedral minerals whereas the so-called septechlorites of Nelson and Roy appear to be always trioctahedral. I hope the authors will not create future troubles by propagating this unfortunate term.

The situation, however, does require us to think seriously and fundamentally about nomenclature. Seven-A chamosites have been shown to exist, (Brindley, 1951; Brindley and Youell, 1953), while a 14A mineral, also called chamosite, exists with a chlorite-type structure; the latter may be incorrectly described and thuringite is perhaps a more appropriate name. The confusion between 7 A and 14 A chamosites is quite serious. Seven-A amesite was described by Gruner (1944), and Brindley, Oughton, and Youell (1951) have given the detailed structure, but it appears now that this 7 A type can be converted to a 14 A chlorite type. The same situation is now found for minerals of serpentine composition. The nomenclature problem is therefore an urgent one. To arrive at a solution which will meet with general approval, however, calls for a wider con-
sideration of mineralogical nomenclature since the problems involved are not peculiar to layer silicate minerals, but often arise when an attempt is made to develop a more systematic mineral nomenclature. Fleischer (1947) has discussed some of the many problems which arise.

The ratio system of designating layer structures, such as 1:1 for 7 A layers and 2:1 for 10 A layers, is useful only in a very restricted sphere of application; it is inadequate for chlorite layers and is inapplicable to the type of layer found in chloritoid. Moreover, it is not a system of general utility in mineralogy.

My personal preference is for a system of names to indicate types of crystal structure, with qualifying prefixes, generally chemical, to indicate compositions. As a principle, this may be acceptable to many mineralogists but opposition is encountered as soon as specific names are suggested. Spencer (1936) has argued that the break with tradition must be kept small, but unless a break is made with some traditions no progress towards systematic nomenclature will ever be made. I have suggested that the 7 A layer consisting of one octahedral and one tetrahedral coordination unit be called the “kaolin-type layer,” but one might usefully make a greater break with tradition and treat this layer in the manner of a chemical radical and name it “kaolin.” Kaolinite then becomes Al-kaolin and serpentine Mg-kaolin. Amesite can be expressed as Mg,Fe,Al-kaolin or, if greater precision is required, as Mg$_{1.5}$Fe$_{0.4}$Al$_{1.1}$-kaolin when the 7 A mineral is implied and Mg$_{1.5}$Fe$_{0.4}$Al$_{1.1}$-chlorite when the 14 A mineral is implied. Chamosite can be similarly treated. The polymorphic forms of kaolinite, (dickite, nacrite), can be adequately described in the same manner as the polymorphic forms of mica or of zinc blende. Dickite then becomes 2-layer Al-kaolin and nacrite 6-layer Al-kaolin. The orthoantigorite described by the writer elsewhere in this symposium would become 2-layer Mg-kaolin, or (if the ortho character must be expressed to distinguish from monoclinic forms) 2-layer Mg-orthokaolin.

I do not, however, advocate the immediate acceptance of this or of any other scheme of nomenclature before its discussion by a sufficiently representative group of mineralogists. The term “septechlorite,” from which this discussion arises, seems to me to be such an unsuitable term that it should be kept in cold storage until opportunity arises for a thorough discussion of nomenclature problems.

REFERENCES


Rustum Roy.—1. The authors are willing to accept any name agreed on by the present group.

2. May I add a few remarks to those by Mr. Nelson in support of our view that a new name is required for these 7A minerals. Since it is a distinct mineral species, actually a whole series such as the micas, a single new name is not suitable. Moreover, several minerals which must belong to this species have been labelled antigorite and, indeed, "antigorites" would be an eminently suitable name were it not for the fact that it has already been applied to a large number of minerals without much discrimination. The term "kaolinite-like" is both too cumbersome and not sufficiently precise. From other detailed studies of synthesis among 2-layer sheet structures we have been able to show that kaolinite is a unique dioctahedral 2-layer assemblage which is not formed by any other ion, and one which will not even admit small amounts of similar ions into its lattice. The name sepetechlorite has been suggested largely because it leaves the reader or user with several desirable connotations. The "septe" prefix is expected to suggest the 7A (i.e., two layer assemblage); the retention of "chlorite" is even more desirable. These minerals are related to the chlorites by a mere polymorphic rearrangement; they often occur intimately mixed with the chlorites; they may be converted to chlorites by proper treatment in the laboratory; they cannot be distinguished from chlorites in the field or in the laboratory without x-ray examination.

3. We heartily agree with Prof. Brindley that a thorough overhaul of the nomenclature of the clay minerals is long overdue. In the absence of such, and even perhaps if it does occur, a case could still be made for the term "sepetechlorite" (or a substitute) as stated in the remarks above and also on the ground that it is not too satisfactory to lump dioctahedral and trioctahedral minerals under one name as he suggests.