

EXPANDABLE CHLORITIC CLAY MINERALS FROM
UPPER MISSISSIPPIAN CARBONATE ROCKS OF
THE CUMBERLAND PLATEAU IN TENNESSEE

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ABSTRACT

The mineral assemblages of upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee may be considered in a six component system: $MgO-CaO-Al_2O_3-SiO_2-CO_2-H_2O$, and within this choice of components, the assemblages may be plotted on a ternary diagram $MgO-CaO-Al_2O_3$. CO_2 and H_2O are considered "perfectly mobile" and SiO_2 is present in excess. Compositional variation of the expandable chloritic minerals, determined by x-ray criteria, lies between the compositions of vermiculite and corrensite, and is consistent with the topologic requirements of the ternary diagram. Mixed-layer ordering, like that found in corrensite, occurs only in chlorite-vermiculite having a composition near a 1:1 ratio of chloritic to vermiculitic layers.

INTRODUCTION

Expandable chloritic clay minerals have been described from a number of localities in the United States and Europe. Many of these clays may be characterized as mixed-layer chlorite-vermiculites (Weaver, 1956). Some are randomly interstratified, and others have a basal spacing (001) near 29 Å, indicating that at least some of the material has a regular alternation of vermiculitic and chloritic layers. Lippman (1954) has proposed the name corrensite for the ordered material.

Table 1 summarizes described occurrences, in sedimentary rocks, of corrensite, or of materials which, on the basis of information given, seem to be corrensite. Two other occurrences of similar material, or hydrothermal origin, have been reported by Sudo *et al.* (1954) and Bailey and Tyler (1960).

Both random mixed-layer chlorite-vermiculite and corrensite have been found in Upper Mississippian rocks of the Cumberland Plateau in Tennessee. They were encountered during a study of the complete mineralogy of this group of rocks. The broad intentions of the study were to determine mineral assemblages, and to relate these assemblages to textures and general stratigraphy (Peterson, 1960).

During the investigation it became apparent that the expandable chloritic minerals displayed significant variations in composition and structure. These minerals will be discussed within the context of the lithologies and mineral assemblages in which they occur.

LITHOLOGY

Carbonate rocks of upper Mississippian strata of the Cumberland Plateau in Tennessee have exceptionally well preserved original sedi-

TABLE 1. PREVIOUSLY DESCRIBED OCCURRENCES OF CORRENSITE FROM SEDIMENTARY ROCKS

Described by:	Spacings in Å:				Lithologic and Mineralogic Associations
	Untreated (001)	Untreated (002)	Glycolated (001)	Glycolated (002)	
Lippman (1954)	28.3	14.2	32-33	16.2	Middle Keuper of southern Germany. Marls show evidence of desiccation.
Earley <i>et al.</i> (1956)	29.		32		Yates formation, Permian of West Texas. Argillaceous siltstone. Quartz, feldspar, mica and dolomite.
Bradley and Weaver (1956)	29.	14.6	31.	15.5	Brazer formation, upper Mississippian of Colorado.
Lippman (1956)	29.	14.5	31.	15.5	Rot member of the Triassic, near Gottingen, Germany. Red and green shales. Siltstone and sandstone. Dolomite, halite and gypsum.
Braitsch, O. (1960)	30.	14.15	31.7	15.6	Stasfurtsalz, Permian, Reyershausen, Germany, Evaporite section.
Grim, R. E. <i>et al.</i> (1960)	30.0	14.48			Salado formation, Permian of Carlsbad, N. M., Evaporite section.
Echle, (1961)	29.4	14.6	31.1	15.44	Keuper near Gottingen, Germany. Dolomitic red bed sequence.

mentary structures; relatively little recrystallization has taken place. Fragments of some shells still have crystallites that appear to be oriented as they originally were in the organism. Also, many oolites have radial structure. Most of these carbonate rocks are very pure. Insoluble residues are usually less than five per cent and commonly only a few tenths of a per cent of the rock.

Strata from which specimens were collected are almost undeformed and dips are of the order of one degree. Younger Mississippian sandstones, shales and carbonates (Pennington group) have a maximum thickness of 500 feet (Vail, 1959); overlying Pennsylvanian formations have a composite thickness of 4,000 feet (Wilson *et al.*, 1956). Disregarding the possibility that rocks younger than Pennsylvanian in age were at one time present, 4,500 feet is a reasonable value for maximum burial. Such a depth of burial would correspond to about 400 bars of load

pressure if the pressure is assumed to have been hydrostatic. Specimens were collected, for the most part, from quarries and new road cuts, particular attention being given to sampling fresh and unweathered material.

These carbonate rocks exhibit a large range of textures including oolitic, fossiliferous fragmental, fine grained or microcrystalline and very fine grained or cryptocrystalline. Dolomitic rocks have proportions of dolomite varying from a barely detectable trace to 100%. Rocks containing an appreciable amount of dolomite are all fine grained, and may or may not contain scattered fragments of fossils or oolites. Many original features, such as thin bedding laminations, micro-cross-bedding, pre-lithification intrusions of soft sediment from overlying or underlying strata, and small pebbles of different lithologies, are present in beds of this type. Commonly these features are visible because of differences in dolomite content. Other rocks containing dolomite in only small amounts are composed, for the most part, of very small oolites.

METHODS

Clays were extracted from carbonates by leaching the finely ground specimen, at room temperature, in a solution of acetic acid buffered at pH 4.5 with lithium acetate. Solution of dolomite is quite slow at this pH; it was usually necessary to allow reaction to proceed for about a day if much of it was present, even if the specimen was finely ground. Specimens that were mainly calcite leached much faster.

The highest possible pH consistent with a reasonable amount of time for leaching was chosen in order to do the least amount of damage to acid soluble clay minerals, especially those of chloritic type. Li^+ was chosen because it would be one of the ions least likely to replace other ions already in the clay structure (Grim, 1953, p. 147, Gedroiz, 1922). During the leaching process Ca^{++} and Mg^{++} ions are also produced. To keep the concentration of these ions low, a large excess of leaching solution was used. The solution was well buffered and change in acidity was less than 0.5 pH unit during the digestion of a specimen. About one gram of rock usually gave enough clay to prepare an oriented aggregate for x -ray diffraction purposes. Diffraction charts of clays left in the leaching solution for a week show no appreciable change from charts of clay minerals from the same specimen allowed to leach for only one hour.

The extracted clays and other insoluble materials were washed in distilled water several times to remove salts, so that the clays dispersed easily in aqueous suspension. Rapid centrifuging was used to expedite the process. Oriented aggregates of the clays were prepared for x -ray

diffraction study by allowing an aqueous suspension of the smaller than two micron fraction to dry on a microscope slide at slightly above room temperature, and then to remain at room temperature and humidity for several hours before study. Separation of the size fractions larger and smaller than 2 microns was done by centrifuging in aqueous suspension. Measurements of clay particles on electron photomicrographs verified that the amount of centrifuging used removed most of the particles larger than two microns; virtually all of the quartz grains were larger than two microns.

Minerals on the slides were identified using a Norelco recording Geiger counter diffractometer. Copper radiation and a nickel filter, scanning speed of $1^\circ 2\theta$ per minute, chart speed of $\frac{1}{2}$ " per minute, tube voltage of 45 kv. and current of 2θ amperes, and a time constant of 4 seconds were used. The divergent, scatter and receiving slits were 1° , 1° , and $.003$ " respectively. Heights of peaks were recorded as proportional to counts per second, rather than on a logarithmic basis. Heat treatment for the selective destruction of clay minerals was accomplished by loosely wrapping the slides in aluminum foil and heating for one hour at 215° C. and then again, after a diffractometer chart had been prepared, for one hour at 550° C.

Dolomite and calcite were identified by the presence of their principal peaks on x -ray diffractometer charts of the samples. The lower detection level, in untreated samples, was 0.2%. The presence of traces less than this was determined from x -ray diffractometer charts of insoluble residues which were prepared by digesting the ground rock, until all calcite was removed, in a solution of acetic acid buffered at pH 5 with ammonium acetate. For specimens containing more than 0.2% dolomite, the pH of the leach was adjusted to 4.5 in order to dissolve the dolomite also. Other trace minerals, such as albite, were identified from these charts. A thin section was prepared for each specimen.

Samples were chosen to be representative of all major lithologies in the stratigraphic sequence. Some of these lithologies contain nodular localizations of certain minerals, such as chalcedony (chert), dolomite and calcite. This introduces a sampling problem if one is trying to describe the typical mineralogy of a rock type. Fortunately such localizations usually form a very small proportion of the total rock, and samples were chosen purposely to avoid them. A total of 77 samples was studied.

CRITERIA OF CLAY MINERAL IDENTIFICATION

10 Å clay

A 10 \AA basal spacing and its associated integral series of higher order (001) reflections, which did not expand upon solvation with ethylene

glycol, was taken to be indicative of a clay with muscovite structure. The basal peak was usually seen to be asymmetric, as is common for "illite." Several determinations of the (060) spacing near 1.51 Å showed these specimens to be dioctahedral. This mineral will hereafter be referred to as muscovite. A small amount of glauconite, the only mineral likely to interfere with this determination, was evident in thin sections of two samples. When found, it was always in specific textural elements, such as inside of foraminifera, and was quantitatively unimportant.

Montmorillonite Containing Some Mixed 10 Å Layers

A broad basal peak, occurring anywhere between 10 Å and 13 or 14 Å, that readily expanded by solvation with ethylene glycol, and collapsed to about 10 Å upon heating to 215° C. was taken to indicate the presence of montmorillonite or montmorillonite containing some mixed 10 Å layers. (It was not necessary that a mineral expand all the way to 17 to 18 Å, as is common for true montmorillonite, for it to be placed in this category.) In some instances, only a small proportion of the clay sample was of this type of mineral, so no attempt was made to distinguish between true montmorillonite and montmorillonite containing non-expanding 10 Å layers.

Non-Expandable Chlorite

An integral series of peaks associated with a basal spacing of about 14.2 Å, that does not expand by solvating with ethylene glycol, identifies normal chlorites. Odd order reflections were weaker than even orders, but they were always clearly present. This is quite different from some of the weathered chlorites of modern sediments, for which the 14 Å peak may be almost completely missing. Commonly the non-expandable chlorite can be detected only after interfering lines of expandable chloritic minerals have been shifted by solvating with ethylene glycol (Fig. 1a, 75-9). The 14 Å and 7 Å peaks of the non-expanding chlorite remain unchanged upon heating to 215° C.

Chlorite-Vermiculite

A basal spacing of from 14.2 to 15.2 Å, that expands to a larger spacing upon solvating with ethylene glycol, and an associated series of peaks that is very nearly integral, indicates the presence of chlorite-vermiculite. Expansion is not the same for all samples, but is related to the spacing of the untreated material, such that the specimens showing the largest original spacing also expand the most (Fig. 1a, 78-6 and 75-9). Shifts in peak position are sufficient to reveal non-expandable chlorite, commonly present only in very small amounts. Heating the specimen to 550° C.

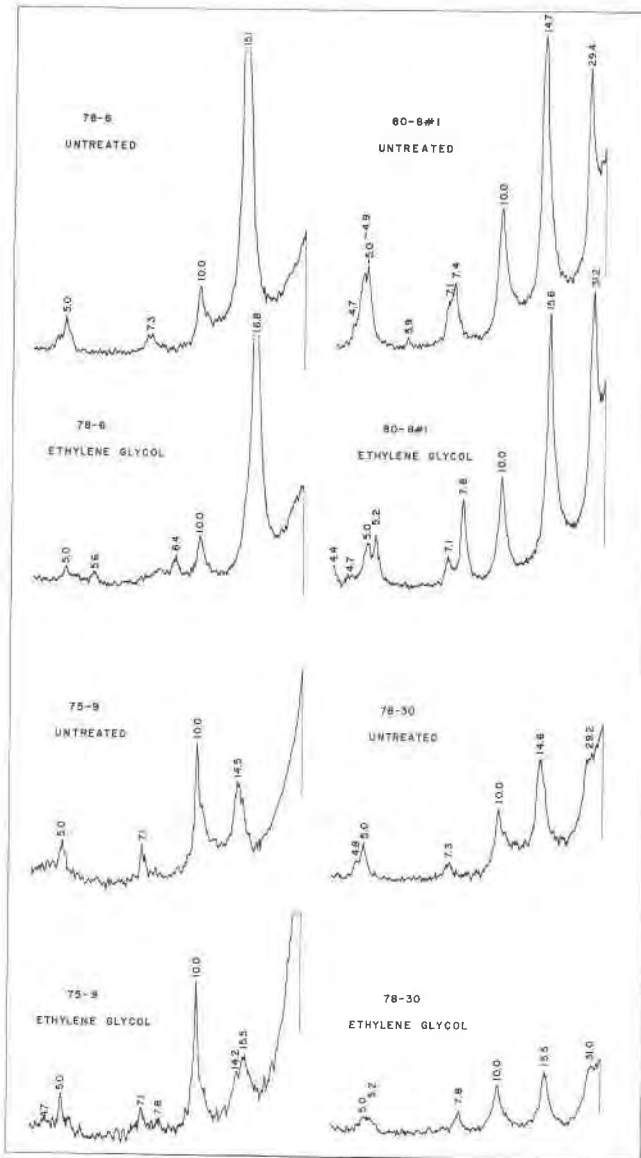


FIG. 1a X-ray diffractometer charts of samples of corrensite (80-8 No. 1 and 78-30) and chlorite-vermiculite (78-6 and 75-9) showing the differences in basal spacings of the air dried and glycolated samples. The specimens having the largest initial basal spacings expand the most upon solvation with ethylene glycol.

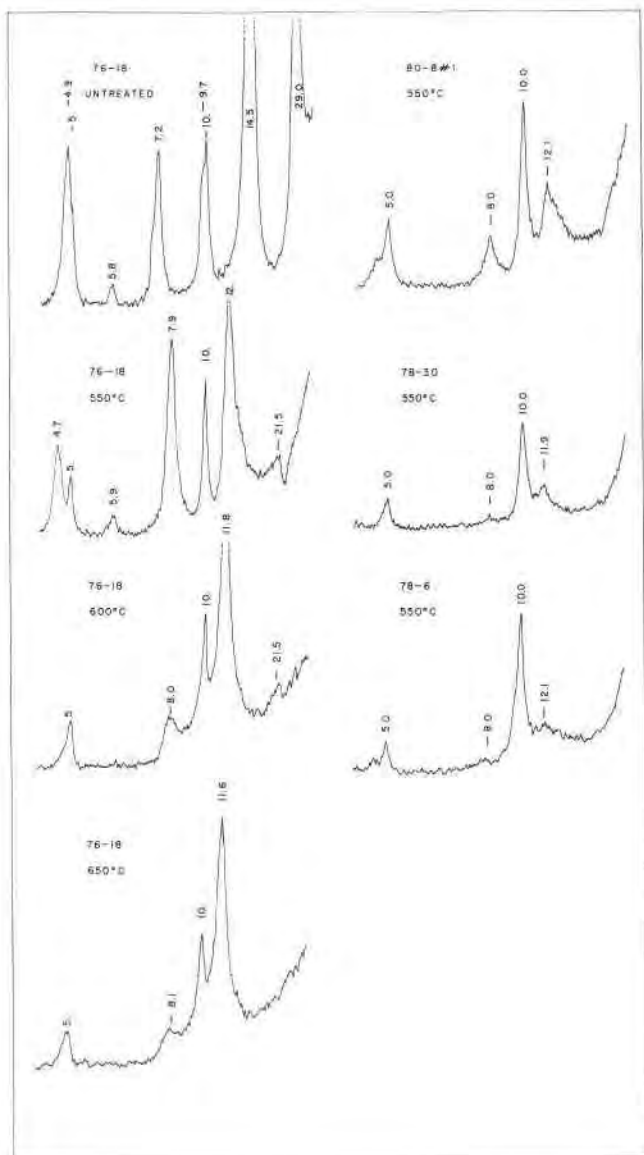


FIG. 1b X-ray diffractometer charts of samples of corrensite (76-18, 80-8 No. 1, and 78-20) and chlorite-vermiculite (78-6), showing the effect of heating. The non-integral character of the basal series is apparent from the manner in which the "7 Å" peak migrates toward lower angles upon heating.

verifies the identification, because the basal series behaves in a non-integral manner as the mineral collapses (Fig. 1b).

Corrensite

A basal spacing of from 28.5 to 29.5 Å is the essential criterion for corrensite (Fig. 1a, 80-8 No. 1, 78-30). The validity of using this spacing as the only feature of the mineral distinguishing it from chlorite-vermiculite will be discussed.

The (060) spacing is represented by an obvious line, in powder pattern, corresponding to 1.55 Å, and indicates that the mineral is trioctahedral. Other sedimentary clays of this type have also been described as trioctahedral by Bradley and Weaver (1956) and Lippman (1956). The chlorite-montmorillonite reported by Earley, *et al.* (1956) also appears to be trioctahedral on the basis of the fairly intense line at 1.54 Å. On the other hand, similar minerals of hydrothermal origin seem to be dioctahedral. Sudo, *et al.* (1954), report such a mineral from a fireclay mine, and Bailey and Tyler (1960) report another from an altered dike in an iron mine, the (060) spacings of which are 1.492 Å and 1.507 Å respectively.

The name corrensite is restricted, in this paper, to the trioctahedral mineral.

Kaolinite

No kaolinite was found in these samples. The important problem in identifying kaolinite is to distinguish its 7 Å basal spacing from the second order peak of non-expanding chlorite and chlorite-vermiculite, and from the fourth order peak of corrensite. Expansion with ethylene glycol will reveal the 7 Å peak masked in the untreated specimen by higher order peaks of corrensite and chlorite-vermiculite. This peak could belong either to non-expanding chlorite or to kaolinite. Well crystallized metamorphic or hydrothermal chlorite breaks down, upon heating, at temperatures above those at which kaolinite loses its crystallinity, whereas more or less degraded sedimentary chlorites break down at lower temperatures than does kaolinite. Some *a priori* judgment of the variety of chlorite is needed before thermal destruction can be used to discriminate between chlorite and kaolinite. Another convenient method for selective destruction of chlorite is leaching in strong, warm acid. Overnight treatment with a warm solution of one part water to one part concentrated HCl is sufficient to completely destroy chlorite. Thus, if the 7 Å peak is reduced in intensity or destroyed, upon acid treatment, the presence of chlorite is more clearly demonstrated. Reduction in intensity of the 7 Å peak, because of disorientation of mineral flakes during treatment, would be difficult to distinguish from destruc-

tion of one of the minerals contributing to it. This difficulty was not encountered, because destruction of the peak was always complete, indicating that no kaolinite was present. The presence of a significant 14 Å peak that does not expand also indicates that some, if not all, of the 7 Å peak is from chlorite.

GENERAL MINERALOGY

Dolomite and calcite are the only two carbonates found. All but three specimens contain some calcite, and about one half of the specimens contain some dolomite. The dolomite, in all but one instance, has between 3% and 6% excess Ca, determined by $d(211)$ (Goldsmith and Graf, 1958). X-ray spectrographic analyses indicate that the iron content of the dolomite is not sufficiently high to invalidate this determination. The calcite has an average $d(211)$ corresponding to a Mg content of 0.5 to 1%. The method employed would have detected either ferroan-dolomite or siderite if they were present in significant quantities but neither was found.

Quartz is present in every specimen studied, either in the form of detrital grains, doubly terminated euhedra, or small authigenic overgrowths on detrital grains, or as cherty replacement of carbonate.

Potash feldspar and albite are present in some specimens. Albite, visible in thin section, is in euhedra that are clearly authigenic. Potash feldspar, not seen in thin section, is detected only in diffractometer charts of insoluble residues, and may be either detrital, authigenic or both; no distinction was made between its different structural states.

Of the clay minerals, a 10 Å phase, probably muscovite, is the only one present in every sample. Glauconite was identified in thin section in two specimens. Non-expanding chlorite, usually present only in very small quantities, was clearly identified in about two thirds of the samples; montmorillonite was distinguished in about one eighth of them. No kaolinite was found. Corrensite or chlorite-vermiculite is present in almost every sample.

MINERAL ASSEMBLAGES

In summary, the major minerals present are calcite, dolomite, corrensite, chlorite-vermiculite, montmorillonite, quartz and muscovite. Of these quartz and muscovite are in all samples. The remaining minerals fall into the following assemblages:

1. dolomite, corrensite
2. dolomite, calcite, corrensite
3. calcite, corrensite
4. calcite, chlorite-vermiculite
5. calcite, chlorite-vermiculite, montmorillonite

The simplicity of these mineral assemblages, and the uniformity with which they occur suggest that methods applicable to the portrayal of certain metamorphic mineral assemblages may also be applicable to these assemblages. These phases may be considered in a six component system, expressed as oxides. These are: CaO, MgO, Al_2O_3 , SiO_2 , CO_2 and H_2O . It is possible and convenient to regard the activities of some of these components as fixed, either because a phase having the composition of the pure component is in the system in excess, or because the component is "perfectly mobile" and its activity is determined by factors not controlled by the bulk composition of the system (Korzhinsky, 1950; Thompson, 1955; Zen, 1959).

The mineral assemblages do not suggest that there were any significant gradients in the activities of either H_2O or CO_2 , at the time the assemblages formed, and thus the system has behaved as if both H_2O and CO_2 were "perfectly mobile." Quartz is present in every sample and therefore SiO_2 is present in excess and need not be considered as a component.

Having eliminated the need to consider three of the six components, it is now possible to plot the remaining three components on a ternary diagram (Fig. 2). The five mineral assemblages are also shown.

The composition of corrensite has been plotted on the basis of two analyses, one of which was reported by Bradley and Weaver (1956). The second analysis, prepared in connection with this study, was of a well crystallized specimen that contained only a small amount of muscovite and from which all quartz and carbonates were removed (Fig. 1*b*, No. 76-18; and appendix at the end of this article). It was assumed that the composition of the mica would be about that of "Fithian illite" (Grim and Rowland, 1942) and all K_2O was assigned to the mica. Recomputing to 100% gives a rough composition for corrensite that corresponds quite closely to that reported by Bradley and Weaver (1956), especially in regard to the Al_2O_3/MgO proportion. The average $MgO/(Al_2O_3+MgO)$ ratio, by weight, for the two analyses of corrensite is 65% (82 mole %). Iron has been ignored in this treatment because of the probability that an amorphous hydrate of Fe_2O_3 would have been concentrated from the large amount of dolomite during the leaching process. The specimen reported by Bradley and Weaver (1956) contained significantly less iron than the specimen analyzed for this study.

This ratio has a value of 67 weight % (84 mole %) for "Pauling formula" chlorite: $Mg_3Al(AlSi_3O_{10})(OH)_8$. Two low iron chlorites from Phillipsburg, Montana and West Chester, Pennsylvania (McMurchy, 1934) give values of 68 and 71 weight % respectively (85 and 87 mole %). Three analyzed low iron vermiculites from Bare Hills, Maryland, Webster, North Carolina (Gruner, 1934), and Kenya (Walter and Milne,

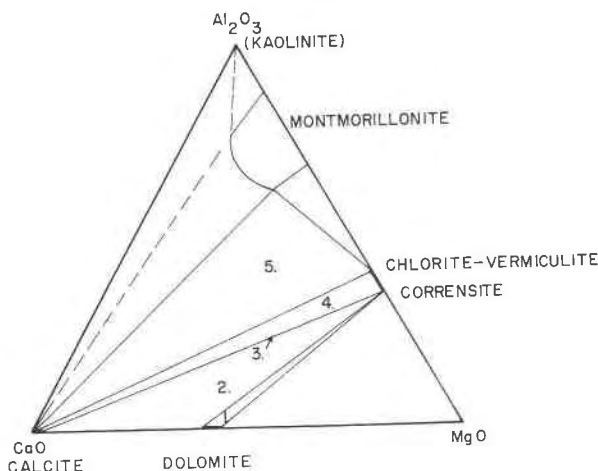


FIG. 2. Mineral assemblages, in the system Al_2O_3 , CaO , MgO , SiO_2 , CO_2 and H_2O , from relatively pure carbonate rocks from the upper Mississippian in the Cumberland Plateau in Tennessee. Quartz and muscovite are also present in every assemblage. The diagram may be considered as a projection from the composition of muscovite. The five mineral assemblages are shown by numbers. The field of montmorillonite has been drawn to include the compositions of several low iron montmorillonites, and has not been extended all the way to the calcite-kaolinite join so as to allow for the possibility of a *calcite, montmorillonite, kaolinite* assemblage, shown in dotted lines. About 0.5% to 1% Mg is in solid solution in the calcite. Temperature and pressure are considered to have been generally low, but variable.

1950), give an average value of about 60 weight % (79 mole %) for this ratio. The inadequacy of these data emphasizes the need for chemical analyses of the sedimentary analogues of these minerals.

The field of montmorillonite in Fig. 2 was drawn to include compositions of three low iron montmorillonites from Tatatilla, Mexico, Otay, California, and Montmorillon, France (Ross and Henricks, 1945). It is indicated as not extending to the kaolinite, calcite join so as to admit the possibility of a *calcite, montmorillonite, kaolinite* assemblage.

RELATIONSHIPS OF THE COMPLEX CHLORITIC MINERALS

The purpose in presenting the mineral assemblages has been to provide a basis for grouping the complex chloritic minerals.

In this study, observed variation in the (001) and (002) spacings of untreated chlorite-vermiculite and corrensite respectively, was from 14.2 to 15.2 Å. In an effort to determine if this variation was at all systematic, the 14.2 to 15.2 Å spacings were plotted in relation to the assemblages in which the mineral occurred (Fig. 3). Those from assemblages 1, 2 and 3 are essentially similar. Those from assemblage 4, however, have a larger

spread of values, and a larger average spacing than those from assemblages 1, 2 and 3; those from assemblage 5 have the largest spacings of all.

The basal spacing of vermiculite is somewhat larger than that of chlorite. Mathieson (1958) attributes the difference between the $d(001)$ of Mg vermiculite (14.36 Å) and Mg chlorite (14.2 Å) to the difference between the $H_2O-Mg-H_2O$ intersheet distance in vermiculite and the $OH-MG-OH$ intersheet distance in chlorite.

The line in Fig. 3 at 14.28 Å indicates the spacing that would be expected for a mineral that was 1:1 mixed-layer chlorite and vermiculite. This value coincides closely with the lower limit of the observed spacings. Bradley and Weaver (1956) demonstrated by a Fourier analysis that a regularly interstratified specimen of this type of mineral was an alternation of vermiculitic and chloritic layers. Earley *et al.* (1956) arrived at essentially the same conclusion; however, they called their mineral a regularly interstratified montmorillonite-chlorite.

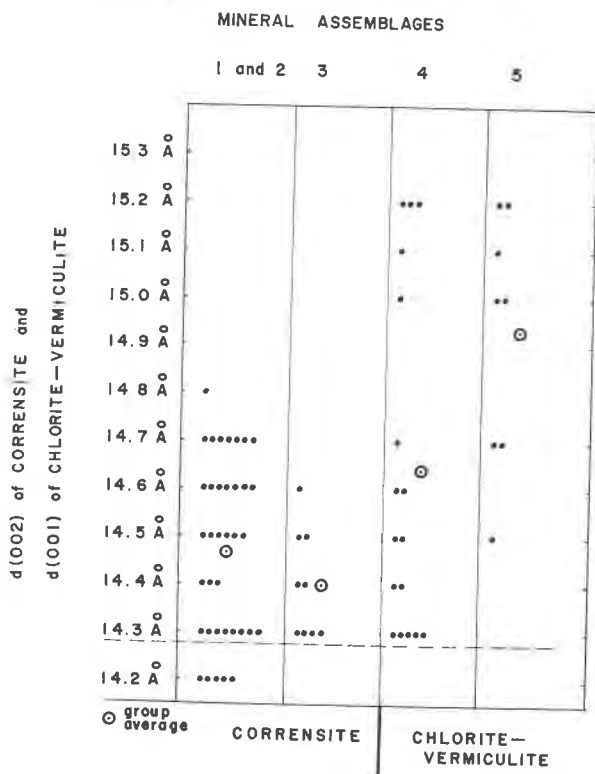


FIG. 3. The relation of mineral assemblages to content of vermiculite in chlorite-vermiculite and corrensite. The measures of content of vermiculite are $d(001)$ of chlorite-vermiculite and $d(002)$ of corrensite.

Increase in relative humidity tends to increase the basal spacing of vermiculite layers of these clays. At low relative humidity, however, the basal spacing of vermiculite stabilizes near a value of 14.4 Å and Weiss and Rowland (1956) have demonstrated in a heating camera that it remains so to a temperature near 80° C. They have also shown that the vermiculitic portion of chlorite-vermiculite behaves in a similar manner.

Variations in relative humidity cause much of the spread of values for spacings. Inasmuch as the data for each group were obtained under the same range of humidity conditions, the average value and relative spread would still be meaningful. Larger spacings would be associated with minerals having more vermiculite than a 1:1 ratio of vermiculite to chlorite, both because of the larger stable spacing of vermiculite at 14.36 Å and because of its ability to expand above this value.

It is therefore evident that the composition of chlorite-vermiculite in assemblage 4 is more nearly that of vermiculite than those of assemblages 1, 2 and 3. Their compositional range is also greater than in the other assemblages. The composition of chlorite-vermiculite from assemblage 5 is most nearly that of vermiculite.

Another measure of the proportion of vermiculitic layers to chloritic layers is the ratio of intensities of the (001) to (002) peaks of chlorite-vermiculite or the (002) to (004) peaks of corrensite (Weaver, 1956). This measure is more sensitive than changes in basal spacing, because the range of values is larger, but it is also more affected by variation in the iron content of the mineral. It is also a more difficult value to determine with accuracy because interfering peaks from non-expandable chlorite are commonly present, and because the 7 Å reflection from specimens near the composition of vermiculite is very weak. For these reasons it was impossible to evaluate this ratio for some specimens.

The (001)/(002) and (002)/(004) peak intensity ratios were plotted in relation to the mineral assemblages (Fig. 4) and demonstrate the same relationships as the basal spacings: that the more vermiculitic minerals are in assemblages 4 and 5, and that the largest spread of values is in assemblage 4.

The regression of one criterion for vermiculite content on the other is illustrated in Fig. 5.

The examples in Fig. 1*a* were chosen to demonstrate the variation found in expandable chloritic clays, and are more or less representative of the mineral assemblages from which they were taken. Samples 80-8 No. 1 and 78-30, both corrensite, are from assemblages 2 and 3 respectively, and have about the same vermiculite content. Samples 75-9 and 78-6 are chlorite-vermiculite from assemblages 4 and 5 respectively: 78-6 has a much larger vermiculite content than the other three specimens.

This compositional variation, in relation to the mineral assemblages, is

consistent with the only topologic possibility in constructing the ternary diagram (Fig. 2). Corrensite that is part of the two phase assemblage *dolomite, corrensite* has also been included in this group, but inasmuch as there are only three specimens from it, their contribution to the spread of values is negligible. Corrensite from the *calcite, corrensite* assemblage also seems to have a narrow range of composition, however, the peak intensity ratio (002)/(004), the most sensitive indicator of vermiculite content, shows it to be of slightly more vermiculitic composition (Fig. 4). In the two phase assemblage *calcite, chlorite-vermiculite*, however, composition of chlorite-vermiculite in the *calcite, chlorite-vermiculite, montmorillonite* assemblage. A paucity of values exists in the 14.7 to 14.8 Å range that may indicate either a compositional gap or inadequate sampling (Fig. 3). This gap may not be present in the distribution of (001)/(002)

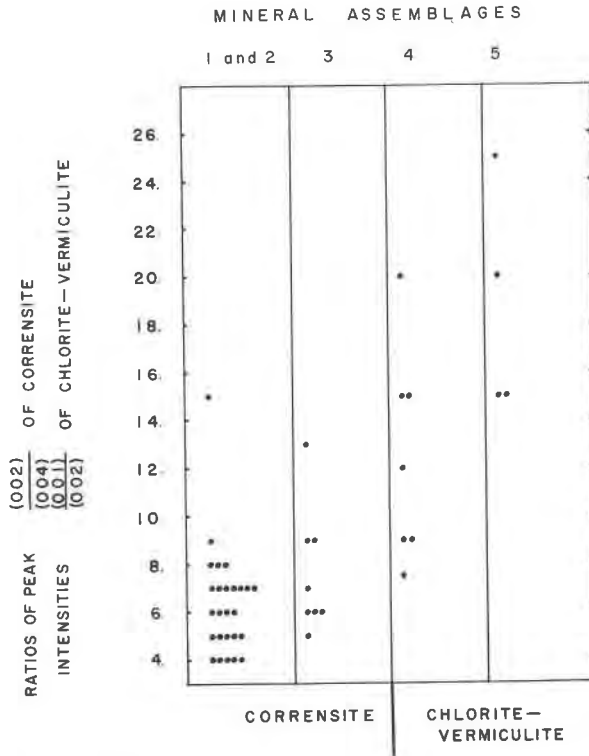


FIG. 4. The relation of mineral assemblages to content of vermiculite in chlorite-vermiculite and corrensite. The ratios of peak intensities (002)/(004) for corrensite and (001)/(002) for chlorite-vermiculite are used as measures of content of vermiculite.

ratios of peak intensities (Fig. 4) in assemblages 4 and 5; moreover, there are no compelling crystallographic reasons to believe such a compositional gap should exist. Chlorite-vermiculite from assemblage 5 should be the most vermiculitic, which it is. Being part of a three phase assemblage, this chlorite-vermiculite should also be invariant in composition. The data do not seem to bear this out, except that there is a suggestion of a decrease in its spread of values (Figs. 3 and 4) compared with that of assemblage 4. It is difficult to evaluate the influence of small amounts of iron and variations in humidity in contributing to this apparent compositional variation. Even the corrensite from assemblages 1 and 2 shows an appreciable spread of values.

RELATIONSHIPS OF CORRENSITE

For the purpose of establishing mineral assemblages, corrensite was distinguished from chlorite-vermiculite by the presence of a basal spacing in the range of 28.4 to 30 Å. It is now of interest to examine variations within the group of minerals showing such a spacing.

Intensities of peaks corresponding to these large spacings vary greatly relative to other peaks in the basal series (Fig. 1*a*, 80-8 No. 1, 78-30) and may be used as a measure of dissimilarity of alternating vermiculitic and chloritic layers, and of the regularity of the alternation.

An independent criterion of dissimilarity of alternating layers is the degree to which the basal series behaves like a non-integral series. If the chlorite-vermiculite is not really a mixed-layer clay, but is composed of layers that are identical, then an integral series will characterize the mineral, even during heat treatment. On the other hand, if some layers are vermiculitic and other layers are chloritic the resultant series will only appear to be integral because the basal spacings of chlorite and vermiculite are so nearly the same. However, heat treatment will selectively increase the thickness of vermiculitic layers and the series will then be conspicuously non-integral.

In every instance heat treatment revealed a clearly non-integral series for both corrensite and chlorite-vermiculite, thus establishing that all the expanding chloritic minerals in these carbonate rocks are truly mixed-layer clays that are composed of dissimilar layers.

Figure 1*b* shows the effect of heat treatment on several specimens. Sample 76-18 is a well crystallized corrensite containing only a minor proportion of 10 Å clay. Heating to successively higher temperatures causes a rather symmetrical migration of the peaks on either side of the 10 Å peak, and illustrates the non-integral behavior of the basal series. Samples 80-1 No. 1, 78-30, and 78-6 are from assemblages 2, 3 and 5, respectively, and show similar behavior. This criterion indicates only that

certain of the layers have a higher thermal stability than others, but does not say how different they are.

If it is assumed that the layers are completely differentiated into ideal chlorite and ideal vermiculite, then the ratio of intensities of (001) to (002) peaks of corrensite is a measure of the proportion of the mineral composed of regularly alternating layers of chlorite and vermiculite. If this assumption is wrong, and the layers of chlorite are somewhat like vermiculite, and the layers of vermiculite are somewhat like chlorite, then a mineral of perfectly alternating layers would have a relatively reduced 28.4 to 30 Å peak and the (002)/(001) ratio would be larger. Inasmuch as magnesium is the only element available in important quantities for interlayer positions, at least in the corrensites that have been analyzed, preferential positioning of a more reflective ion, such as divalent iron, in alternating layers does not seem to be an important possibility.

The (002)/(001) ratio of intensities has been chosen therefore as a meas-

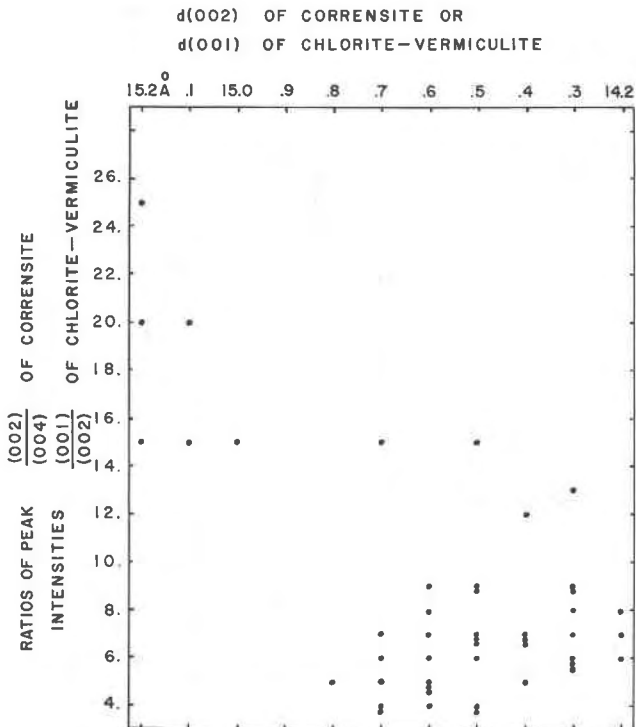


FIG. 5. The mutual relation of the two measures of vermiculite content in chlorite-vermiculite and corrensite.

ure of ordering of corrensite. Disorder would be present either as deviation of the individual layers from pure chlorite or vermiculite, or as a lack of perfect regularity of alternation of the layers. A well ordered mineral would have maximum differentiation of its layers and perfect alternation.

Height of peaks was used as the measure of intensity, and is somewhat difficult to determine with precision because the 28.4 to 30 Å peak is superimposed on a background that is rapidly descending from the direct x -ray beam. Intensity was measured above the interpolated background at the point of maximum height. The Lorentz-polarization factor and the area of irradiation were assumed, for this approximation of the degree of ordering, to be the same for all samples. Values of the ratio were determined only to the nearest 0.5.

Corrensite from assemblages 1, 2 and 3 has a much more limited range of compositional variation than that of the chlorite-vermiculite from assemblages 4 and 5, as can be seen from the small spread of values of both d (002) (Fig. 3) and (002)/(004) peak intensity ratios (Fig. 4). This limited variation may also be predicted from the fact that the portion of the mineral contributing to the 28.4 to 30 Å peak must have a 1:1 proportion of chloritic to vermiculitic layers. Variation does exist, however, and a plot of d (002) as a measure of vermiculite content, against (002)/(001) peak intensity ratio, as a measure of ordering, shows several interesting relationships (Fig. 6).

An abrupt upper limit to the degree of ordering exists, and probably represents a maximum ordering that can be achieved by the mineral with respect to chlorite and vermiculite alternation and differentiation.

Most of the specimens approach rather closely this maximum ordering; however, there are five specimens that do not. These fall in the more vermiculitic range, as indicated by their generally larger d (002). Poor ordering would also result if a mineral were more chloritic than the 1:1 ratio, but inasmuch as none of the poorly ordered specimens has a d (002) less than 14.4 Å, it would seem that compositional variation of expandable chloritic minerals in these carbonate rocks is between the compositions of corrensite and vermiculite. This generalization also includes the chlorite-vermiculites from assemblages 4 and 5.

Most of the specimens of corrensite occur in rocks containing dolomite, although some are from rocks that have only calcite as the carbonate. A plot of d (002) of corrensite against the proportion of dolomite in the rock in which it is found (Fig. 7) demonstrates that the composition of corrensite is not dependent on the bulk composition of the rock within the limits of the assemblages *dolomite, corrensite*; and *calcite, dolomite, corrensite*. A plot of (002)/(004) peak intensity ratios would demonstrate the

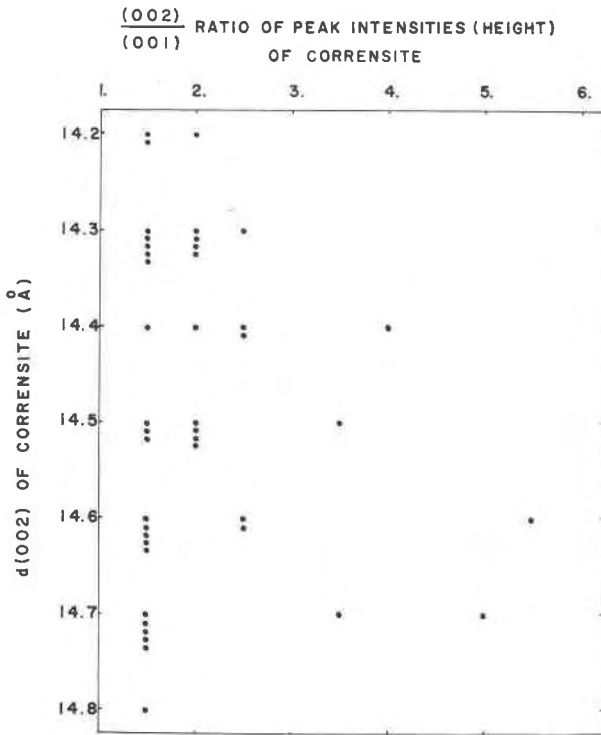


Fig. 6. A plot of $d(002)$ of corrensite, a measure of the vermiculite content, against the $(002)/(001)$ ratio of peak intensities, a measure of ordering.

same relationship. Minor exception to this generalization is found in the five examples of corrensite that show poor ordering with respect to chloritic and vermiculitic layers. A plot of the ordering criterion, $(002)/(001)$ peak intensity ratios, against dolomite proportion of the host rock (Fig. 8) demonstrates that the better ordered corrensites show no relation to bulk composition of the rock. On the other hand, four of the five poorly ordered specimens fall on or near the join separating assemblages containing corrensite from those not containing it.

Important considerations concerning the relation of corrensite to the other expandable chloritic minerals are: (1) can chlorite-vermiculite of the same composition as a perfect 1:1 corrensite exist in these rocks without ordering, and (2) can ordering similar to that in corrensite exist in a mineral that is not very close to the ideal 1:1 composition? Using $d(002)$ as the criterion for vermiculite content (Fig. 3) it can be seen that compositions of chlorite-vermiculite approach very closely that of corrensite, but are, in general, more vermiculitic. Ratios of peak intensities $(002)/$

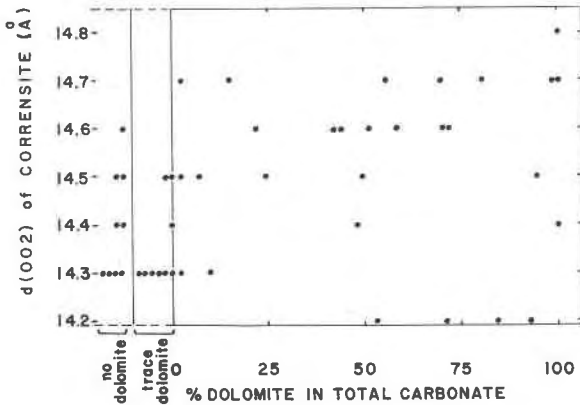


FIG. 7. A plot of $d(002)$ of corrensite against the proportion of dolomite for each specimen, showing that there is no systematic variation in the proportion of vermiculite to corrensite in relation to the amount of dolomite also in the rock.

(004) for corrensite or (001)/(002) for chlorite-vermiculites of assemblages 4 and 5 really are more vermiculitic (Fig. 4). Unfortunately it was not possible to determine these ratios for all specimens. Evidence at hand seems to indicate that when the mineral has a composition very near that of corrensite, it tends to be ordered. The poorly ordered corrensites have (002) spacings within the range, although on the more vermiculitic side, of the well ordered corrensites. Humidity variations obscure some of the relations here, but it is safe to say that none of their compositions is far from that of well ordered corrensite.

It is also necessary to entertain the possibility that these poorly ordered

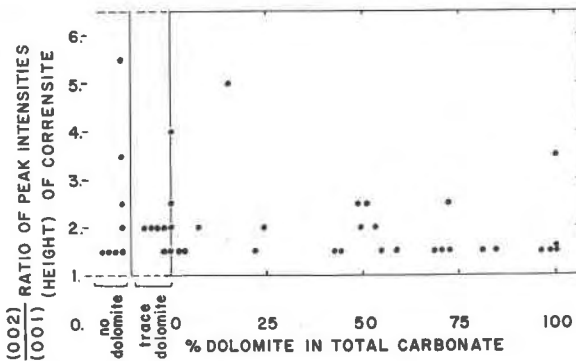


FIG. 8. A plot of (002)/(001) ratios of peak intensities against the proportion of dolomite for each specimen. The specimens containing poorly ordered corrensite, as shown by large (002)/(001) peak intensity ratios, also contain little or no dolomite.

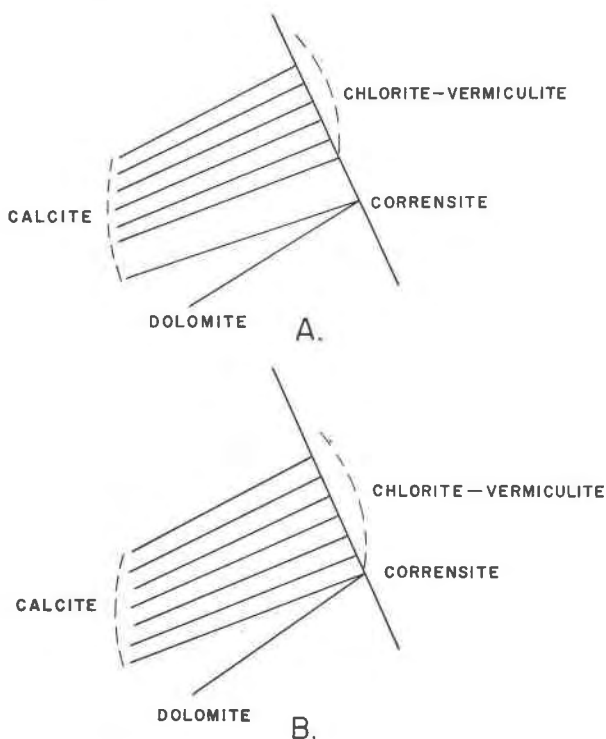


FIG. 9. Two alternative ways of constructing the portion of the ternary diagram Al_2O_3 , MgO , CaO near corrensite in the system Al_2O_3 , MgO , CaO , SiO_2 , CO_2 and H_2O . There is no evidence for a compositional gap in the chlorite-vermiculites near the composition of corrensite. This fact would favor the interpretation shown in B.

corrensites are really mixtures of the well ordered mineral and chlorite-vermiculite of more vermiculitic composition. This possibility can be illustrated in the ternary diagram as shown in Fig. 9A. Alternatively this assemblage might be illustrated (Fig. 9B) as part of a two phase field *calcite*, *chlorite-vermiculite*, corrensite being somewhat variable in composition, grading into chlorite-vermiculite. Sufficient information is not available to revolve this point, except that there is no evidence of a compositional gap, however small, between chlorite-vermiculite of very nearly 1:1 composition and corrensite. Therefore, what evidence there is would favor the interpretation of a two phase field, *calcite*, *chlorite-vermiculite*. Corrensite would be an ordered member within the phase region of chlorite-vermiculite. Within the context of this study, corrensite assumes the role of an end member. The more magnesium rich part of the system is currently being investigated by the author. If it is assumed that

these assemblages are equilibrium products, and if the components have been sorted out properly, it is interesting to note that the mixed-layer minerals chlorite-vermiculite and corrensite have behaved as single thermodynamic phases, so far as satisfaction of the phase rule is concerned, because both are found as members of assemblages containing the maximum permissible number of phases, the variance having been arbitrarily set at two.

The purpose of this paper has been to present the information as it bears on compositional and structural variations in the complex chloritic minerals; however, the meaning would be quite incomplete without considering the question of what relation the mineral assemblages may bear to the true equilibrium products. The simplicity of the mineral assemblages, the uniformity with which they occur, and the fact that they can be used to construct an internally consistent phase diagram, which may be thought of as a graphic statement of the phase rule, all imply that the assemblages are the result of a mineral paragenesis, but not necessarily a complete equilibration, that took place during and after deposition. The fact that the compositional variations of the complex chloritic minerals are consistent with the topologic requirements of the phase diagram also carries the implication that these variations are indeed meaningful, and are related to the mineral paragenesis. The demonstration that minerals have formed or altered during or after deposition, or that they have been in some form of reactive equilibrium, does not prove that the rock in which they are found constitutes an equilibrium assemblage. Such a demonstration, however, does illustrate the importance of chemical processes in producing the properties of these carbonate rocks, and of the minerals forming them, even those minerals traditionally regarded as detrital. The question of whether these assemblages are true equilibrium products or are metastable assemblages will be discussed in more detail in a paper devoted to the geological implications of this study (Peterson, in press).

The processes contributing to this mineral paragenesis took place at temperatures and pressures far below those traditionally associated with metamorphism. Processes and conditions usually regarded as diagenetic grade with complete continuity into those regarded as metamorphic, and no clear distinction is possible. It is clear that diagenetic readjustment of sedimentary mineral constituents does take place, and can be thought of as the very beginning of metamorphism.

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TABLE 2. CHEMICAL ANALYSIS OF CORRENSITE
Analyst: J. Ito

	Weight % Determined	Weight % Re-calculated		Weight % Determined	Weight % Re-calculated
SiO ₂	37.2	34.	Na ₂ O ^b	0.2	—
Al ₂ O ₃	15.5	13.	TiO ₂ ^b	0.4	—
Fe ₂ O ₃ } ^a	6.7	7.	MnO ^b	0.01	—
FeO			V ^b	0.0001	—
MgO	18.9	24.	Zr ^b	0.0001	—
K ₂ O	1.4	—	Cu ^b	0.001	—
CaO	1.0	—	H ₂ O	18.4	22.
			Total	99.7	100.

^a Total iron as F₂O₃.

^b Determined spectrographically.

for their helpful guidance and friendly criticism, with regard to this part of the research. I would also like to thank Professors E. C. Dapples and L. L. Sloss of Northwestern University under those instruction I first became interested in this group of rocks.

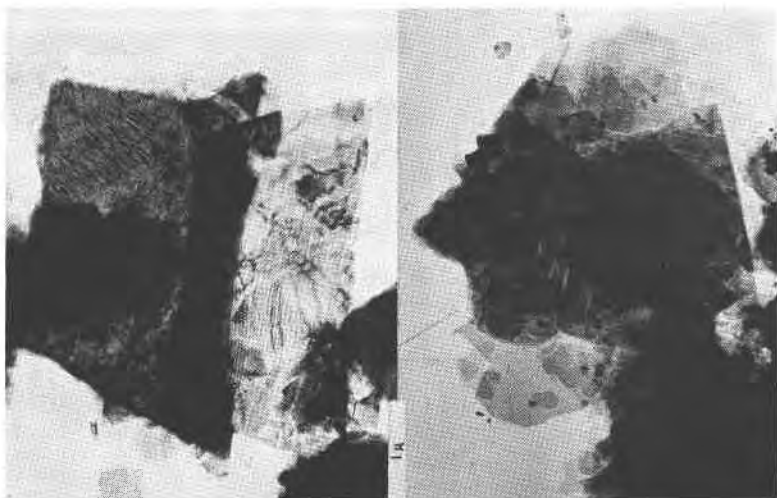


FIG. 10. Electron photomicrographs of corrensite from Sparta, Tennessee. Moiré patterns are clearly visible. (Courtesy of Dr. C. B. Chapman, Department of Biology, Harvard University).

TABLE 3. X-RAY DIFFRACTION DATA OF CORRENSITE
(County Rock Quarry, Sparta, Tennessee)

	Air Dried d Å (observed)	Solvated with ethylene glycol d Å (observed)
(001)	29.5 (29.0 computed)	32. (31.0 computed)
(002)	14.5	15.5
(003)	9.7	10.3
(004)	7.25	7.76
(005)	5.83	6.24
(006)	4.85	5.16
(007)	4.15	4.43
(008)	3.63	3.87
(009)	3.25	3.44
(00.10)	2.89	?
060	1.54	

APPENDIX

ANALYZED SPECIMEN OF CORRENSITE

The sample was collected from the county rock quarry four miles west of Sparta, Tennessee, on State Highway 42, about seventy-four feet above the floor of the quarry. It is from unit 18 of measured section number 76, descriptions of which are on file at the Division of Geology, G-5 State Office Bldg., Nashville, Tennessee. The carbonate fraction of the rock is composed of 96% dolomite and 4% calcite.

The clay was chosen for analysis because it was a relatively pure, well-ordered clay, as seen by x -ray diffractometer traces and was well crystallized, as seen from electron photo-

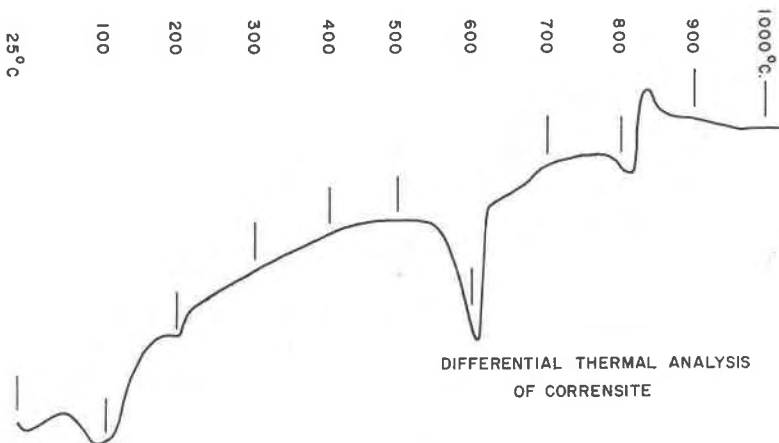


FIG. 11. Differential thermal analysis trace of corrensite from Sparta, Tennessee.
The rate of heating was 5° C. per minute.

micrographs (Fig. 10), and was present in sufficient quantities in the rock. It was extracted by leaching the carbonate from the rock in a solution of acetic acid buffered at pH 4.5 with lithium acetate. Quartz was removed by size fractionation, leaving a small amount of muscovite, or "illite," as the only impurity detected by x-ray diffraction methods. Iron would be the least reliable part of the analysis because of the probability that it would be concentrated as an amorphous hydrate of Fe_2O_3 during the leaching of the dolomite. A faint brownish tinge to the dominant grey-green of the mineral may have been caused by uncombined Fe_2O_3 . All K_2O was assumed to be in the mica, of the composition of "Fithian illite." Recomputing to 100% gives a rough composition for corrensite, as shown in Table 2.

Differential thermal analysis produces a curve essentially similar to that of the Brazer limestone corrensite (Bradley and Weaver, 1956) and is reproduced here for comparison (Fig. 11). The heating rate was 5°C . per minute.

X-ray diffraction data for this specimen are given in Table 3. A value of 1.54 \AA for d (060) is within the range associated with trioctahedral phyllosilicates.

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