

DIAGNOSTIC CRITERIA FOR CLAY MINERALS*

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ABSTRACT

The value of the utilization of complex formation between clay minerals and suitable types of organic liquids in the identification and characterization of clay minerals is illustrated by means of a series of such complexes between ethylene glycol and various clay minerals. Particular attention is devoted to mixed layer minerals involving intergrowth of montmorillonite with illite.

Recent observations on molecular associations between organic liquids and the montmorillonite type of clay minerals (1) have suggested that similar associations may be used to classify the other clay minerals. Not only is it true that many organic materials are available which associate with montmorillonites in a clearly characteristic manner, but there is an extensive list of incompletely characterized clays in which low-temperature water seems sufficiently important that one might anticipate similar associations.

For the limited number of observations reported here, the following thoughts have guided the choice of illustrative examples. The associations of poly oxygen compounds with montmorillonite are assumed without the complicating factor of base exchange, and of these, the complex that contains ethylene glycol, the simplest molecule, invariably gave an excellent clearly characteristic x -ray diffraction diagram. Ethylene glycol is both small enough to minimize possibilities of steric hindrance and sufficiently non-volatile to keep clay specimens damp during the registration of diffraction patterns, even though no complex may have been formed.

THE MONTMORILLONITE GROUP

Associations of montmorillonites with organic materials have been studied from time to time (2, 3, 4, 5) and have been the basis of Hendricks and Alexander's color reaction for the group (6). X -ray diffraction diagrams represent only one of the methods by which montmorillonites are habitually recognized. Justification for the further complication of utilizing x -ray diffraction from chemically treated preparations must come from the characteristically more clean-cut appearance of patterns. Natural minerals of the montmorillonite group afford diffraction patterns which vary enormously in the relative prominence of the basal reflections (commonly used as the diagnostic criterion) and of the prismatic reflections, to say nothing of the variations in diffraction angle for the first order of the base, and the vast differences in the perfection of develop-

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ment of succeeding orders. Montmorillonites soaked in glycol and drained dry before registration of the diffraction diagram have invariably afforded a clear sequence of higher orders of diffraction from the base, of greater intensity relative to prismatic reflections than are observed for natural materials, and representing a c -axis length not appreciably affected by previous history or humidity. This configuration has been interpreted to represent individual montmorillonite layers interleaved with double layers of glycol molecules, comprising a periodicity along c^* of

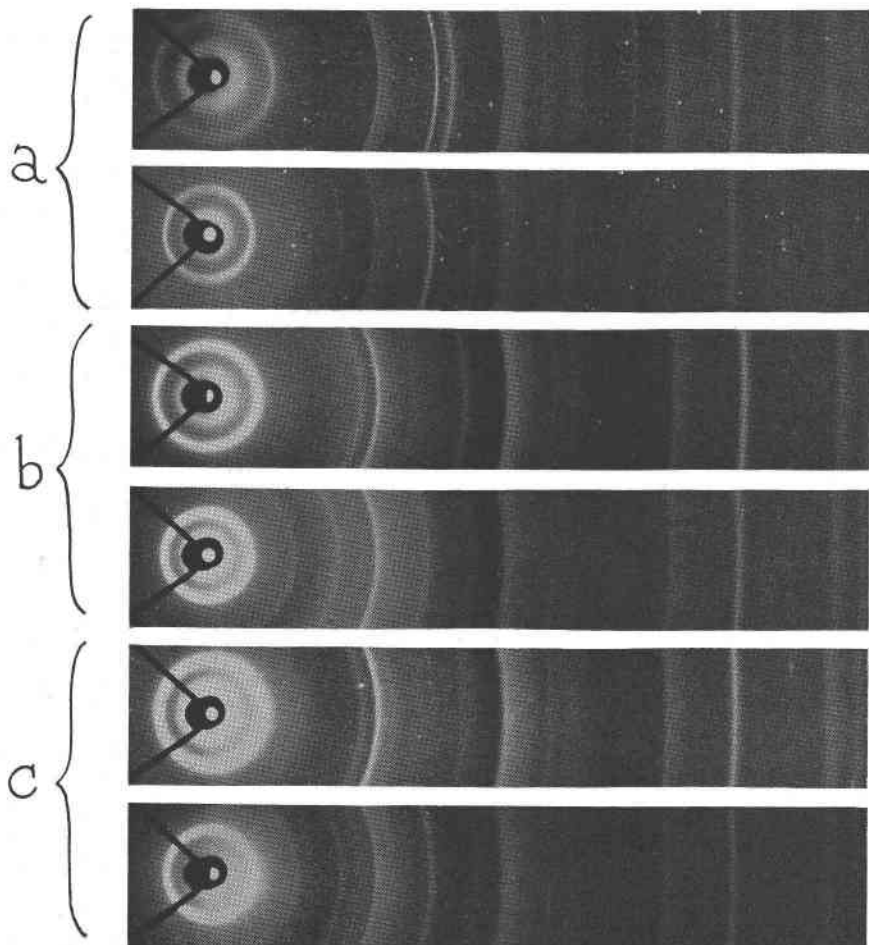


FIG. 1. X-ray powder diffraction diagrams of natural montmorillonites compared with the diagrams after glycol treatment. (a) Wyoming bentonite; (b) pink montmorillonite from Tatatila, Vera Cruz, Mexico, U. S. Nat. Mus. no. 101836; (c) montmorillonite from Rodeout, Utah. Natural clay above, and treated material below for each.

17 Å. Diagrams have looked about equally clear for glycol complexes prepared from natural materials for which, when untreated, the higher orders of the base were: (a) clear and related to a 12.5 Å periodicity; (b) clear and related to a 15 Å periodicity; or (c) poorly defined or missing. Illustrative examples are shown in Fig. 1. In cases where montmorillonite is only a minor component in the presence of other material, diffraction effects from the complex are also more easily discerned than are those of the untreated material.

THE KAOLINITE GROUP

The kaolinite group of minerals, kaolinite, nacrite, and dickite, include no molecular water in their crystallizations, and exhibit no reactions with liquids which can be followed by diffraction methods. It is undoubtedly true that there is strong adsorption of organic liquids on the crystallite surfaces, as shown in the properties of materials like plasticene (or modelling clay), but the actual crystallization (and diffraction patterns) are unaltered.

ENDELLITE AND HALLOYSITE

An unfortunately confused state of nomenclature with regard to halloysite has recently been resolved by the proposal of "endellite" as a name for the hydrated member (7).

Both minerals are recognized readily enough on the basis of their normal diffraction diagrams, but their behavior toward the organic liquids is interesting. The displacement of molecular water from endellite by ethylene glycol (and by other solvents) both serves to confirm its structure and is an unmistakable criterion of identity.

The characteristic strong diffraction line of endellite at 10.1 Å is displaced to 10.8 Å in the ethylene glycol complex. First, third, and fifth orders from this spacing, which is the complex thickness, are apparent in each case. These thicknesses represent the thickness of a kaolinite layer plus, respectively, one water layer of about 3.0 Å and one glycol layer of about 3.6 Å. In contrast with the montmorillonite complexes, which have two layers of glycol, it is pointed out that endellite has only one oxygen surface and montmorillonite has two oxygen surfaces available. It is assumed that the stability of each configuration is governed by the attraction of the oxygen surfaces for the slightly active methylene groups.

The dependence of the mean refractive index of endellite on the constitution of the index oils was noted by Correns and Mehmel (8) but was questioned by Faust et al. (7). It is clear that the indices of complexes of the sort here described must differ appreciably from those of the natural

mineral. The calculated mean index for endellite is 1.49, and an estimated index for the glycol complex, based on the molecular volume of liquid glycol is 1.52, probably ± 0.01 . The observed index for the complex is 1.525, determined by rapid comparison with liquids made up from mineral oil and monochloronaphthalene. The endellite for this preparation was selected from material from Eureka, Utah, and did not contain more than 5 or 10 per cent of halloysite. Complexes of endellite with

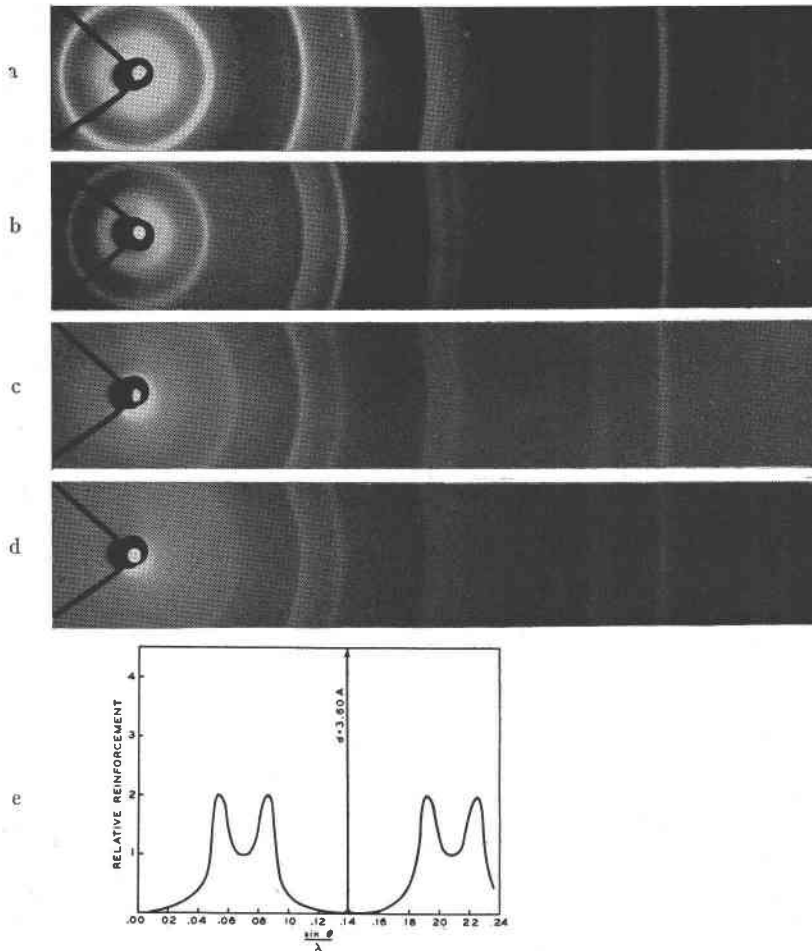


FIG. 2. The association of ethylene glycol with halloysite. (a) natural endellite; (b) endellite treated with ethylene glycol; (c) halloysite resulting from aging of (a); (d) halloysite treated with ethylene glycol; and (e) a plot of Hendricks and Teller's function for units of 10.8 and 7.2 Å, plotted to the approximate scale of the diffraction diagrams. The arrow indicates the position of normal reflection.

other active liquids (1) would also have indices ranging from 1.52 to 1.55.

Halloysite derives from endellite upon loss of the molecular water. The resultant material is very porous, retains its original bulk, and readily absorbs water, but the structural change from the endellite crystallization to a kaolinitic crystallization is irreversible, or at best incompletely reversible. Wet halloysite specimens give essentially the halloysite diffraction diagram.

The diffraction diagram of halloysite wet with ethylene glycol differs in a distinctive way from those of endellite, halloysite, or kaolinite. The prismatic interferences of endellite and halloysite are unchanged, but of the possible interferences related to the base, only one line, at 3.6 Å, appears sharp and well-defined. In the region corresponding to periodicities from about 11 to about 7 Å, there appears only a broad weak band, in which the intensity seems to be somewhat higher near its edges.

The function derived by Hendricks and Teller (9) for mixed layer minerals applies only to equally probable units of the same form factor. In the absence of suitable information about the form factors it is impractical to attempt to compute a theoretical intensity distribution for this case (as will later be done for a more apt example), but a comparison of the plot of Hendricks and Teller's function with the diffraction diagram in Fig. 2 indicates clearly that a random or near random interleaving of 10.8 and 7.2 Å units would produce the same sort of diagram as is observed. Actually, it seems indicated that simple 7.2 Å units outnumber the complex 10.8 Å units, but the characterization of halloysite as the collapsed structure subject to random penetration of active liquids, seems justified.

ILLITE

Although illites invariably contain more or less molecular water, as is apparent from thermal analysis curves (10), the crystallization is determined by mica principles, and the position in the structure of any water not merely absorbed on exterior surfaces is not known. Treatments of illite with organic liquids do not therefore result in any structural changes, and diffraction diagrams do not differ from those of the untreated materials. The frequently encountered instances in which illites are observed to be mixed with extraneous layers are discussed in connection with the mixed layer minerals.

MIXED LAYER MINERALS

Several instances have been reported (11, 12, 13, 14, 15) in which it seemed that a specimen under consideration was actually composed of irregularly alternating layers of two distinct minerals. The treatment of

diffraction effects from such mixed layers by Hendricks and Teller (9) has afforded a basis on which one can hope to examine in detail some of these suspected instances.

A particularly fortunate case has been that of some bravaisite from the type locality, U. S. Nat. Museum Specimen No. 4918.* A study has shown not only that this material is about equally divided between two species, but also that the two form factors are similar enough to permit a reasonably accurate construction of the calculated diffraction effects.

Grim and Rowland (10) concluded from thermal analysis curves that this material included both illite and montmorillonite. If it be assumed, then, that this material be made up of a random stacking of equally probable illite and montmorillonite layers, one case can be developed for the natural material itself, and a second case can be developed for the mixture of illite with glycol-complexed montmorillonite which would result from glycol treatment.

In connection with the previous study of complexes of montmorillonite with various types of organic liquids (1), observed $00l$ diffraction sequences from a series of complexes of varying cell heights have been available. Estimated intensities for the powder diffraction rings for this entire group have been plotted together against $\sin \theta/\lambda$, and Fig. 3 is a

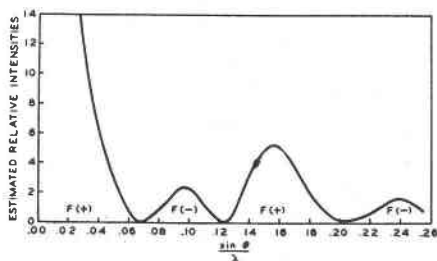


FIG. 3. Composite curve of estimated relative intensities of $00l$ powder diffraction rings versus $\sin \theta/\lambda$ taken from a group of organic molecule-montmorillonite complexes of various c -axis periodicities.

smooth average curve summarizing the composite data. Although each individual diagram has been rather strongly influenced by the organic matter, the allowable degree of error for the present purposes is so great that this curve adequately represents not only the contribution of the montmorillonite layers, but also the contribution of the similarly constituted, but rigid, illite layers.

To arrive at the angular distribution of scattered radiation from the random mixed layer sequences assumed, then, it is only necessary to

* Furnished through the courtesy of Dr. W. F. Foshag.

multiply the ordinates of Hendricks and Teller's function for each case by the ordinates of Fig. 3. In Fig. 4 curves derived in this way for a mixture of 10 Å and 15 Å units, and of 10 Å and 17 Å units are compared with the diffraction diagrams of bravaisite and of glycol treated bravais-

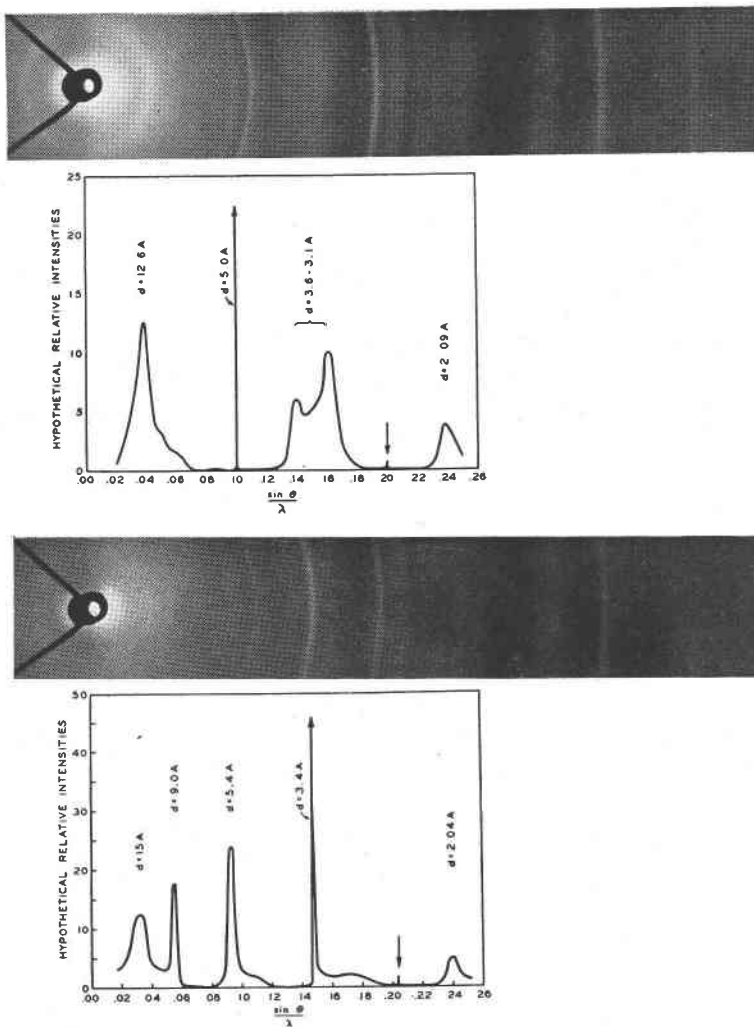


FIG. 4. Bravaisite, Noyant Allier, France, U. S. Nat. Mus. no. 4918 (above) and the same treated with ethylene glycol (below), each compared with its synthesized curve for random mixed layers to scale approximately equivalent to the diffraction diagram. Erect arrows indicate positions of normal or near normal reflection. Inverted arrows indicate normal reinforcements in the mixing function which are extinguished by the form factor.

ite, respectively. Reasonable agreement in the position, relative intensity, and apparent breadth of all the important maxima is evident.

No other instance has been encountered in which the relative frequencies of illite and montmorillonite layers are nearly enough equal to conform to Hendricks and Teller's equation. However, the principle can probably be extended in a qualitative way to cases in which one species predominates over the other to a moderate extent. If for example, illite occurred more frequently than montmorillonite, we would expect from

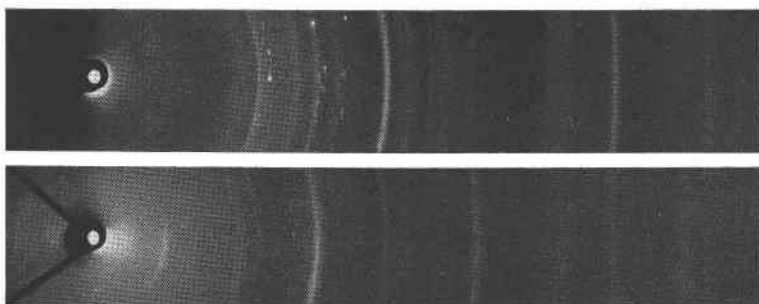


FIG. 5. Powder diffraction diagram of "glimmerton," Sarospatak, Hungary, from U. Hofmann, treated with ethylene glycol (above), compared with illite purified from shale from Alexander County, Illinois, after the same treatment (below).

inspection of the function that in general maxima would approach the position of the sharp interference maxima of illite. For the natural material, where the form factor extinguishes one of the small-angle maxima of the complex function, the diagram would only more nearly resemble illite. For glycol-treated material, however, both of the small-angle maxima should persist and should merely approach each other.

Among the natural materials in which two small-angle maxima are developed by glycol treatment are several which have heretofore been described as illites or at least as mica-like clays. These include the "glimmerton" from Sarospatak, Hungary (16), the illite purified from an underclay in Grundy County, Illinois (17), a "metabentonite" from High Bridge, Kentucky (10), and possibly some glauconites. In Fig. 5 the diagram for glycol-treated "glimmerton" is reproduced. For specimens with lesser proportion of montmorillonite layers the diagrams are less clear. The ratio of mica to montmorillonite layers in the "glimmerton" is probably near 2; in the other cases, somewhat higher. A diagram of a glycol-treated illite, unmixed with extraneous layers, is included for comparison.

Mixed layer minerals of other types also no doubt exist, of which par-

ticularly a mixture of montmorillonite and illite with montmorillonite predominating should be amenable to interpretation by this method, but no clear cut occurrence has yet been recognized.

MISCELLANEOUS MINERALS

The number of hydrous clayey or clay-like minerals which have been described and named is too great to attempt to catalogue them here. Probably the greatest number of these are the varieties which are actually members of the montmorillonite group. Most of the specimens of this sort reported on by Grim and Rowland (10) have been made available for examination in this study. The characteristic 17 Å glycol complex is readily prepared from all of the so-called beidellites discussed by them, except their number 8 Å (U. S. Nat. Museum no. R7595), from the nontronites, the white Hector magnesium clay, smectite, chloropal, and volkonskoite.

Loosely related to these materials are two other mineral types in which comparable structural units appear, the vermiculites and attapulgite.

Vermiculites.—Although the ideal structure of vermiculite (12) immediately suggests that the interlayer water could be displaced by organic liquids, no attempts to make such complexes from the familiar crystalline materials have yet been successful. However, a series of cryptocrystalline weathered amygdules collected by Dr. R. M. Grogan from basic Keweenawan flows along the north shore of Lake Superior, which have been identified as vermiculites by x-ray diffraction methods, do form the same sort of 17 Å glycol complex as is observed for montmorillonites. In view of the known tendency for vermiculites to occur mixed with chlorites, it seems quite possible that such mixing, particularly if it were lateral within layers, might inhibit the introduction of glycol into the natural large crystals even though it would be readily introduced into a fine-grained, or into an ideal specimen.

Attapulgite.—The association of any individual water molecule with the silicate portion of attapulgite is probably due to hydrogen bonding, analogous with that exhibited by the water associated with montmorillonite, but the disposition of the silicate chains (18) confines the water to narrow channels and precludes the changes in dimensions that are observed for swelling clays. The water channels have cross sections of about 3.7×6.0 Å, which might accommodate single strings of ethylene glycol, but in the absence of dimensional changes, only minor intensity variations are to be expected upon glycol treatment, and no obvious variations were noted in the diffraction diagrams. Refractive indices, however, are sharply reduced. Well-oriented flakes with $\gamma = 1.540$,

$\gamma - \alpha = .032$, showed after treatment $\gamma = 1.50$ with comparable birefringence. The calculated mean index for the silicate skeleton above is about 1.44. The observed indices can therefore apparently be considered to arise from extensive extraction of the hydrogen-bonded water accompanied by only very limited penetration of glycol into the channels.

SUMMARY

The association of certain organic liquids with clay minerals affords a basis for the classification of such minerals into the principal groups, and at the same time serves to confirm the general features of the respective structures.

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REFERENCES

1. BRADLEY, W. F., *J.A.C.S.*, **67**, 975-981 (1945).
2. GIESEKING, J. E., *Soil Sci.*, **47**, 1-13 (1939).
3. HENDRICKS, S. B., *J. Phys. Chem.*, **45**, 65-81 (1941).
4. DAVIDSON, R. C., EWING, F. J., AND SHUTE, R. S., *Natl' Pet. News*, **35**, No. 27, R318-321 (1943).
5. MACÉWAN, D.M.C. *Nature*, **154**, 577-578 (1944).
6. HENDRICKS, S. B., AND ALEXANDER, L. T., *J. Am. Soc. Agron.*, **32**, 455-458 (1940).
7. ALEXANDER, L. T., FAUST, G. T., HENDRICKS, S. B., INSLEY H., AND McMURDIE, H. F., *Am. Mineral.*, **28**, 1-18 (1943).
8. CORRENS, C. W., AND MEHMEL, M., *Zeits. Krist.*, **94**, 337 (1936).
9. HENDRICKS, S. B., AND TELLER, E., *J. Chem. Phys.*, **10**, 147-166 (1942).
10. GRIM, R. E., AND ROWLAND, R. A., *Am. Mineral.*, **27**, 746-761, 801-818 (1942).
11. GRUNER, J. W., *Am. Mineral.*, **19**, 557-575 (1934).
12. HENDRICKS, S. B., AND JEFFERSON, M. E., *Am. Mineral.*, **23**, 851-862 (1938).
13. GRUNER, J. W., *Am. Mineral.*, **29**, 422-430 (1944).
14. JACKSON, M. L., AND HELLMAN, N. N., *Proc. Soil Sci. Am.*, **6**, 133-145 (1941).
15. NAGELSCHMIDT, G., *Mineral. Mag.*, **27**, 59-61 (1944).
16. MAGDEFRAU, E., AND HOFMANN, U., *Zeits. Krist.*, **98**, 31-59 (1937).
17. GRIM, R. E., AND BRADLEY, W. F., *J. Am. Cer. Soc.*, **22**, 157-164 (1939).
18. BRADLEY, W. F., *Am. Mineral.*, **25**, 405-410 (1940).