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CORRENSITE: Mineralogical Ambiguities and Geologic Significance

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## ABSTRACT

This paper is a summary of the information available on the mixed-layer clay mineral corrensite. For 30 years corrensite and corrensite-like phases have been reported in the literature. The best-known occurrences are in the German and English Keuper Marl, the German Zechstein, the French Jura Basin, and the Texas-New Mexico Delaware Basin. Corrensite is defined as a 1:1, regularly, interstratified, probably trioctahedral clay mineral species composed of a 14A chlorite and a swelling-clay layer. The latter has been variously defined as a vermiculite, a montmorillonite, a saponite, and a swelling chlorite. The most common constituent of the swelling layer appears to be a smectite with swelling chlorite the next most common. Vermiculite does not seem to be a valid species name for the swelling layer. Differential Thermal Analysis curves show endothermic peaks at 100<sup>o</sup>-200<sup>o</sup>C, 550<sup>o</sup>-660<sup>o</sup>C, and 830<sup>o</sup>-850<sup>o</sup>C with an exothermic peak at 850<sup>o</sup>-900<sup>o</sup>C. The eleven chemical analyses for corrensite, taken from the literature, can be separated on an environmental and chemical basis; hydrothermal samples lie in the vermiculite field; sedimentary samples cluster into the saponite field. Corrensite is found in three types of environment--sedimentary, hydrothermal, and low-grade metamorphic. It has a definite distribution through geologic time with the major sedimentary occurrences being in the Paleozoic and early Mesozoic while the hydrothermal occurrences are grouped in the Cretaceous and Tertiary. Sedimentary corrensite is hypothesized to form by ion aggradation of a less-ordered species. Sedimentary corrensites are shown to exist in evaporite-bearing rocks, in carbonate-bearing host rocks, and in transitional marine lithologies. In general, the shallow marine conditions of a warm, epicontinental sea seem to favor corrensite formation.

## INTRODUCTION

This article is a survey of the corrensite dilemma--the unfortunate assignment of the mineral name "corrensite" to at least four discrete mixed-layer clay species; chlorite-vermiculite, chlorite-montmorillonite, chlorite-swelling chlorite, and chlorite-saponite. It is the author's intent to present a summary of the ambiguities and contradictions encountered in the literature under the heading of "corrensite or corrensite-like" phases.

There is considerable reference material available on corrensite. Unfortunately, many researchers have been confronted with the problems of duplicitous definitions and much of the subsequent work has been poorly defined tending to compound the confusion.

It is not the objective of the author to offer any definite solutions at this time. Additional research, compilations and data integration must be carried out on representative samples and an extensive research project to this end is being implemented. However, it is the intent of this work to summarize the available information in as useful detail as is practical, outline specifically the existing problem areas, offer some guidelines for phase identification, and discuss why the dilemma exists.

As many literature citations as possible are included in this paper. However, some references have been excluded. The criteria used for exclusion were duplications, incomplete data, and lack of time to translate or to abstract. It was not the intention to slight any researcher. The author would appreciate that oversights be brought to her attention so that subsequent work can be as complete as possible.

## HISTORY OF THE STUDY OF CORRENSITE

Corrensite has appeared in the literature as a recognized species for nearly thirty years. A mixed-layer phase with what was later defined as corrensite characteristics was synthesized by Calliere and Henin in 1949. As a naturally occurring species it was first documented from the Triassic Keuper Marl in England by I. Stephen and D.M.C. MacEwan in 1950 and 1951. Honeyborne (1951) also reported it from this locality. Two excellent and more detailed characterizations of corrensite from the Keuper in England were done in Davis (1967) and MacNeill (1978).

The term "corrensite" was first used by Friedrich Lippmann in his 1954 paper on the German, Triassic, Keuper Marl. The mineral was named in honor of Professor C. W. Correns of Gottingen, Germany. Dr. Lippmann, in his own research (1954, 1956, 1976) and in that of his various countrymen (Lippmann and Savascin, 1969; Echle, 1961; Becher, 1965; Schlenker, 1971), presented detailed examinations of corrensite occurrences in the primarily evaporite sequences of the Keuper and associated formations.

Corrensite was reported from another evaporite deposit, the famous Permian Zechstein of Germany by Dreizler (1962) and Braitsch (1960, 1971). It was found in the evaporite-bearing Permian Salado Formation of the Delaware Basin, of New Mexico by Grim and his co-authors (1960) with additional work done by Fournier (1961), Madsen (1978, personal communication), Bodine (1978) and Loehr (1979).

Another famous basin occurrence for corrensite is that of the Jura in France. Here corrensite was documented by Millot and his associates (1963); by Martin Vivaldi and MacEwan (1957), Lucas and Ataman (1968), by Lucas (1962); and Tardy, et al. (1972).

There are also numerous reports of this mineral from hydrothermal environments. Japan, in particular, hosts many corrensites and corrensite-like minerals formed as byproducts of ore deposition. Corrensite species have been identified from widespread geographic localities: South West Africa, Iceland, Japan, Mozambique, Italy, India, Austria, Russia, Spain, Scotland, and in the United States, Nevada, North Carolina, Colorado, Tennessee, Kansas, California, Illinois, and Arizona; and from diverse geologic environments such as pegmatites, geothermal systems, ore-rock alteration zones, dike-intruded shales, hydrothermally altered calcareous argillites, altered basalts, various low-grade metamorphic alteration regimens, transitional marine and near-shore marine environments, and shallow marine carbonates. Most of these occurrences have been summarized in tables which appear later in this paper.

This brief historical summary of documented corrensite occurrences indicates that the mineral has been recognized by, relatively speaking, a great number of workers in the last thirty years.

#### DEFINITION OF "CORRENSITE"

The most confusing aspect of the corrensite problem is in the definition of corrensite. In general, the literature is in agreement that "corrensite" is a 1:1, regular, interstratified, probably trioctahedral, species composed of a chlorite layer and a swelling-clay layer. Disputation arises, however, when attempts are made to characterize the swelling-clay layer.

Corrensite has been documented as regularly interlayered: chlorite-swelling chlorite, chlorite-saponite, chlorite-montmorillonite, and chlorite-vermiculite. These different species do seem superficially to conform to the definitions given by their authors. The lattice spacings, in angstroms, shown in Table 1, attempt to define numerically the components of the various mixed-layer species. This is a generalized version, as variations on these spacings seem the rule rather than the exception. The swelling-chlorite variety expands with glycol, but does not collapse with heat. The montmorillonite layer both expands with glycol and contracts with heat, as does the saponite, although the saponite may expand more with glycol than does the montmorillonite. The vermiculite constituent does not expand with glycol but does collapse with heat. Each of these, therefore, seems to be a distinct definable phase.

To simplify nomenclature, throughout this paper the terms "smectite," "montmorillonite," "vermiculite," and "swelling-chlorite" will be used without the "chlorite" modifier to mean the nonchlorite layers of a corrensite species. Unless otherwise noted, the species designations used are those assigned by the original authors. Although corrensite is defined as possessing a 1:1 relationship between its layers, this is seldom true, as will be shown through the compilations in the section on X-ray diffraction data. There are usually minor discrepancies, and many times, major ones.

Table I.--The reactions of various corrensite species to standard clay analyses tests shown by the superorder angstrom positions derived by X-ray power diffraction methods. Spacings given in the last column apply to values of the collapsed structure after heating to 550° C.

LAYER COMPONENT SPACINGS				
CORRENSITE SPECIES	UNTREATED	ETHYLENE GLYCOL	550°C	SPACINGS
CHLORITE/ SWELLING-CHLORITE	28Å	31Å	28Å	(14Å + 14Å = 28Å)
CHLORITE/ MONTMORILLONITE	28Å	31Å	24Å	(14Å + 10Å = 24Å)
CHLORITE/ SAPONITE	28Å	31Å	24Å	(14Å + 10Å = 24Å)
CHLORITE/ VERMICULITE	28Å	28Å	24Å	(14Å + 10Å = 24Å)

From the numerical values for the layer components listed in Table I, it becomes apparent that the "C" axis dimension can vary with species type. The assumption is made that the chlorite component remains a constant 14A. The variation is then attributed to the interlayer space between the two components and/or the octahedral layer of the swelling-clay component. These variations and their potential causes will be discussed after some of the physical and chemical information for corrensite has been presented.

Dr. Lippmann of the University of Tübingen in Germany prefers that the controversial layer be referred to as a "swelling clay layer" without a species name (personal communication, 1979). He is currently researching the thermodynamic properties of corrensite from the Keuper Marl in Germany to define the mineral more precisely (Lippmann, 1977a, b; 1979).

#### PHYSICAL AND CHEMICAL CRITERIA FOR THE IDENTIFICATION OF CORRENSITE

An examination of the various physical and chemical criteria used to identify this mineral will be helpful toward an understanding of it. The following sections assess the literature data and present research performed by the author and assistants using X-ray diffraction, differential thermal analyses, scanning electron microscopy, and chemical analyses of various corrensite species. Unfortunately there is very little cross-referencing of samples between the different types of analyses compiled from the literature. However, interesting trends do appear and some new perspectives on corrensite can be gained.

#### X-Ray Diffraction Analysis Criteria

The most commonly used method for the identification of corrensite is X-ray diffraction. A comprehensive study by the author of powder-diffraction data presented in the literature as identification criteria, however, shows that the values given are anything but consistent. Considering the inconsistent nature of the mineral under discussion, this inconsistency is not surprising.

Selected X-ray powder diffraction patterns of corrensite samples given to the author by other researchers are shown in Figure 1. An attempt has been made to present a cross section of types and environments for the readers' comparison. The corresponding numerical data from these patterns are tabulated in Table II. The patterns were run on the less-than-2 micron fraction; carbonates, sulphates, and other silicates were removed by routine processes (Jackson, 1974).

The sample in Figure 1A is from the Permian, evaporite-bearing Salado Formation of New Mexico. It is termed "chlorite-vermiculite" by Madsen (personal communication, 1979). The mid-Tertiary evaporite layers of nonmarine red beds from the California Sespe Formation (Flemal, 1970) yielded the chlorite-montmorillonite of Figure 1B. Sample 1C comes also from an evaporite deposit, the famous Triassic Keuper Marl of Germany (Lippmann, 1954, 1956, 1976). The swelling-layers have been called swelling-chlorite, vermiculite and montmorillonite. The chlorite-montmorillonite of the Pennsylvanian and Permian Supai Group of the Grand Canyon, Arizona is shown in Figure 1D (McKee, ed., in press). This is a transitional, marginal marine

Figure 1.--X-ray diffraction patterns of various corrensite samples. Machine parameters were: Copper K-alpha radiation scanned at one degree 2-theta per minute; two degrees 2-theta per inch (samples D and F were run at four degrees 2-theta per inch); counts per second varied with the samples.

- A. Chlorite-vermiculite from the Salado Formation, New Mexico.
- B. Chlorite-montmorillonite from the Sespe Formation, California.
- C. Chlorite-swelling chlorite from the Keuper Marl, Germany.
- D. Chlorite-montmorillonite from the Supai Group, Arizona.
- E. Chlorite-swelling chlorite from the Crescent Formation, Washington.
- F. Chlorite-saponite from the Elena Formation, Nevada

Figure 1

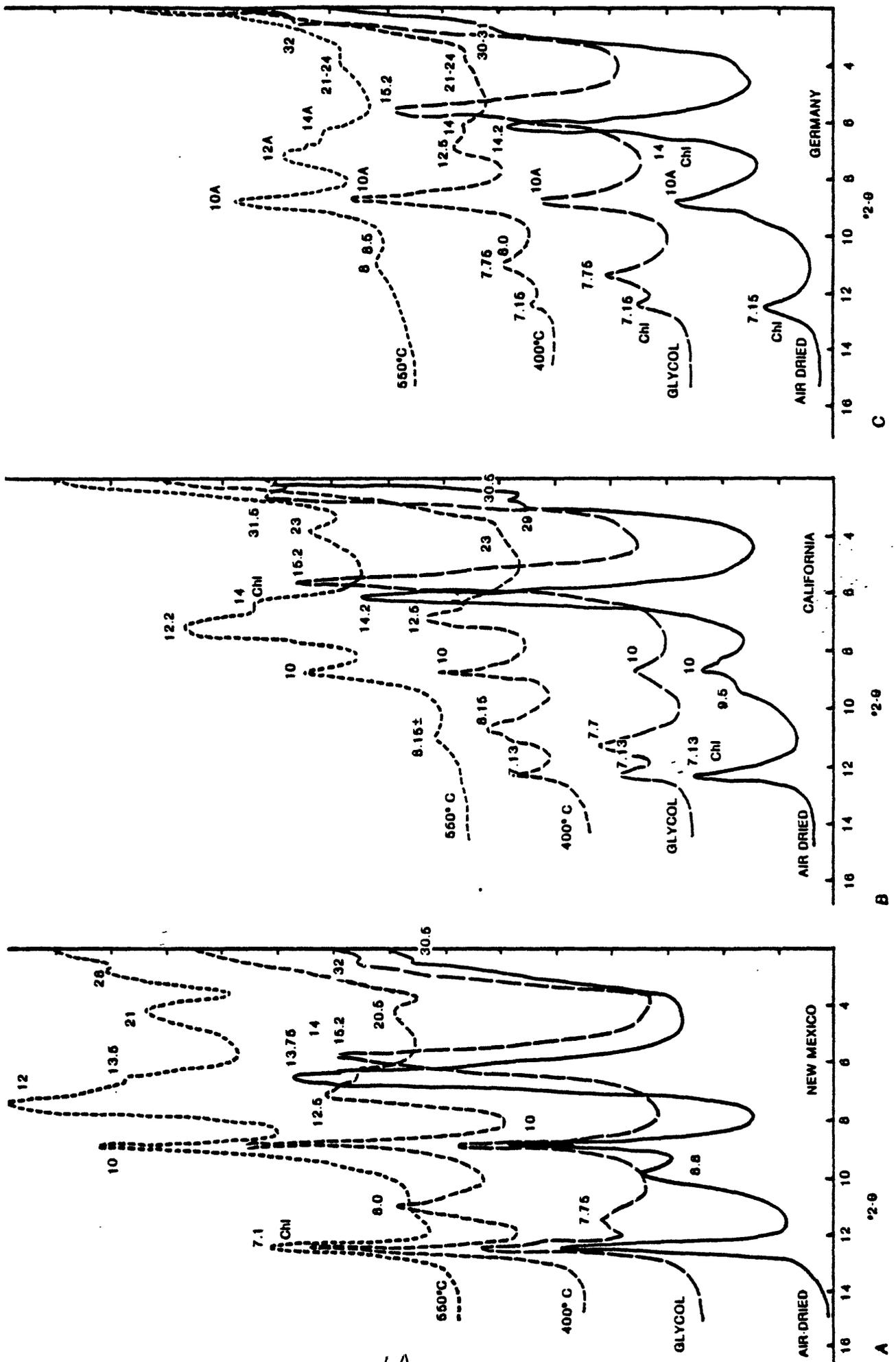
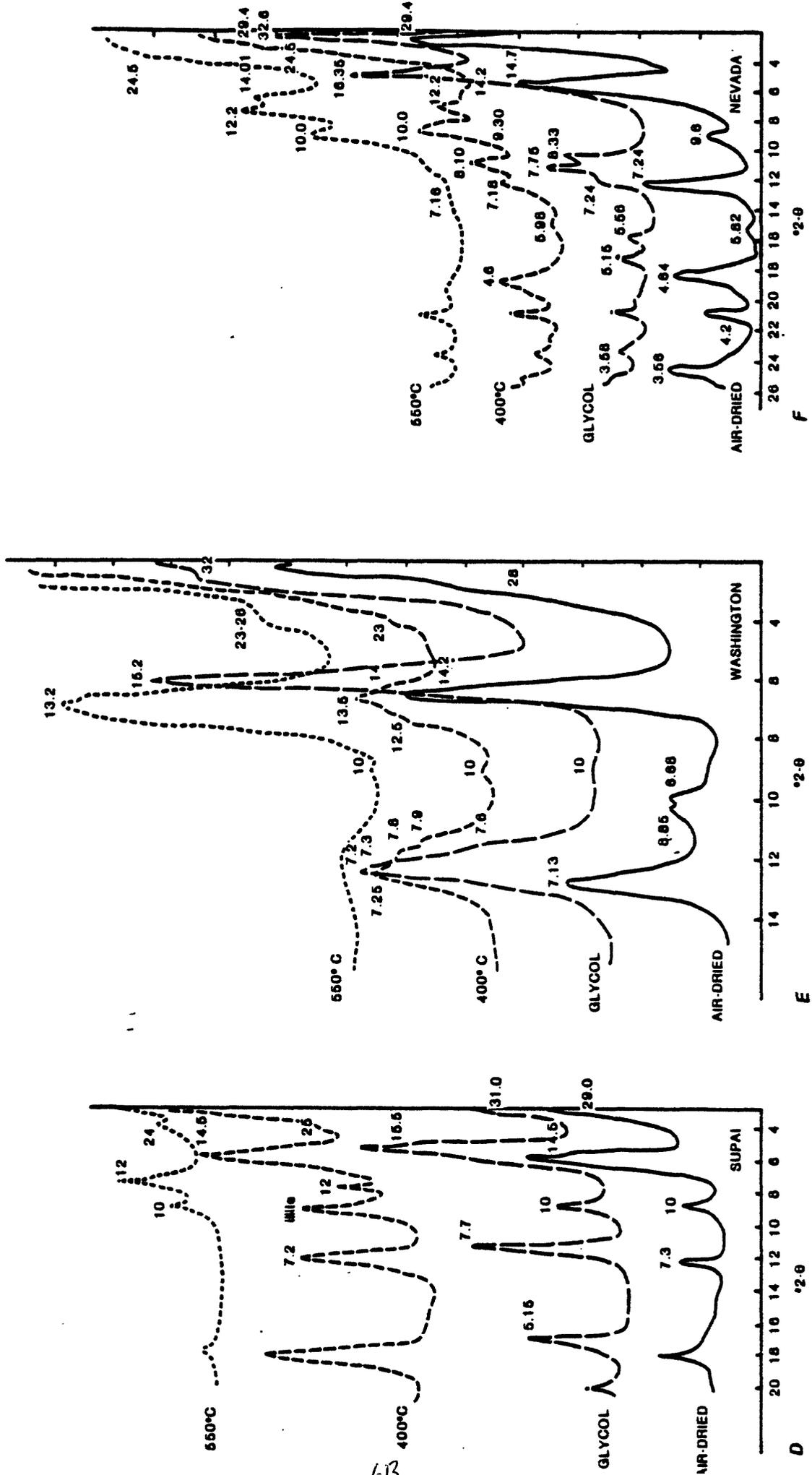


Figure 1





environment. The chlorite-swelling chlorite of Figure 1E is a low-grade metamorphic variety of corrensite from the Eocene Crescent Formation of the Olympic Peninsula, Washington (Pevear, written communication, 1979). This corrensite occurs in volcanoclastic lenses of a sea floor basalt unit. Figure 1F illustrates the pattern of a chlorite-saponite variety from the hydrothermally altered argillites of the Devonian and Mississippian Eleana Formation in Nye County, Nevada.

Six X-ray patterns provide insufficient data for more than just a discussion of their identification. If the criteria shown in Table I are applied to the "superorders" tabulated in Table II, the first conclusion is that very few of these samples conform exactly to the criteria. Samples B, C, D, and F give fairly good fits and probably can be classified, from the X-ray data, as smectites (montmorillonites, saponites). Sample C and especially sample F show greater swelling characteristics than do samples B and D. This swelling might indicate that they are saponites. However, sample A, which swells significantly ( $32A=14A+18A$ ), and collapses insignificantly ( $28A=14A+14A$ ), does not exhibit the acceptable criteria for a vermiculite (that is nonswelling and collapse to a  $24A=14A+10A$  phase). This nonconformity also applies to sample E. It collapses more than A, but not as low as the vermiculite required 10 angstroms. Subsequently, sample A and more certainly sample E are probably of the "swelling-chlorite" variety. One problem with the identification of these phases is that, due to degree of crystallinity and instrument limitations, superorders cannot always be resolved adequately. Unfortunately, the superorder positions are the real key to the identification of these different species.

It appears that, based on the X-ray diffraction data, the species types could be reduced from four to two (smectite and swelling chlorite). The literature data compiled for this study and other data presented in this paper suggest such a trend.

An examination of literature data by species is in order here. A clarification of X-ray identification criteria may not be possible from this, but at least a better understanding of the source of the confusion should emerge. The majority of the "vermiculite" species of corrensites reported in the literature swell where they should not and/or do not collapse enough. A compilation of these data is given in Table III. Some references have been omitted because either no data from X-ray analysis were reported or they were inconclusive; even some of the data included are many times insufficient for a valid identification. When considering this compilation, please recall the criteria shown in Table I, i.e.: a phase (untreated,  $28A=14A+14A$ ) that does not swell with glycolation (glycol = 28A) but collapses with heat to 24A ( $14A+10A$ ) is probably a vermiculite. Certain interpretive latitudes must be allowed but 30 and 31 angstroms is very generous for the untreated values. However, other variables such as the retention of additional interlayer waters due to high humidity conditions can also affect these superorder spacings. The presence of interlayer aluminum hydroxyl complexes could also influence the reactions of the clay structure to glycol and heat.

All the samples, presented in this table, except one, swell to varying degrees, which vermiculites should not do. Of the 12 samples in the table, 6 collapse to 24A or less as those with vermiculite (or smectite) layers should, and at least 4 collapse with heat to values greater than 24A, indicating that the swelling layers might be more validly considered to be swelling chlorites.

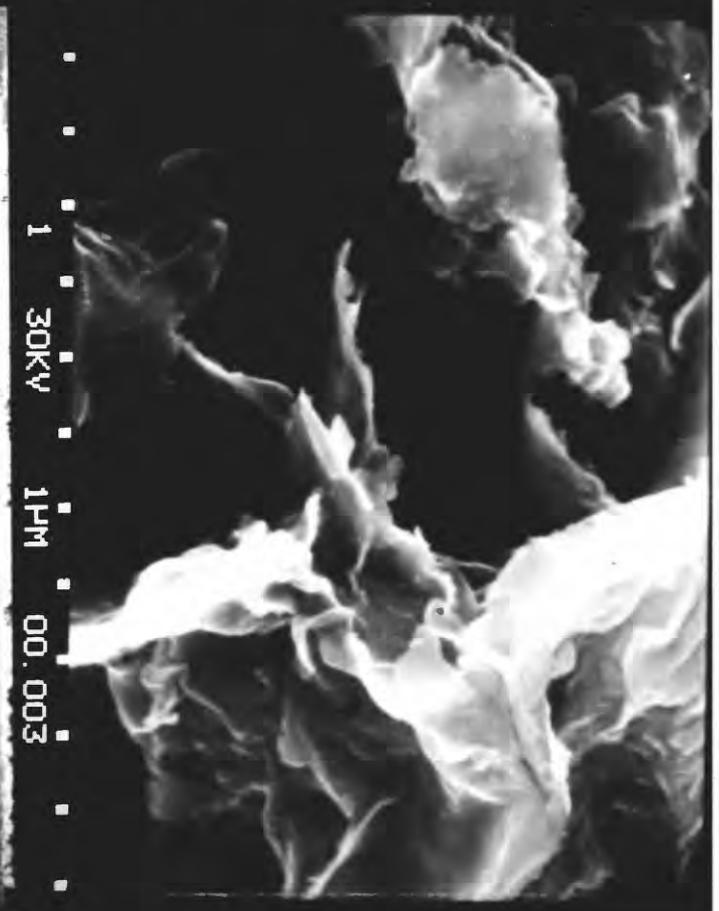
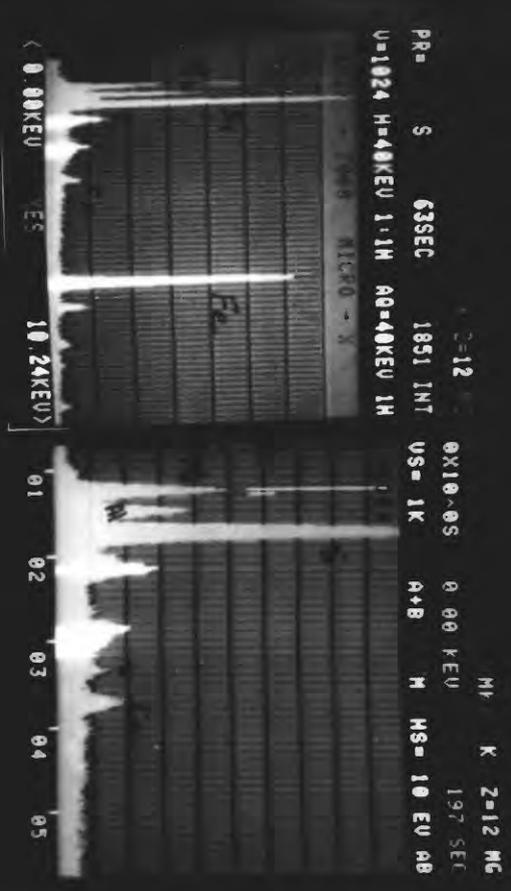
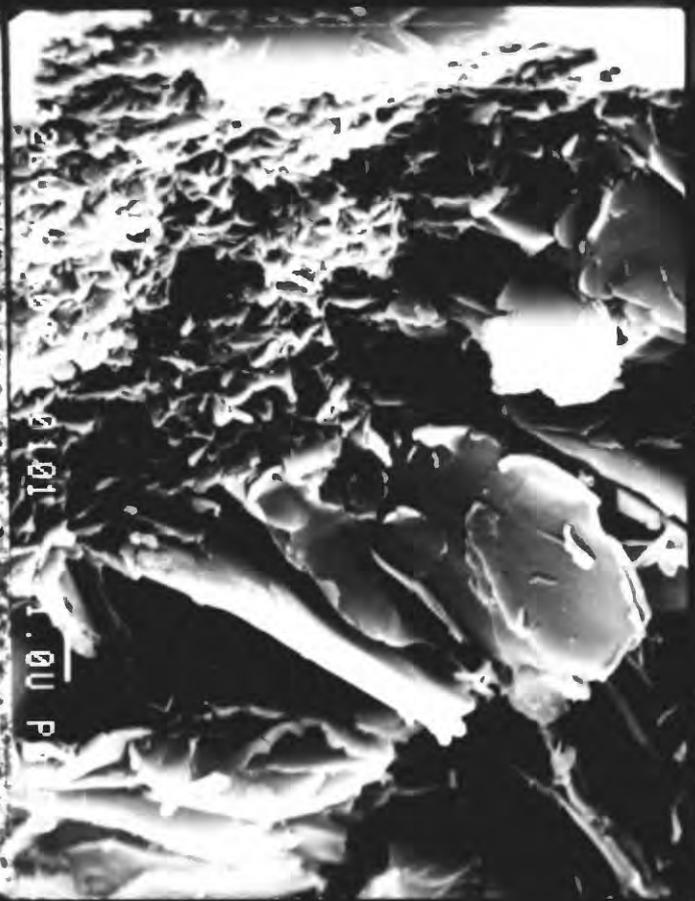


Table III.--X-ray diffraction data for corrensite species from the literature  
which cite vermiculite as the "swelling layer" constituent

[Numerical values are given in angstroms]

Reference	Untreated	Glycol	550°C
Bradley and Weaver 1956	29.2	31.0	(24) ?
	14.7	15.5	12
	9.7	10.2	8
	7.3	7.7	6
Alietti 1958	29.0	31.0	29.0 12.0
Grim et al. 1960	30.0 14.48	15.49	not given
Fournier 1961	30.5 14.26	31.5 15.5	21.55 13.81 (chl)?
Peterson 1961	29.4	31.2	
	14.7	15.6	12.0
	10.0	10.0	10.0
	7.4	7.8	8.0
Johnson 1964	28.5	28.5	24
Becher 1965	28.5	32-33	27.7-28
	14.2	16.2	13.9
		14.2	
	7.08	8.1	
Gradusov 1969	29.0 14.3	31.9	23.65
Rao and Bhattacharya 1973	30.9	31.5	
	14.9	15.2	13.7
	7.2	7.2	
Kopp and Fallis 1974	13.8	15.8	12.1
	9.0	7.9	8.0
	7.1	7.1	7.1 (chl)?
Lippmann 1956	29.0	31.0	
	14.5	15.5	13.0
	7.2	7.75	
	4.79	5.15	

There is only one sample in the table that adheres to the vermiculite parameters--that of Johnson (1964).

Therefore, what emerges from the perusal of Table III, is that perhaps the term "vermiculite" applied to the swelling layer of a corrensite species identified by X-ray diffraction techniques is not necessarily a valid usage. This conclusion assumes acceptance of the premise that "vermiculites do not swell." Some of these samples (Bradley and Weaver, 1956; Fournier, 1961; Peterson, 1961; Gradusov, 1969; Kopp and Fallis, 1974) might be reclassified as falling closer to the smectite variety whereas the samples of Alietti (1958), Becher (1965), Rao and Bhattacharya (1973), and Lippmann (1956) seem to act more as a swelling-chlorite variety.

If one next examines various "swelling-chlorite" samples as presented in the literature and compiled here in Table IV, they seem to hold slightly more true to their definition of 28A (untreated) swelling to 31A (14A+17A) with glycol and collapsing to 28A (14A+14A) with heat. Of the nine data sets in Table IV, four are fairly close to the 28A untreated value; nearly all swell greater than the theoretical value of 31A and all, except the two of Kimbara and Sudo (1973) in which the swelling layer behaves more like a smectite, collapse to 26-28A.

The literature values for the montmorillonite-cited species of corrensite are tabulated in Table V. These samples show the best fit to the established criteria with few digressions. The same applies to the saponite variety samples listed in Table VI.

If one calculates the distribution and percentages of all the values given for the samples in Tables III, IV, V, and VI on an unweighted, volume basis, the values having the higher percentages are:

untreated	29A	38.5% of the samples
	30A	20.5%
-----		
glycol	31A	29%
	32A	23.7%
	31.5A	16%
	33A	16%
-----		
550°C	24A	43%
	28A	16%

Choosing the highest from each group yields:

untreated	= 29A	(14A + 15A)
glycol	= 31A	(14A + 17A)
550°C	= 24A	(14A + 10A)

Table IV.--X-ray diffraction data for corrensite species from the literature  
that cite swelling-chlorite as "swelling layer" constituent

[Numerical values are given in angstroms]

Reference	Untreated	Glycol	550°C
Honeyborne 1951	14.5	16.4	13.8
Lippmann 1954	28.3 14.2	32.33 16.2	28.0 (14)
Martin Vivaldi and MacEwan 1957	30.0 14.7 30.0	35.0 16.8 32.7	13.1 28.5 13.6 8.8
Martin Vivaldi and MacEwan 1960	28	31	28
Heckrodt and Roering 1965	30.0 14.4	31.0 15.0	13.64
Kimbara and Sudo 1973	31.5 14.97 30.2 14.77	32.9 15.71 32.5 15.44	22.6 12.1 23.9 11.9
MacNeill 1978	28.5 14.3 7.05	32.72 15.5 7.8	27.61 13.8 6.86
Pevear 1979 Personal communication	28.0 14.2 8.88	32.0 15.2 8.0	23-26 13.2

Table V.—X-ray diffraction data for corrensite species from the literature  
that cite montmorillonite as the "swelling layer" constituent

[Numerical values are given in angstroms]

Reference	Untreated	Glycol	550°C
Earley and Milne 1956	29.0	31.7	23.3
Earley et al. 1956	29.0 14.1	32.0	24.0 12.0
Sudo and Kodama 1957	30.0 15.0 9.96 7.52	31.8 15.5	24.0 11.9
Sudo 1959	29.8	32.3	11.7
Lucas 1962	28.5 14.2 9.5 7.1	30.5 15.2 9.9 8.8	24 12 8.0
Wyart and Sabatier 1967	29.1	30.9	23.7 13.7
Flemal 1970	28.5 13.65 7.14	33.0 15.55 7.81	28.5 13.2
Wilson and Bain 1970	29.0 13.9-14	32.0 15-15.1	24 12.4
Schlenker 1971	29.0 14.6	31.5 15.5	23.5 12.1
Tomasson and Kristmannsdóttir 1972	14-14.6	15.3-15.8	12-14 12-12.9
Blatter et al. 1973	29.0 14-15	31.0 17 14	23-24 12
Sawatzki 1975	28-29.5 14-14.5	30-31.5 15.2-15.5	24 11.8-12.2
Almon et al. 1976	29 14.48 7.23	31 15.23 7.62	23.8 11.9 7.9
McKee, ed. (in press)	29 14.5 7.2	31+ 15.5 7.75	24 12

Table VI.—X-ray diffraction data for corrensite species from the literature  
that cite saponite as the "swelling layer" constituent

[Numerical values are given in angstroms]

Reference	Untreated	Glycol	550°C
Alietti 1958	29.4	31.6-.7	23.5 11.8 8.75
Kimbara 1973	30.4 14.72 9.82 7.31	31.5 15.49	23.9 11.94
Kimbara and Sudo 1973	30.0 15.8 9.8 7.4	32.7	23.0
Blackmon 1979 Personal communication	29.4 14.7	32.6 16.35 8.33	24.5 12.2
Loehr 1979	29.0 13.7 9.6	32.0 15.4	(24.9)? 12.45

This does not necessarily support a conclusion toward corrensite being primarily a smectite-type species but does indicate that the majority of the samples researched to date seem to have smectite-like characteristics. It would also seem less confusing to refer to this species as having "smectite" rather than "montmorillonite" or "saponite" layers, at least until more specific identification criteria are developed, or chemical analyses are available.

The swelling-chlorite variety as opposed to vermiculite appears to be the other common species. This hypothesis is supported by the trend shown in Table II and Figure 1 and will be given further credence with data presented in later sections.

#### Differential Thermal Analysis Criteria

Differential thermal analysis (DTA) is another useful technique for characterizing clay minerals. Unfortunately, not a great deal of work has been done on the corrensite species. In MacKenzie's book on DTA curves for clays (1957), Caillere and Henin present a helpful summary on DTA curves for corrensite and related types. As would be anticipated, there is a distinctive suite of peaks that can be used effectively to characterize some of the components of corrensite phases. One specific reaction range is a direct manifestation of the brucite layer, which may be most useful structurally toward identifying corrensite.

There is first a lower temperature endothermic peak between 100<sup>o</sup>-200<sup>o</sup>C, closer to 150<sup>o</sup>C, which indicates loss of absorbed water. The hydroxyls of the brucite layer are lost between 550<sup>o</sup>C to a little more than 600<sup>o</sup>C, and sometimes as high as 660<sup>o</sup>C. The structure still maintains integrity, however, until the mica layer is also dehydrated, around 830<sup>o</sup>-850<sup>o</sup>C. The exothermic peak of recrystallization also falls very close here, between 850<sup>o</sup>C to near 900<sup>o</sup>C.

Table VII is a compilation of some of the published DTA curves. Most of these values are estimates from the published diagrams. They generally conform to the criteria postulated by Caillere and Henin (in Mackenzie, 1957). However, there are no apparent species correlations. Until the more definite parameters of chemical composition, X-ray diffraction data and interlayer configurations can be established, these temperature values can only serve as guidelines for future investigations.

The DTA curves in Figure 2 are from Bradley and Weaver (1956). They were chosen to be included here because they not only illustrate the corrensite species under discussion, but also its hypothesized constituent parts. The bottom curve is indicative of these represented by numerical values in Table VII. The X-ray data in Table III for the Bradley and Weaver sample has smectite characteristics. Because corrensite is defined as a trioctahedral species, those samples designated dioctahedral have been labeled "questionably corrensite."

Table VII.--Compilation of DTA data for corrensite-like phases from literature sources  
 [( ) indicate values estimated from diagrams. \* indicates a dioctahedral phase which is questionably  
 corrensite]

Species	Endothermic		Exothermic		Reference
	150°C	660°C	830°C	850°C	
Chlorite-saponite					Alfietti, 1958
Chlorite-vermiculite	150	655	830	850	Alfietti, 1958
Chlorite-montmorillonite/ Chlorite-vermiculite	(150)	(550+)	(850)	(875)	Grim and Johns, 1953
*Chlorite-swelling layer	100,200	555	850	880,915	Heckroodt and Roering, 1965
Chlorite plus chlorite-vermiculite	(150+)	(580)	(850)	(890)	Heystek, 1955
Chlorite-vermiculite	(180)	(580)	(850)	(900)	Heystek, 1955
*Chlorite-montmorillonite	(150)	(610)	(870)	(940)	Sudo and Kodama, 1957
*Chlorite-swelling layer	(150) broad	510	(850+)	(950)	Klages and White, 1957
Chlorite-swelling chlorite	(120)	(610)	(830)	(860)	Lippmann, 1954, 1956
Chlorite-vermiculite	(100,200)	(610)	(820)	(840)	Peterson, 1961
Chlorite-vermiculite	100,210	550	(850+)	(890)	Bradley and Weaver, 1956

## Chemical Criteria

There are only a few chemical analyses for corrensite type minerals in the literature. This is understandable when the difficulty in obtaining a pure representative separate is considered. Table VIII is a compilation of these chemical analyses. It was not always clear from the text what was being analyzed, a clay separate or the whole rock; or how refined the analytical sample was.

The elemental percentages were calculated from these data and projected onto the ternary diagrams shown in Figure 3.

Approximate fields for montmorillonite, saponite, vermiculite, and magnesium-bearing chlorites have been plotted on Figure 3A. The Mg-bearing chlorite field is included for comparison because there was insufficient chemical analyses to plot a "swelling-chlorite" field. The chemical data were taken from analyses reported in Deer, Howie, and Zussman (vol. 3, 1962), Grim (1968), Weaver and Pollard (1973), Starkey and Blackmon (1979).

The effect of the chlorite constituent has not been considered and the chlorite most likely varies in composition among the samples, although it is probably magnesium-bearing. If the chlorite layer can be characterized with any confidence, and its influence subtracted, a shift to the left would be postulated.

Until there are more corrensite chemical data generally available, it is rather pointless to speculate too far on the distribution shown in Figure 3. However, some inferences can be drawn from these diagrams. In general there is credible separation between samples from hydrothermal environments and those from sedimentary environments except for sample 5 (which was identified as coming from a sedimentary environment). The term "hydrothermal" is an author designated one. There were no chemical data reported for "low-grade metamorphic" corrensite occurrences. Another very interesting observation is the scattered pattern of the various species. Using the authors' designations, there is only some consistency to species distribution. This could suggest that there are perhaps fewer discrete phases than previously identified.

It is interesting to note that the majority of the hydrothermal corrensites fall into the vermiculite field even though only two of them (no. 8 and no. 9) have been identified as having vermiculite layers while no. 6, a sedimentary chlorite-vermiculite, plots on the fringe of that field. The saponite variety of no. 2 falls definitely into the vermiculite field. No. 4, identified as a chlorite-saponite, seems by this criteria to be one. However, neither of the "montmorillonite" species (no. 5 and no. 7) are close to the montmorillonite field.

Figure 2--Differential Thermal Analysis Curves from a corrensite sample. These show a corrensite of the vermiculite variety and its constituent parts. Reproduced from Bradley and Weaver (1956, p. 502) with the permission of the authors.

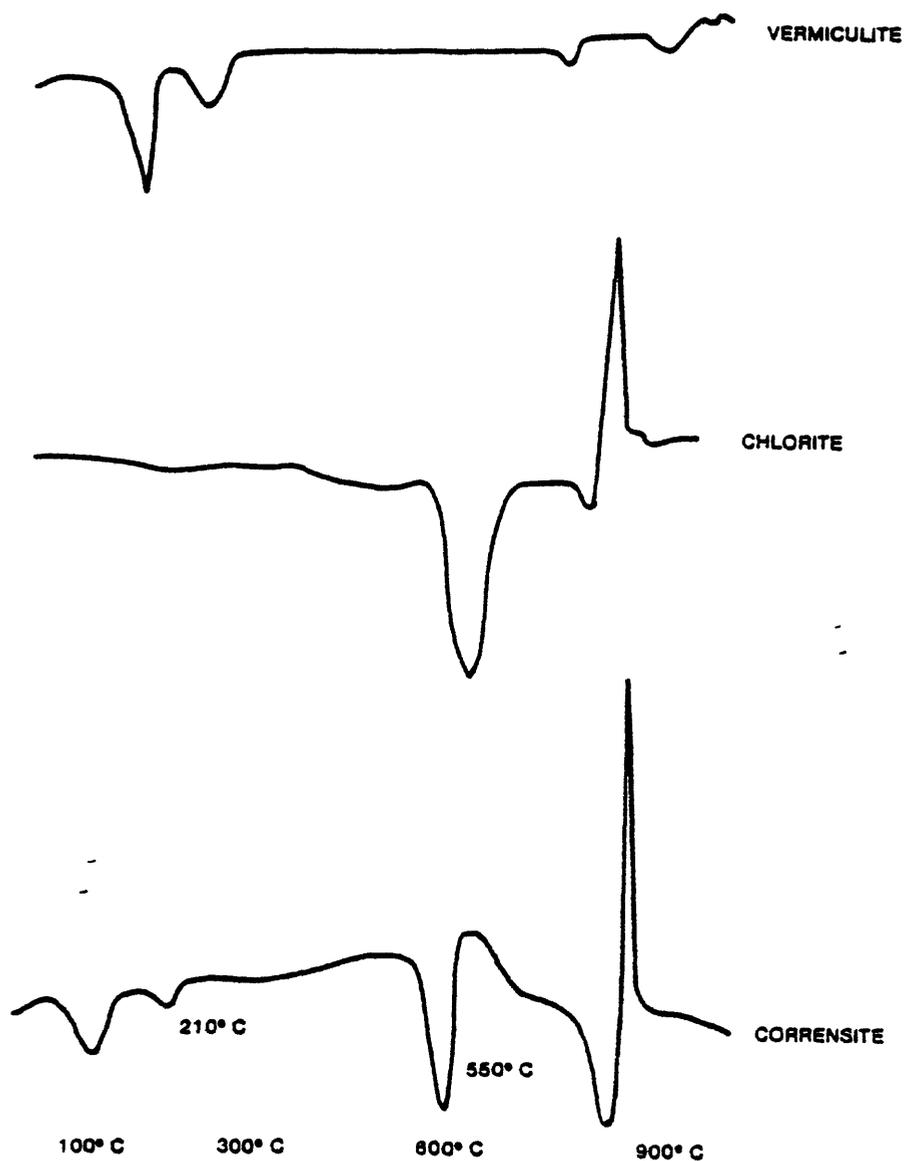


Table VIII.--Chemical analyses of some corrensite samples from the literature

Composition	chlorite-									
	1 swelling hydro	2 hydro	3 hydro	4 dol	5 dol	6 ls	7 CO <sub>3</sub> -slt	8 hydro	9 hydro	10 ls
SiO <sub>2</sub>	32.72	36.12	35.95	39.46	48.2	37.2	43.1	33.95	32.96	41.2
Al <sub>2</sub> O <sub>3</sub>	20.28	13.67	15.13	12.59	10.3	15.5	16.6	19.20	17.07	12.1
MgO	24.47	25.16	14.76	24.91	27.7	18.9	17.65	26.31	23.01	22.0
Fe <sub>2</sub> O <sub>3</sub>	1.00	2.14	6.65	.31	1.98	6.7	6.32	.71	2.79	1.74
FeO	--	6.85	9.15	.14	--	13.5	--	.69	8.68	.39
CaO	1.97	1.70	1.86	.06	.12	1.06	.94	.70	.58	1.4
Na <sub>2</sub> O	.25	.37	1.13	.22	1.24	1.32	.2	.74	.58	.07
K <sub>2</sub> O	Tr	.10	1.13	.03	1.12	.67	1.4	.05	.16	.22
TiO <sub>2</sub>	.03	.23	.30	.02	.3	.13	.4	Tr	.47	.04
MnO	.06	--	.38	--	.02	.32	--	--	--	--
H <sub>2</sub> O <sup>-</sup>	7.02	4.81	6.62	10.94	--	--	--	6.55	2.63	6.80
H <sub>2</sub> O <sup>+</sup>	12.57	9.25	7.30	11.2	--	12.13	7.40	11.26	11.28	15.4
TOTAL	100.37	100.4	100.00	99.88	--	99.63	100.48	100.16	100.21	101.36

These are arranged relative to species types and environments are given for each sample. The numbers at top of the columns refer to literature citations.

1. Shimoda, in Sudo and Shimoda, 1978
2. Allietti, 1958
3. Kimbara et al., in Sudo and Shimoda, 1978
4. Takahashi, 1959
5. Almon et al., 1976
6. Peterson, 1961, 1962
7. Earley et al., 1956
8. Sugitara, 1962
9. Allietti, 1958
10. Bradley and Weaver, 1956
11. Bodine, 1978

The numerical values are reproduced exactly as given in the source documents. Inaccurate totals have not been corrected.

ls = limestone; dol = dolomite; hydro = hydrothermal; slt = siltstone; evap. = evaporite

Figure 3--Ternary diagrams showing elemental relationships from some corrensite samples documented in the literature. A. Si-Al-Mg; B. Si-(Al + Fe (total)) - Mg; C. Si-Al-(Fe + Mg); D. Si-Al-(Fe + Mg). Numbers on the plots refer to the following references: 1. Shimoda, in Sudo and Shimoda, 1978 (swelling chlorite); 2. Alietti, 1958 (saponite); 3. Kimbara et al., in Sudo and Shimoda, 1978 (saponite); 4. Takahashi, 1959 (saponite); 5. Almon et al., 1976 (montmorillonite); 6. Peterson, 1961, 1962 (vermiculite); 7. Earley et al., 1956 (montmorillonite); 8. Sugiura, 1962 (vermiculite); 9. Alietti, 1958 (vermiculite); 10. Bradley and Weaver, 1956 (vermiculite); 11. Bodine, 1978 (saponite). The species given in parentheses are the authors' designation for the swelling layer constituent; circles refer to sedimentary occurrences, squares to hydrothermal occurrences.

Figure 3

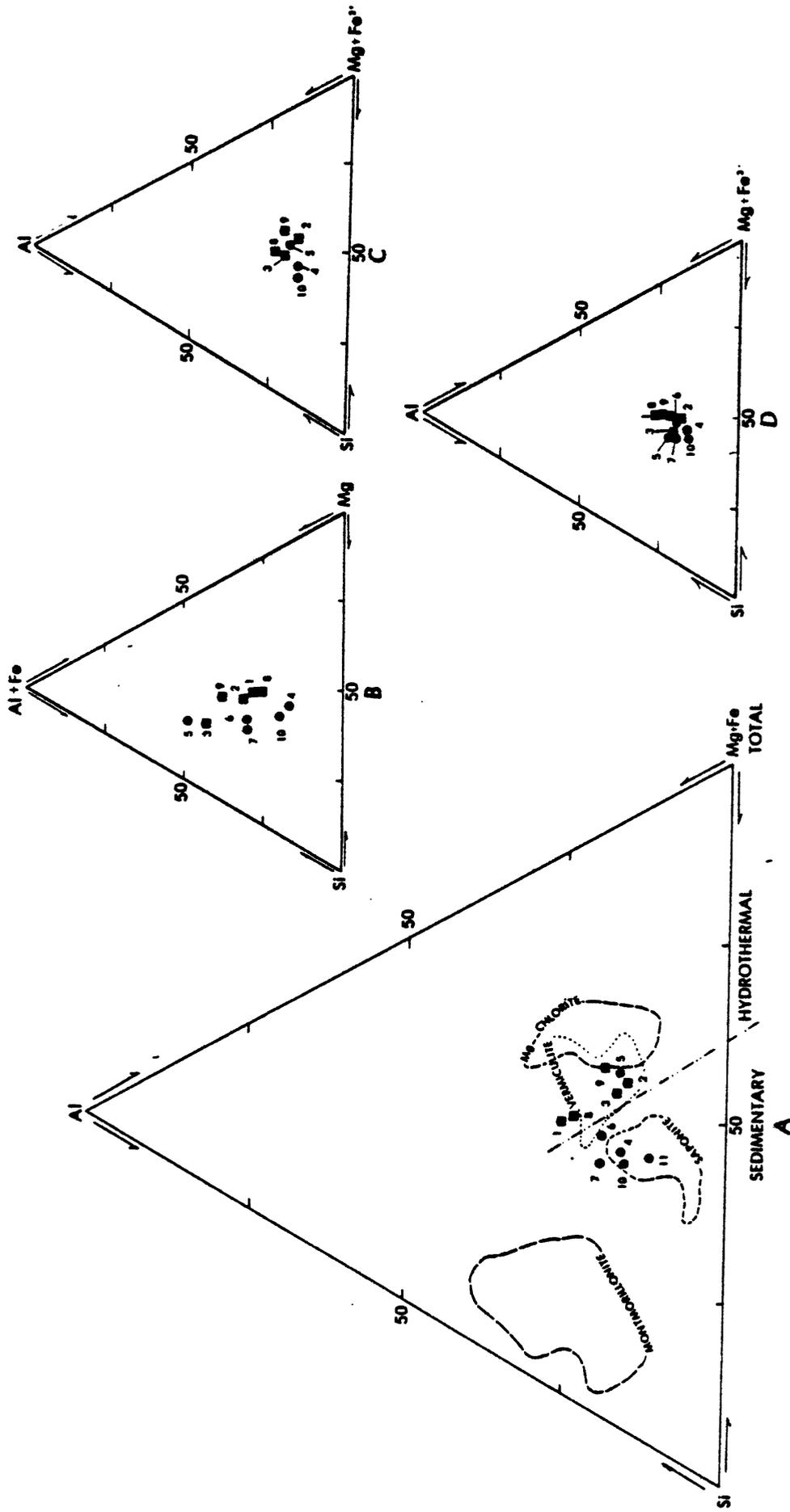


Table VIII also provides some additional generalizations. The corrensite samples found in the sedimentary environment have a higher silica content. The hydrothermally produced corrensites have both higher magnesium and aluminum contents than their sedimentary counterparts. For the most part, the range within the magnesium percentage for hydrothermal corrensites is small (about 3% from 23%-26%), whereas there is a greater latitude for the Al content with a 7.6% range. In a hydrothermal environment where Mg is a less-common element but restrictions on Al are not as stringent, this relationship is not surprising. The reverse trend appears in the sedimentary environments where there is a wide range of magnesium content (nearly 12%) but a restricted range for Al (4.4%).

It might be generalized that it takes less aluminum and less magnesium to make a sedimentary corrensite; however, sedimentary samples have more silica than the hydrothermal varieties. This might suggest different basic mechanisms of formation or at least different precursors.

Iron is the confusing chemical variable. Theoretically, if it is in the structure itself, the iron potentially substitutes into the cation positions of the octahedral layer. In Figure 3B, the plot of Si, Mg, (Al + Fe<sub>total</sub>), has a distribution relative to the other figures toward the Al + Fe end, which would seem to indicate that the iron is at least in part substituting into the Al positions. Both iron and aluminum may also substitute into the magnesium positions. This was substantiated by a plot of Mg-Fe-Si, which is not shown here. The separation of the sample points shown in the Si-Al-(Fe<sup>2+</sup> + Mg) plot in Figure 3C could imply that the iron is within the structure because a division between hydrothermal and sedimentary samples is evident. This is in contrast to Figure 3D, the Si-Al-(Fe<sup>3+</sup> + Mg) plot, where the clustering indicates, but still with environmental segregation, that the iron is more likely external to the structure, potentially an oxide coating or impurities in the sample.

To summarize, the chemical data suggest that depositional environment is an important consideration toward the determination of species type.

### Scanning Electron Microscopy Criteria

Few scanning electron microscope (SEM) photographs of corrensite phases have been published because they are difficult to obtain. Sample crystallinity is usually poor; grain size is small; mixed-layer configurations are notorious for poorly defined morphology; and corrensites, especially from sedimentary environments, appear to be so fragile that concentration processes tend to alter their morphological characteristics. The best SEM picture published to date of corrensite is that of Almon, et al. (1976). This portrays a chlorite-montmorillonite variety found in a transitional marine environment of calcareous sandstones. The corrensite was found here as pore and vein fillings, thus making it easier to visually locate and also giving it some protection. Figure 4 contains photographs of two previously unpublished corrensites with accompanying energy dispersive system (EDAX) spectra. In figure 4A, the corrensite is the darker band of near-vertical "grains" through the center of the picture. Figure 4B is an enlargement of the lower right corner of Figure 4A. This sample is the low-grade metamorphic chlorite-swelling chlorite from Washington. The curled edges are probably an artifact of the electron beam. The configuration shown in these two pictures is

Figure 4.--Scanning electron microscope photographs and energy dispersive spectra of corrensite specimens.

- A. Chlorite-swelling chlorite from Washington  
magnification = 2,400X.
- B. Chlorite-swelling chlorite from Washington  
magnification = 6,600X; this is an enlargement of A.
- C. Chlorite-saponite from Nevada  
magnification = 10,200X.
- D. Energy dispersive spectra for A and B.
- E. Energy dispersive spectra for C.

similar to the "cornflake" habit described by Almon, et al. (1976). Figure 4D is the corresponding energy dispersive spectra for the Washington corrensite. The first three peaks shown are Mg, Al, Si, respectively, and most probably relate to the corrensite. Figure 4C represents the hydrothermal chlorite-saponite from Nevada. EDAX spectra of this saponite is shown in Figure 4E and also shows Mg, Al, Si as the major elemental constituents. This habit is similar to a smectite.

These pictures are included here to illustrate one more potential method that can be used to characterize corrensite. Until numerous samples of corrensite are studied with the SEM, no valid conclusions relative to habit can be drawn.

#### SWELLING LAYER CHARACTERISTICS

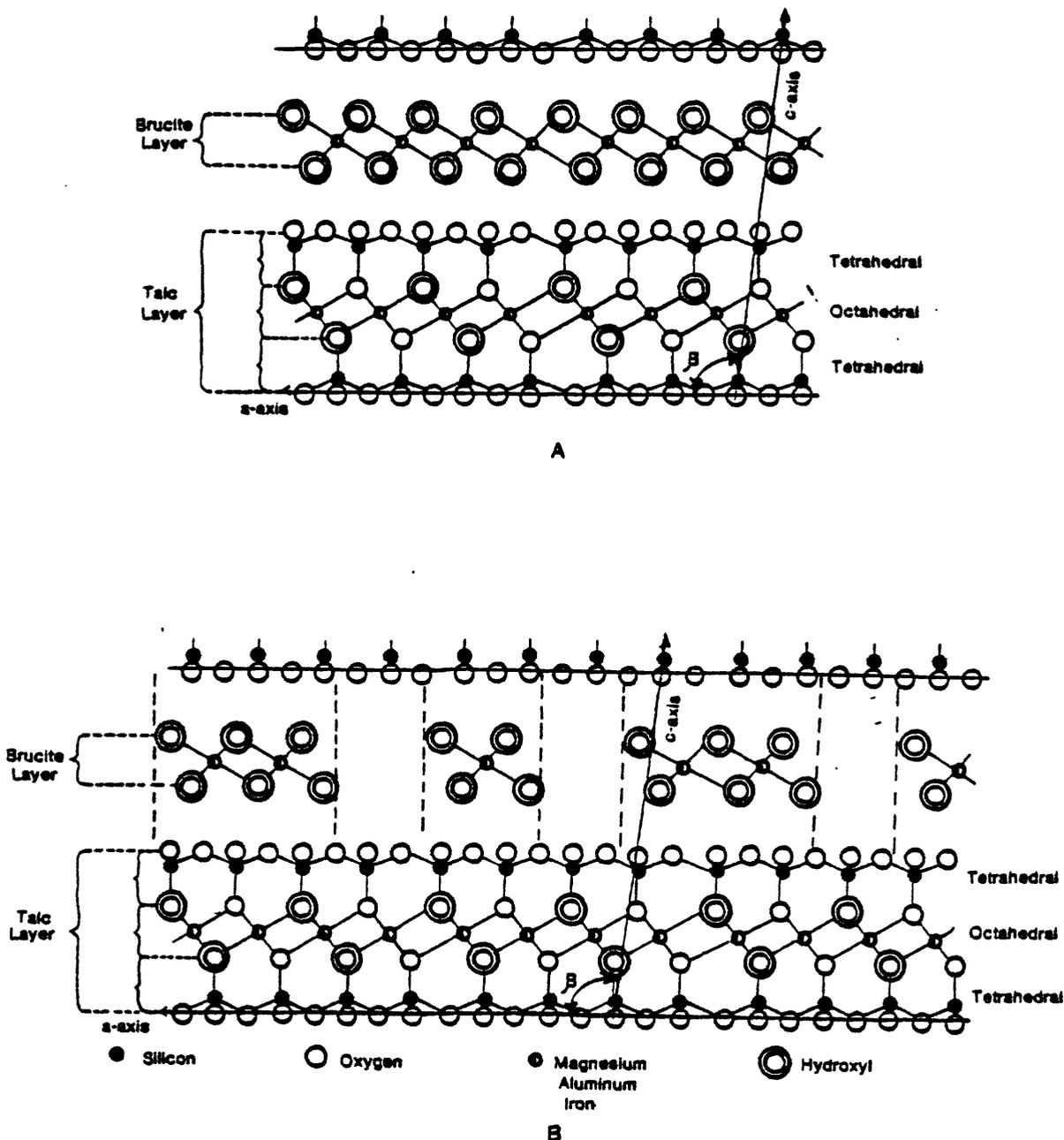
An explanation for the behavior of the swelling layer of the corrensite species was proposed by Martin Vivaldi and MacEwan (1960). These researchers hypothesized that the brucite layer within the swelling-layer component of the mixed-layer species was gapped having lost magnesium and hydroxyl ions resulting in an island or pillar configuration. Twenty years later this explanation seems less sophisticated than required to explain the behavioral idiosyncracies of this complex mineral.

Utilizing a simplified projection of the basic structure of a 14A-chlorite, shown in part A of Figure 5, and that same chlorite with a gapped brucite layer (Figure 5B), some speculations can be made about the mixed-layer configuration of corrensite.

The interlayer domain between the intact chlorite layer and the swelling clay layer must be considered at this time. Comparing the magnitude of the peaks of the DTA curves represented numerically in Table VII, interlayer water appears minimal compared to the hydroxyl content of the structure. Because its presence could be a function of ambient laboratory humidity conditions, a high weight percentage for interlayer water can be misleading. The interlayer cation composition is important in the ultimate characterization of corrensite. Until cation exchange work is done, what lies within the interlayer positions and its effect on the behavior of the various species becomes conjecture. If the swelling layer is also considered to equal 14A, then the X-ray data indicate that there exists an additional 0.3A to 3.5 angstroms (greater than 28A--air-dried value) along the "c" axis which could be explained by the presence of interlayer cations, interlayer hydroxyls, and/or adsorbed water. It is in this interlayer position that the polar molecule glycol could penetrate causing the swellings to 30A-34A that have been observed.

The octahedral layer of the swelling layer should also be considered as it is here that most isomorphous substitution occurs. The values in Table VIII show that there is a 10% and greater difference in both Al and Mg values, indicating some latitude for substitution. The greater variability in percentage content of magnesium and aluminum exists in the sedimentary environment.

Figure 5.--A diagrammatic representation of the chlorite layer of an intact structure (A) and a swelling layer which has been breached or not completed (B). This is a modification from Brindley and Robinson in Grim (1968, p. 101). No attempt has been made to balance layer charge in this representation.



The brucite layer of the swelling layer of the hypothetical corrensite structure merits consideration because it is potentially the weakest link--the Mg-OH bonds are relatively easier to create or destroy than the bonds holding the tetrahedral and octahedral layer elements together. If the brucite sheet is indeed incomplete, as some researchers believe, then this gapped structure, such as that idealized in Figure 5B might explain some behavioral idiosyncracies of the various corrensite phases--why they swell and collapse as they do. It is not inconceivable that the glycol molecule could also invade the "gapped" regions of the brucite layer causing expansion of the structure here also. However, since this organic molecule is 3.5A in diameter, it would probably have to be stacked to have any swelling effect. A discontinuous brucite layer would weaken the entire structure. Obviously there would be limitations to the number of "gaps" the brucite layer could support before the integrity of the structure is damaged to the point where collapse after heat treatment (less than 800°C) is to a spacing between 14-12A. X-ray diagrams have been run which show this progressive collapse with heating. Although this collapse with heat could be a function of the percentage of gaps in the brucite layer of the swelling layer component, it could also be the manifestation of Al-hydroxyl complexes precipitated into the interlayer domain. They could prop the structure up withstanding temperatures close to 800°C.

The possibilities available to explain this swelling layer are somewhat overwhelming. The swelling layer could take on the characteristics of a vermiculite, of a smectite, or a swelling chlorite depending on several variables and/or their combinations: the degree to which the brucite layers have been breached; the chemistry of the octahedral layer cations; the components and behavior of the interlayer domain and, not to be forgotten, the configuration and composition of the "seed" phyllosilicate mineral, i.e., the precursor of the corrensite phase. Figure 3, even with only 11 data points, shows little definite distribution pattern relative to species type, as designated by the authors; however, a definite trend relative to environment is noticed. The chemistry puts these species closest to vermiculites and borderlining saponites. However, vermiculite theoretically does not swell. Based on the X-ray data reported in the literature, every documented corrensite species, except the vermiculite variety of Johnson (1964), swells. Some swell by less than an angstrom, but there is definite movement toward a higher angstrom position with the introduction of glycol into the lattice. This upward shift may indicate an ability to accommodate the larger, organic molecules and therefore gaps in the structure or interlayer positions do exist into which these polar molecules can slip. The shift may also show the presence of adsorbed water--the function again of localized humidity conditions in the air-dried sample.

The DTA data shows a range for loss of OH from 550°-660°C. The more hydroxyl in the structure, the more intact and durable it would be potentially requiring higher temperatures for complete collapse. A weakened structure with gaps in the brucite layer could lose integrity at lower temperatures. There are only two samples from Figure 3 that also appear in the DTA table. From their chemical analyses they fall in the vermiculite field; from the DTA data, they require higher temperatures to remove OH, thus suggesting logically that they contain more OH and likely therefore fewer gaps in their structure. These observations obviously are not proof of a theory, but only the beginnings of a trend to be investigated. These temperature reactions

could also be explained by the presence of interlayer hydroxyls. Some work of this nature has been done on the English Keuper corrensites by MacNeill (1978).

The conclusion here is unavoidable--contradictions from chemical and X-ray data indicate that the present nomenclature and identification criteria for corrensite are in error and misleading. None of these identification techniques, by themselves, seem sufficient to characterize this highly complex mineral.

#### SUMMARY OF MINERALOGICAL DATA IMPLICATIONS

From the compilations presented in the preceding sections on X-ray diffraction, DTA, SEM, and chemical data, the most obvious conclusion is that a good deal more work must be done on corrensite before this ambiguous mineral can be characterized with any confidence. That conclusion was foregone and the inspiration for this paper.

X-ray data indicate that the swelling layers of the majority of documented corrensites exhibit the characteristics of a smectite while the few chemical analyses reported indicate that this is a saponite variety. Chemistry also shows that there are two species of corrensite. One is a saponite as defined by X-ray data and occurs exclusively in sedimentary environments. The other, although chemically a vermiculitic variety, has the X-ray diffraction characteristics of a swelling chlorite and exists solely in a hydrothermal regime. There are, of course, discrepancies in the preceding correlations in that many of the samples chemically classified as having vermiculite layers show the smectite-variety X-ray characteristics. The reverse is not true. Those samples chemically classified as having saponite layers do have smectite X-ray traits. These are trends based only on 11 data points but the distribution is strikingly consistent.

DTA techniques can add to the information on corrensite species but probably could never be used by itself to identify more than generally the existence of corrensite. SEM, even with the assistance of energy-dispersive spectra, also has limitations as there are so many variables which can determine or alter the morphology of a mixed-layer species. The lines for future investigation are now somewhat clearer. Corrensite species obviously will require more than one method of analyses for definite identification.

#### GEOLOGIC SIGNIFICANCE OF CORRENSITE OCCURRENCES

Until the mineralogical ambiguities of corrensite discussed in the preceding sections are more satisfactorily resolved, the geologic significance of this mineral will also be in question to some extent. However, a great deal can still be said about the usefulness of corrensite as an indicator of primary depositional environments from the data now available.

Corrensite has been documented from three general environments: sedimentary, hydrothermal, and low-grade metamorphic. Corrensite occurrences from each of these environments and subfacies will be summarized in tables and briefly discussed in later sections.

## Distribution of Corrensite Occurrences through Geologic Time

Further evidence toward the theory that corrensite species are directly related to their originating environments comes from a study of their distribution through geologic time. Figure 6A is a reproduction of an illustration taken from Weaver and Beck (1977, p. 216) which was used to show in a general way the relative abundance of corrensite and some associated authigenic magnesium minerals.

Some interesting generalizations emerge from this figure. Corrensite is shown to be relatively abundant at the beginning of the Mesozoic (Triassic) and during the Paleozoic. The major deposits of the French Jura Basin, and those of the English and German Keuper Marl are Triassic; the evaporite sequences of the Delaware Basin in North America and the famous German Zechstein are of Permian age. The corrensite-bearing evaporites of the Supai Group (Grand Canyon, Arizona) are also Permian. Most of the Supai corrensites are found earlier in the transitional marine environment of Pennsylvanian age. There are three Upper Mississippian occurrences documented in North America: the carbonate-rich environments of the Cumberland Plateau of Tennessee (Peterson, 1961, 1962); the Brazer Limestone from Colorado (Bradley and Weaver, 1956); and the marginal marine tidal flats and lagoons of southern Illinois (Fraser et al., 1973). These comprise the majority of the recorded sedimentary corrensite occurrences. As can be seen from the tables in a later section, there are Tertiary sedimentary corrensites reported from California (Flemal, 1970), and from India (Rao and Bhattacharya, 1973). However, nowhere else through geologic time has there been an abundance of sedimentary corrensite such as that observed during the late Paleozoic and early Mesozoic ages.

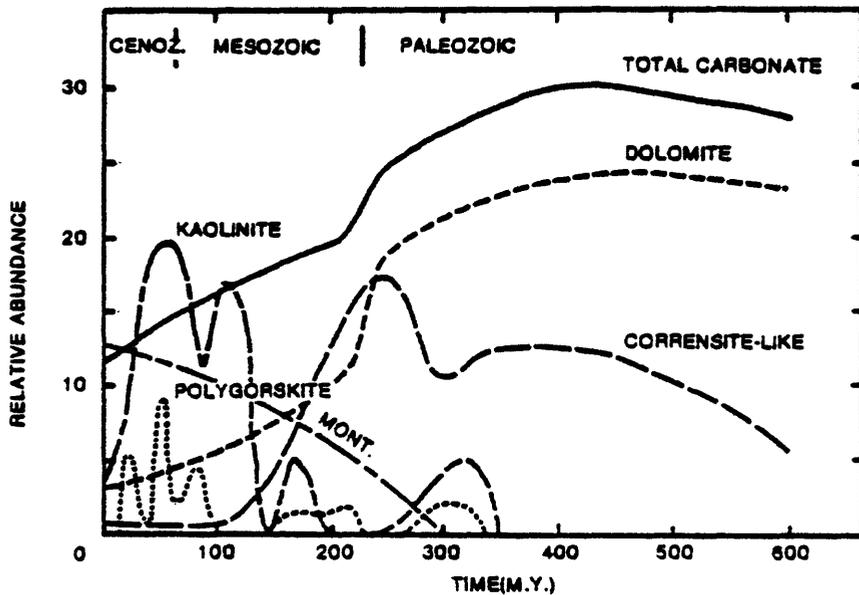
If these corrensites are environmentally linked as hypothesized, this distribution is quite logical. The climate at the time of major sedimentary corrensite deposition was warm and dry with arid conditions prevailing (Schwarzbach, 1961); sediment deposition occurred in shallow, epeirogenic seas with hypersaline waters (Shaw, 1964) and hypothesized lower concentrations of silica. All of these factors favored the deposition of dolomite with its attendant silica-poor corrensite. Weaver and Beck (1977) further pointed out that as the Mesozoic advanced, humidity increased, silica became more abundant, carbonate precipitation dropped off, and the silica-rich palygorskite was favored over corrensite.

Another interesting distribution is shown in Figure 6B which is a modification of Figure 6A. Here the hydrothermal and low-grade metamorphic corrensites have been incorporated in the sedimentary corrensite curve, and they fall almost exclusively in the Tertiary. The exceptions are low-grade metamorphic occurrences in the Precambrian to Cambrian of Scotland (Wilson and Bain, 1970); the Thones syncline of France (Sawatzki, 1975); and the Lower Cretaceous dike-intruded shales in Montana (Blatter et al., 1973). There are no other documented hydrothermal occurrences that have been found by the author.

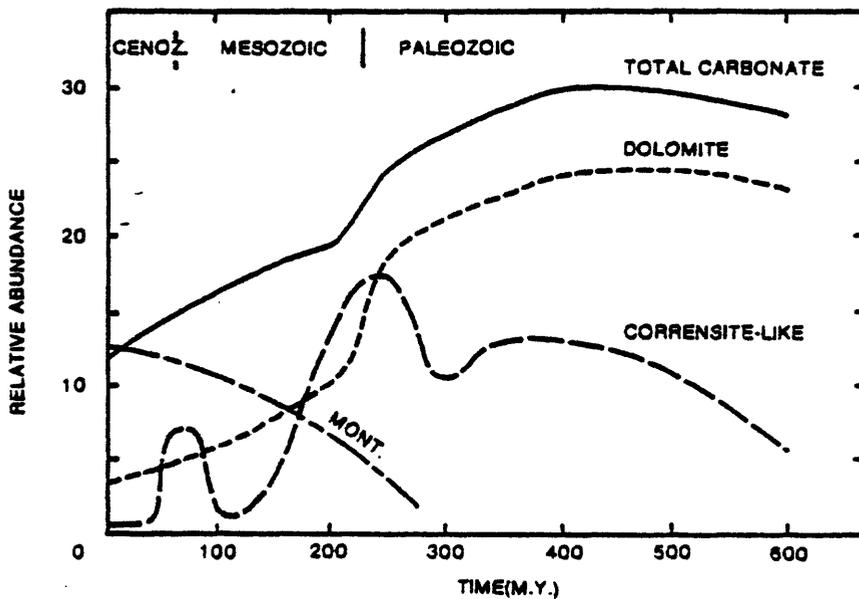
These figures very graphically illustrate the time and subsequent climate-environment association of corrensite occurrences.

Figure 6.--Distribution of corrensite and associated magnesium-bearing minerals through geologic time. (A) shows sedimentary corrensite occurrences plotted with other sedimentary minerals. In (B) the sedimentary curve is supplemented with a smaller hydrothermal curve in the Tertiary part of the time scale. These figures are reproduced and modified from Weaver and Beck (1977) with the authors' permission.

Figure 6



A



B

## Hypothesized Origins of Sedimentary Corrensite Species

From the previous sections of this paper has come the idea that there are only two discrete corrensite species, but with permutations, and that these species may be environmentally controlled. Some conjecture is in order here relative to the geochemical conditions required for the formation of sedimentary corrensite species.

Figure 7 was developed to explain the hypothesized origins of the corrensite formed in the Supai Group rocks of the Grand Canyon region in Arizona, an occurrence with which the author is most familiar (McKee, ed., in press). However, this diagram is flexible and applicable here. In their work on the Miocene of the southeast United States, Weaver and Beck (1977) postulated that some form of illite is a necessary precursor of corrensite. The illite structure would supply the required higher tetrahedral layer charge of corrensite. Unfortunately, the Supai study can neither prove nor refute this theory although an unsupported but logical hypothesis is that the random mixed-layer source of the authigenic Supai clays did originate from weathered detrital micas and feldspars.

As the flow of Figure 7 is followed, the theory of corrensite formation that emerges is one of ion aggradation of random mixed-layer phases in a magnesium-enriched environment as proposed by the French clay mineralogists and geochemists and applied to the studies of the Jura Basin of France (Lucas, 1962; Millot et al., 1963, 1966; Millot, 1964; and Lucas and Ataman, 1968).

The "Equivalence theory" that Powers (1959) developed explains the preferential adsorption of magnesium over potassium into the random mixed-layer structure. The ratio of the concentration of the  $Mg^{+2}$  to  $K^{+}$  ions is about 5 to 1 in seawater. From the water-sediment interface to a variable depth within the unconsolidated bottom sediments (this depth Powers calls the "Equivalence level") magnesium, because it is present in greater amounts, is adsorbed first. At this "Equivalence level"  $K^{+}$  and  $Mg^{+}$  are theoretically present in equal amounts while below this level potassium becomes the dominant ion and  $K^{+}$ -bearing clays are formed. Above the "Equivalence level" not only will the magnesium be adsorbed onto the degraded material, but it unites with free silica tetrahedra. This silica actively competes for the magnesium, capturing enough to form corrensite (which is a silica-deficient phase) but not a consistently sufficient amount to complete all the chlorite layers of the structure. A deficiency in aluminum, which is relatively insoluble and immobile in this environment, may be a further consideration relative to corrensite formation over chlorite.

With the incorporation of the magnesium ion into the lattice, water is lost, a higher level of ordering of the structure occurs and the number of expansible layers decreases. Magnesium substitution is favored at shallower water depths. This theory involves ion migration from the surrounding solutions to interlayer cation positions and then into the octahedral layer sites and finally to the tetrahedral layer sites (Millot et al., 1966). This is a process that can be followed from detrital random mixed-layer clays through a corrensite phase to a well-crystallized chlorite. In the Supai Group clay study this progression was observed. There is an abundance of random mixed-layer material which it is hypothesized, is being upgraded by ion aggradation into various authigenic clays. There are well-crystallized

# DIAGRAMMATIC REPRESENTATION OF CORRENSITE FORMATION

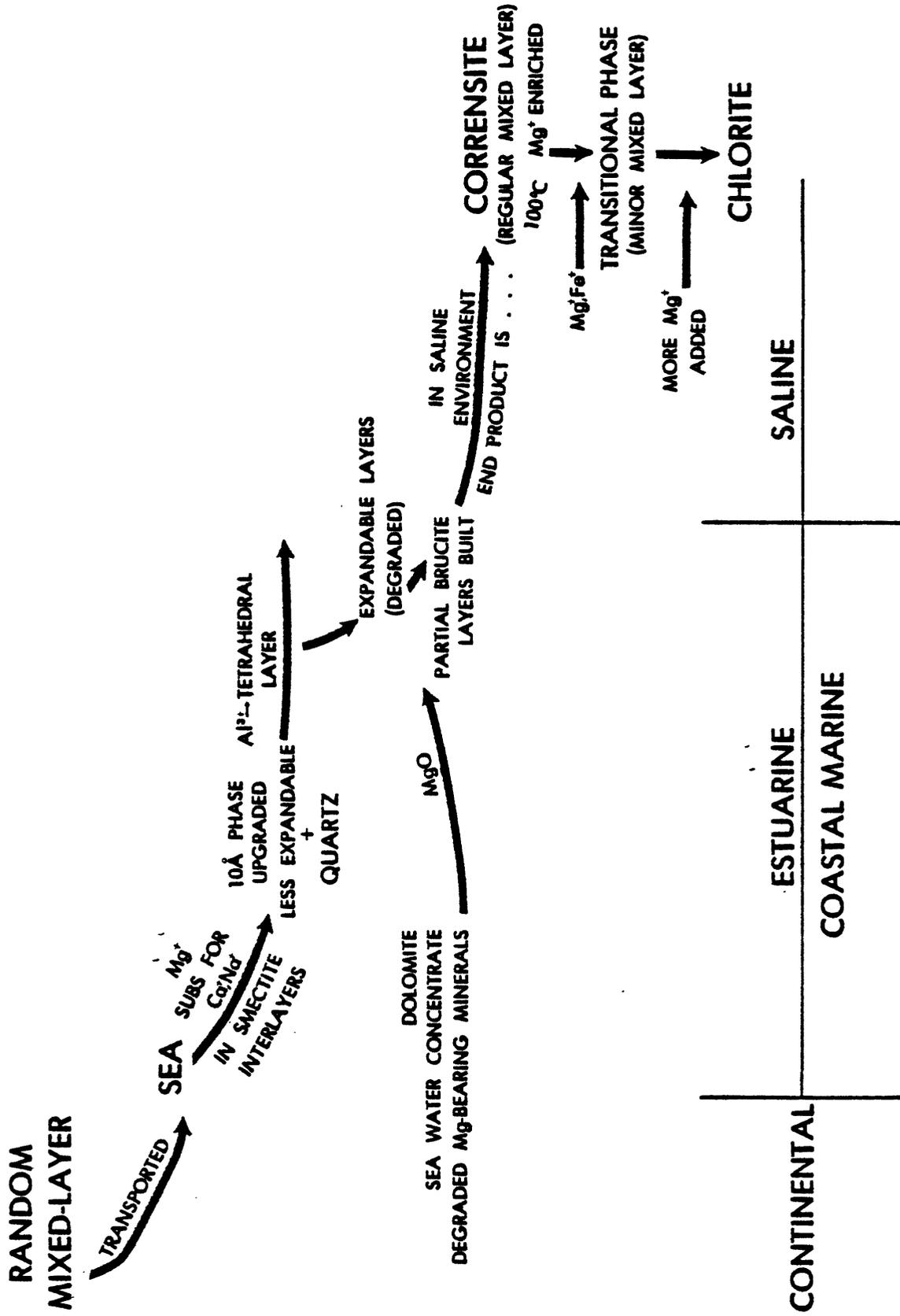


Figure 7.--Diagrammatic representation of the hypothesized origins of authigenic, sedimentary corrensites.

corrensites and there are transition corrensite-like phases. These phases do not expand as much as "true" corrensites with glycol (usually only 14.5-15.0A) nor do they collapse as far as does "corrensite" with heat (13.5-14A).

The implication is that this transition phase has fewer gaps in the brucite layer, has less water replacing the hydroxyls, has less, if any, interlayer waters or cations and, therefore, is a more tightly bonded transitional phase between corrensite and chlorite. The existence of this phase strongly suggests that the mixed-layer configuration of the corrensite is upgrading toward a nonexpanding chlorite, supporting the aggradation theory and corresponding with the summary of Dunoyer de Segonzac (1970).

Early work on corrensite led some researchers, Martin Vivaldi and MacEwan (1960) among others, to hypothesize that corrensite might form by weathering or degradation of a higher-ordered phase such as a chlorite. If the chlorite were put into an acidic environment with free hydrogen ion, the  $H^+$  could combine with the  $OH^-$ 's of the brucite layer forming water and freeing  $Mg^{2+}$  ions. This mechanism was used to explain their hypothesized "pillar" or "island" configuration for the brucite layer.

There is little substantiating evidence in modern literature for this degradation theory: the chlorite-vermiculite of Johnson (1964) might be cited. However, its validity as a corrensite species is in question since it does not swell and all other corrensites do.

The "swelling-chlorites" that Post and Janke (1974) describe as weathering products of California Mesozoic slates are also in question as no superorder values are reported from the X-ray diffraction work, and subsequently a valid identification of corrensite cannot be made.

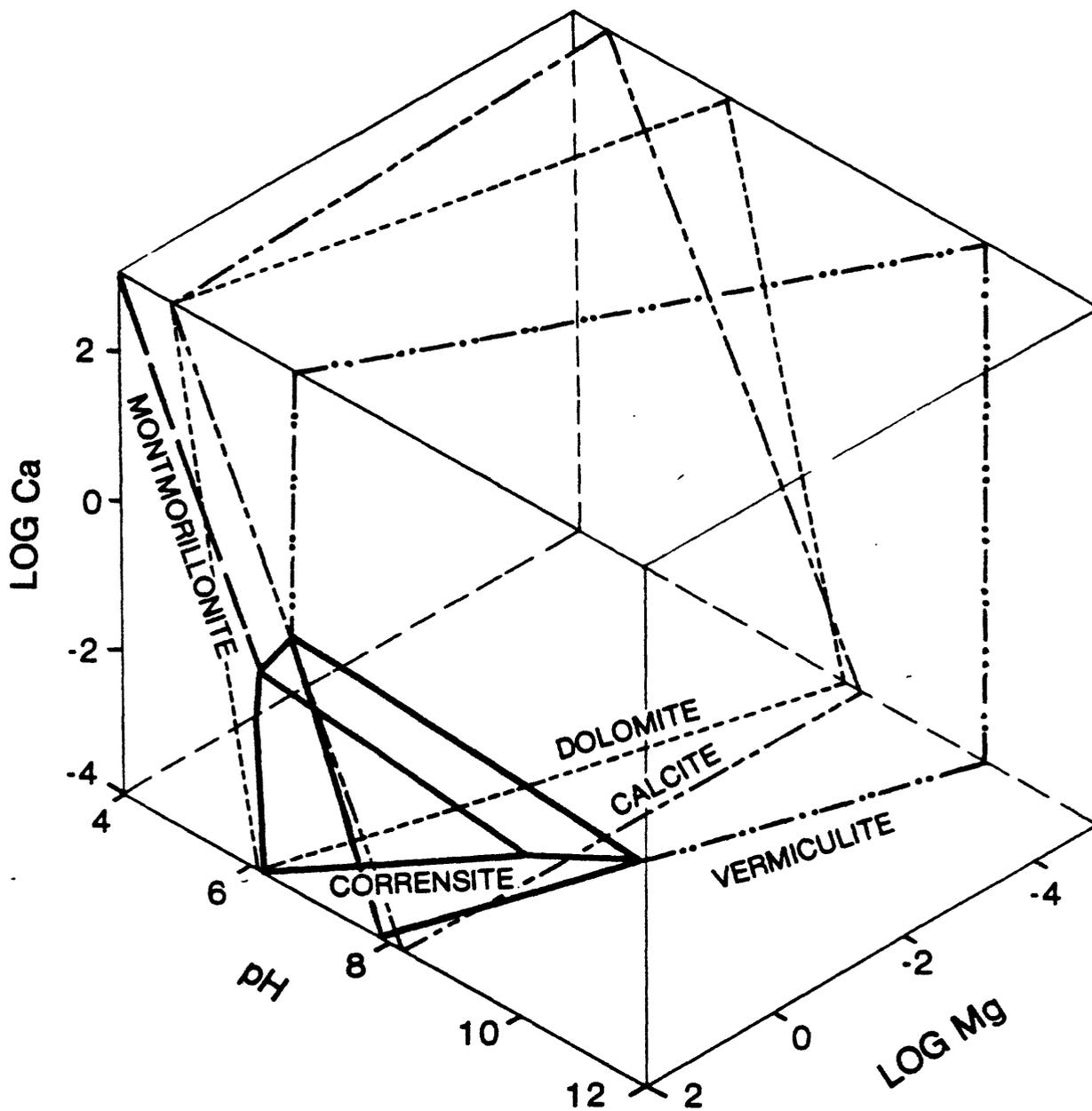
The mixed-layer configurations of "chlorite-vermiculites" and similar species in soil profiles are many times random interstratifications rather than the regular interlayering required for a corrensite. They also do not always possess the superorder lattice values, again a corrensite requisite.

Whatever the true mechanism of corrensite formation is the majority of current evidence seems to favor aggradation over degradation.

The stability field and associated mineral relationships for authigenic corrensites are shown in Figure 8, which is a modification of an illustration by Almon et al. (1976, p. 95). The parameters derived by these researchers indicated that corrensite is stable within a pH of 7.5-8.8 with a high magnesium to calcium ratio. This limited field makes corrensite a potentially useful indicator of depositional environments. These relationships are in agreement with the work done by Peterson (1961, 1962) in the Cumberland Plateau area of Tennessee.

Stability temperature from Velde (1977a, b) appears to be from 100°C to possibly as high as 280°C. Corrensite has been synthesized from montmorillonite in a magnesium-enriched solution at temperatures between 300°C and 600°C by Wyart and Sabatier (1967).

Figure 8—Stability fields for authigenic corrensites and associated minerals. Modified from Almon et al. (1976, p. 95).



### CORRENSITE STABILITY RELATIONSHIPS

## Occurrences of Corrensite in Sedimentary Environments

An observation to be drawn from the preceding section and one which will be substantiated by the numerous tables to follow in this section is that corrensite is commonly found as a primary phase; it has not yet been observed to be detrital. The distribution and mineralogical associations of corrensite through geologic time strongly indicates that the known occurrences are potentially all authigenic.

Sedimentary corrensite, with which the author is most familiar from studies of the Supai, seems to fall into three subfacies: those of evaporite sequences listed in Table IX; those in which the host lithology is primarily carbonate-bearing, shown in Table X; and those which are transitional marine, given in Table XI. Each of these tables contains a summary of the pertinent literature giving references to the phase, citation, brief environmental description, mineralogical associations, formation, locality, and age.

Evaporite-Bearing Host Rocks.--Originally corrensite was thought to be restricted to a hypersaline environment. As Table IX shows, a good deal of work, especially by the Europeans has been done on corrensites from evaporite sequences. The best-known corrensite occurrences are listed in this table: the Texas-New Mexico Delaware Basin; the German Zechstein Formation and Keuper Marl; the French Jura Basin. All the localities in Table IX, except one, are Permian or Triassic. Mineral associations for these evaporite-corrensites are consistent. Aside from the evaporite minerals, dolomite and illite seem to be always present, while quartz and chlorite are commonly present. This association suggests a magnesium-rich, restricted, quiet, shallow-water environment.

Carbonate-Bearing Host Rocks.--Another host rock for corrensite is one that is primarily carbonate. This is usually, but not exclusively, dolomite with calcite a common constituent. Quartz, chlorite, and illite are other frequently associated minerals. These occurrences are also mostly found in the Paleozoic and early Mesozoic. Again the environment suggests warm to hot, semidesert conditions with lagoonal to shallow marine waters. These localities are summarized in Table X.

Transitional Marine Environments.--The last type of sedimentary corrensite environment is that of transitional marine with still, shallow, warm, semirestricted waters, probably with some magnesium-enriched pockets. There is more interfacing with muds and silts. Dolomite and calcite are also requisite associated minerals as are illite, chlorite, and quartz. Feldspars and mica may also be present. This environment is, in some respects, less well defined than the preceding two. However, it is the environment with which the author is most familiar and a brief discussion of the Supai occurrence of corrensite is included here.

## Occurrence of Corrensite in the Supai Group Rocks

In the Supai Group of the Grand Canyon of Arizona, corrensite is found in the evaporite layers associated with dolostones of the Permian Esplanade Sandstone and in the two older formations of the group, the Pennsylvanian Watahomigi and Manakacha. In the latter two, corrensite occurs in the

Table IX.--Corrensite occurrences in evaporite-bearing rocks

[The arrangement is by species type]

Name	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Chlorite/vermiculite	Grim et al., 1960, Fournier, 1961, Madsen, 1979 Personal communication Loehr, 1979	mildly acidic Mg <sup>+2</sup> , Na <sup>+</sup> , K <sup>+</sup> -rich environment clays have accumulated and remained in this environment since Permian	dolomite, quartz, muscovite, chlorite, montmorillonite, halite, sylvite, polyhalite, magnesite, anhydrite, carnallite, illite, anhydrite Fe-oxide	Salado Formation, Carlsbad, New Mexico	Permian
Chlorite/vermiculite	Kopp and Fallis, 1974	hypersaline environment	dolomite, gypsum, anhydrite, quartz, illite or mica chlorite	Wellington Forma- tion Hutchinson salt Lyons, Kansas	Permian
Chlorite/vermiculite	Draizler, 1962 Braitsch, 1971	saline environment	quartz, albite, dolomite, talca, chlorite, montmor- illonite, anhydrite, illite, chlorite (penninite), halite, quartz, K-feldspar, magnesite	Zechstein Forma- tion, Germany Stassfurt rock salt	Permian
Chlorite/vermiculite "swelling chlorite"	Lippmann, 1956 Becher, 1965	continental salt-lake and salt-flat environ- ment, red and green shales, siltstone, sandstone	dolomite, calcite, illite, Gypsum, quartz, hematite, halite	Buntsandstein, Germany	Lower Triassic
Chlorite/montmorillonite (trioctahedral) chlorite/swelling chlorite	Echle, 1961, Schlenker, 1971 Lippmann, 1954 Lippmann, 1956 Lippmann, 1976	shales, marls, dolomitic carbonates, gypsum, sandstone argillaceous sediments dolomitic red beds	illite, chlorite, quartz, dolomite, anhydrite, plagi- oclase, mica, gypsum	Keuper Marl Gipskeuper Member Stuttgart, Germany	Triassic
Chlorite/montmorillonite	Milot et al., 1963 Lucas and Ataman, 1968 Tardy et al., 1972	saline...lagoonal marine deposits becoming marly, dolomitic or saline carbonates, evaporites, argillaceous sandstones	chlorite, illite, calcite, halite, gypsum, dolomite, anhydrite	Muschelkalk Forma- tion Keuper Formation Jura Basin, France	Triassic
Chlorite/montmorillonite	Flemal, 1970	evaporite layers of a nonmarine red bed	gypsum, chlorite illite smectite in noncorrensit horizons	Sespe Formation S. California near Santa Barbara	Mid-Tertiary
Chlorite/montmorillonite	McKee, ed. (in press)	evaporite layers associ- ated with the dolomite beds of the Esplanade Sandstone	dolomite, gypsum, illite	Supai Group Grand Canyon Region Arizona	Permian

Table X.--Corrensite occurrences in primarily carbonate-bearing rocks

Name	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Chlorite/swelling chlorite	Martin-Vivaldi and MacEwan, 1957	rocks corresponding to Keuper, Muschelkalk, Runter of Germany-- carbonates, shales, muds	calcite, dolomite, quartz, chlorite	Catalan Formation, Triassic Spain Jura Formation, France	
Chlorite/swelling chlorite	Honeyborne, 1951, Stephen and MacEwan, 1951, Davis, 1967, MacNeill, 1978	hot, semi-desert conditions; warm sea-shales dolomites; sandstones with coal stringers; basic saline and supersaline waters; lagunal or basic continental waters, fairly stagnant, few fossils, calcareous lakes, sepiolite/polygorskite appears in higher salinity	clays: illite, chlorite, swelling chlorite corrensite, sepiolite nonclays: quartz, dolomite, calcite, hematite <1%: Gypsum, halite, "celestine"	Keuper Marl, England	Triassic
Chlorite/vermiculite (trioctahedral)	Bradley and Weaver, 1956	carbonate	calcite, quartz (incomplete data)	Brazer Limestone Moffat Co., Colo.	Upper Mississippian
Chlorite/vermiculite and corrensite (trioctahedral)	Peterson, 1961, 1962	carbonates...formed by salinity variations caused by evaporite conc. of normal marine water	dolomite, calcite, quartz, K-spar, albite, illite-mica, montmorillonite(?), chlorite, authigenic assemblages	Cumberland Plateau Tennessee	Upper Mississippian
Chlorite/vermiculite	Rao and Bhattacharya, 1973	microdolospirite, limestone and shales, some hypersaline considered diagenetic	dolomite, clays	Sirban Limestone Riasi Himalayas, India	Tertiary

Table XI.--Corrensite occurrences in transitional marine or near-marine environments

Name	Compositional Description	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Chlorite/montmorillonite	Chlorite/montmorillonite	Grim and Johns, 1953	Recent--bay, continental shelf, open gulf ongoing sedimentation	illite-mont-chlorite chlorite/montmorillonite	Texas Gulf Coast	Holocene
Chlorite/montmorillonite (trioctahedral)	Chlorite/montmorillonite (trioctahedral)	Earley et al., 1956	argillaceous siltstone Mg <sup>+</sup> rich environment	dolomite, quartz, clay, mica, feldspar, organics	Yates Formation West Texas	Permian
Chlorite/vermiculite	Chlorite/vermiculite	Fraser, et al., 1973	carbonate rocks, tidal flats, lagoons, marine banks, shallow open-marine	details not given calcite +?	Southern Illinois	Upper Mississippian
Chlorite/montmorillonite	Chlorite/montmorillonite	Almon et al., 1976	volcaniclastic sandstone delta distributary channels and distributary mouth bar environment	calcite, dolomite (poor cement with corr)	Horseshief Formation, Montana	Upper Cretaceous
Chlorite/montmorillonite	Chlorite/montmorillonite	McKee, ed. (in press)	mudstones, siltstones, calcareous, transitional marine, shallow, lagoonal	calcite, quartz, dolomite, feldspar, illite, chlorite	Supai Group: Watahomigi and Manakacha Formations, Grand Canyon region, Arizona	Pennsylvanian

calcareous mudstones and in the carbonate rocks. It is hypothesized to be authigenic, a product of ion aggradation of the random mixed-layer clays which are thought to be originally detrital. Corrensite is associated almost exclusively with illite and often with chlorite. It is never found with the random mixed-layer clays, nor with kaolinite, which implies an acidic, high-alumina environment and is considered in the Supai to be of continental origin. The transitional swelling-chlorite type minerals, mentioned in a previous section, occur in stratigraphic proximity to corrensite and are additional indicators of the authigenic origins of the assemblage.

This probable authigenic origin is also supported by the lithologic associations of corrensite as it occurs throughout the marine facies of the Watahomigi and Manakacha Formations, the lowest energy formations of the group.

The Watahomigi is composed of carbonates, calcareous mudstones, and minor sandstone layers. The general impression of the Watahomigi environment is that it was mostly marine, low-energy, quiet water. There were transitional marine embayments with fluctuating water levels, some of which became restricted and were cut off from freshening waters. There was possibly a river forming a delta containing many distributaries that migrated across marine tidal flats to the open sea.

The Manakacha Formation is largely carbonate and mudstones, but does contain an appreciably greater amount of sandstone than the Watahomigi. The clay mineralogy of the Manakacha shows that in some respects its environment of deposition was similar to the Watahomigi, but in others quite different. The land-sea interface is more clearly defined in the Manakacha because of less intertonguing of marine and continental facies. The large amount of marine clay minerals such as illite, chlorite, and corrensite indicates the continuing and dominant role of the saltwater facies. The marine waters still prevailed to the west but the continental environment was starting to encroach on the sea.

Corrensite has been used in the Supai as an indicator of marine or transitional facies. Its distribution shows formation in near-shore locales restricted lagoons which are now narrow limestone units surrounded by calcareous silt and mud units. No evidence of hypersaline conditions is seen in the Watahomigi and Manakacha, but rather evidence for a relatively normal marine salinity with localized areas of high magnesium concentrations.

#### Summary of Sedimentary Occurrences

In general the shallow marine conditions of a warm, epicontinental sea seem to favor corrensite formation. There are localized salinity changes where slightly hypersaline conditions occur, and large concentrations of magnesium buildup (possibly due to calcium precipitation into calcite), as in lagoonal settings behind barrier bars. The "Equivalence level" concept of Powers (1957, 1959) can again be cited in support of shallow-water deposition of corrensite as magnesium substitution is favored at shallower depths.

Corrensite can also exist in restricted, large evaporite basins, and it is found in deltaic channels and distributary mouth bars (Almon, et al., 1976). These locales imply low-energy environments and impounded waters. Corrensite indicates a magnesium-enriched, silica-poor environment.

The conclusions of Lucas and Ataman (1968) suggest that corrensite is stable in a carbonate facies where much of the magnesium is relegated to the dolomites. Too little magnesium is then left to form a true chlorite, but the silica tetrahedra acquire some of the remaining  $Mg^{2+}$  ions and form corrensite. Silica deficiency is also a consideration. The fact that corrensite is found associated with evaporites may only be a function of whatever silica has managed to infiltrate the sulphate-chloride environment. This silica actively competes for the magnesium, capturing enough to form corrensite, an intermediate phase, but not a sufficient amount to complete all the chlorite layers of the structure.

#### Occurrence of Corrensite in Hydrothermal and Low-Grade Metamorphic Rocks

Corrensite also has been found in hydrothermal and low-grade metamorphic rocks. Information on these occurrences are summarized in Tables XII and XIII. The mineralogic constituents of the suites shown in both these tables are similar. Chlorite, calcite, prehnite, laumontite, serpentines, zeolites, saponite, illite, mixed-layer clays, and epidote seem common to both environments. These mineralogic assemblages are those of the zeolite and greenschist facies described by Turner and Verhoogen (1960). This facies is a low-temperature environment, with temperatures probably less than  $300^{\circ}C$ . In this environment there is little real distinction between sedimentary diagenetic processes and low-grade metamorphic activity. The two tables were compiled separately because of the designations made by the authors rather than because of dissimilarities in descriptions. These "hydrothermal" corrensite occurrences should be examined in much greater detail than possible here to identify the significance of corrensite in this environment.

#### SUMMARY AND DISCUSSION

Sedimentary corrensite is considered to be a progressive mineral--one that is being built from components of lesser order toward a higher degree of order; not a mineral that forms from the destruction of a more ordered phase. Corrensite is most likely a transition phase formed under limited geochemical conditions existing as an intermediate to a more ordered phase--that of a "true" chlorite.

Corrensite, under certain conditions, has survived through great periods of Geologic time showing remarkable longevity for a mixed-layer mineral. Corrensite has prevailed because its host rocks have been little affected by tectonism or modifying diagenetic fluids. Detrital corrensite is not known to occur nor is there documentation of true corrensite in soil-weathering profiles. In sedimentary rocks, therefore, corrensite appears to be authigenic--it forms in place at the time of deposition or shortly thereafter and subsequently mirrors the conditions of the primary depositional environment.

The relationship between environment and geologic time, shown by the clustering of sedimentary localities in the Paleozoic and early Mesozoic, indicates a definite correlation of the existence of corrensite with environmental parameters such as salinity, pH, temperature, climate, chemical composition, and energy levels. The sedimentary environments manifest the results of the limitations on these parameters with similar, almost exact mineralogic, lithologic, and geomorphic associations. The environmental

Table XII.--Hydrothermal corrensite occurrences

Name	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Compositional Description					
Chlorite/swelling chlorite (dioctahedral)	Hekrodt and Roering, 1965	deuteric altered beryl pegmatite in quartzites	beryl, albite, Li-bearing mica, amblygonite, tantalite	Dernburg pegmatite Karibib, S.W. Africa	
"Strongly expanding" chlorite (trioctahedral)	Tomasson and Kristmannsdottir, 1972	lava flows, geothermal system with saline groundwater circulating	zeolites, calcite, quartz, illite, anhydrite, epidote, prehnite, glass, plagioclase, montmorillonite, chlorite	Reykjanes geothermal area, Iceland	"post-glacial"
Chlorite/swelling chlorite	Kimbara and Sudo, 1973	hydrothermal alteration acidic to basic pyroclastic sediments-- cements tuffaceous sandstone; closely associated with laumontite	laumontite, prehnite, epidote, calcite, sericite, chlorite	"Green Tuff" Yamanaka District, Ishikawa Prefecture, Japan	Miocene
Chlorite/montmorillonite (trioctahedral)	Earley and Milne, 1956	hydrothermal alteration amygdaloidal basalt	mica (data incomplete)	Mozambique	
Chlorite/montmorillonite	Tomasson and Kristmannsdottir, 1972	lava flows, geothermal system with saline groundwater circulating	zeolites, calcite, quartz, illite, anhydrite, epidote, prehnite, glass, plagioclase, montmorillonite, chlorite	Reykjanes geothermal area, Iceland	
Chlorite/montmorillonite	Blatter et al., 1973	dike-intruded shales, siltstones, corrensite in shales and dike rock. It is thought to develop with the carbonate veining by hydrothermal action from the intrusive.	M.L. (illite-smectite) illite dike = pyroxene, plag. carbonate (calcite) veining	Montana Group and Colorado Group Western Montana	Early Cretaceous
Chlorite/montmorillonite	Blackmon, 1979 Personal communication	hydrothermal alteration argillite; altered and calcareous argillite	chlorite, trioct saponite, M.L. quartz, fsp, calcite, siderite, brucite, serpentine, magnetite, pyrophyllite	Eleana Formation, unit "J" Nye County, Nevada	Mississippian
Chlorite/vermiculite (trioctahedral)	Alletti, 1958	hydrothermal alteration serpentine masses calcareous	serpentine, chlorite, talc, calcite, quartz, saponite/talc chlorite/saponite; chl/verm	Monte Chiaro, Italy	
Chlorite/vermiculite	Harvey and Beck, 1960	hydrothermal alteration andesites and dacites formed by alteration of hornblende	chlorite, calcite, antigorite, plagioclase, montmorillonite, tobermorite, pyroxene, penninite, pyrophyllite	Goldfield, Nevada	Early Tertiary

Table XII.--Hydrothermal corrensite occurrences--Continued

Name	Compositional Description	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Chlorite/vermiculite	Bodine, 1971	hydrothermal porphyritic basalt flow interbedded with evapor- ites	magnesium-chlorite, K-spar, magnetite, anhydrite, halite	Haselgebirge evaporite sequence in the Hallstatt salt deposit Upper Austria		
Chlorite/vermiculite (trioctahedral)	Furbish, 1975	deuteric action in a sill-like gabbro - replacement product of chlorite in chlorite- prehnite or chlorite- laumontite alteration zonea in the gabbro; also in hydrothermal fracture filling	chlorite-prehnite chlorite-laumontite group of Ca-Mg-Na-Al-Si minerals	Durham, North Carolina		

Table XIII.--Low-grade metamorphic corrensite occurrences

[Arrangement is by species type]

Name	Reference	Environmental Description	Mineral Association	Formation Locality	Age
Compositional Description					
Swelling chlorite phase "precorrensite"	Sawatzki, 1975	volcanic graywackes, andesites, diabasic corrensite in low-grade metamorphics...laumontite zone of the zeolite facies; CO <sub>2</sub> cemented rocks	laumontite, illite, chlorite, illite/smectite M.L., swelling chlorite, carbonate cement	Thones Syncline Haute-Savoie, France	Jurassic Eocene Oligocene
Swelling chlorite	Wilson and Bain, 1970	meta-limestone clays formed as low-temperature diagenetic products or low-grade retrogressive metamorphic	saponite, illite, talc, calcite, kaolinite, muscovite, chlorite, tremolite, diopside	Dairadian Rocks, Scotland	Late Precambrian to Cambrian
Chlorite/swelling chlorite	Pevear, 1979 Personal communication	volcaniclastic sandstone seafloor basalt unit	"prehnite-pumpellyite facies	Crescent from Olympic Peninsula, Washington	Eocene
Chlorite/smectite	Wilson and Bain 1970	meta-limestone clays formed as low-temp. diagenetic products or low-grade retrogressive metamorphic	saponite, illite, talc, calcite, kaolinite, muscovite, chlorite, tremolite, diopside	Dairadian Rocks, Scotland to Cambrian	Late Precambrian
Chlorite/saponite	Kimbars, 1973	low-grade metamorphism replaces glass shards pyroclastics zeolite - amphibolites laumontite zone; prehnite-pumpellyite zone	chlorite, laumontite, prehnite, pumpellyite, epidote, montmorillonite, zeolites, Fe-saponite	Tanzawa Mountains, Japan	Early Miocene
Chlorite/montmorillonite	Sawatzki, 1975	volcanic graywackes andesites, diabasic corrensite in low-grade metamorphics...laumontite zone of the zeolite facies; CO <sub>2</sub> cemented rocks	laumontite, illite, chlorite, illite/smectite M.L., swelling chlorite, carbonate cement	Thones Syncline, Haute-Savoie, France	Jurassic Eocene Oligocene
Chlorite/vermiculite (trioctahedral)	Gradusov, 1969	asbestos rock	talc, asbestos, chrysotile anthophyllite	Zerveta deposit, S. Urals, USSR	

components for corrensite become predictable, supporting the conclusion that corrensite is a reliable indicator of certain depositional conditions.

Hydrothermal corrensites are apparently different from those found in sedimentary environments. They differ chemically. They are found almost exclusively in far younger rocks occurring in the Tertiary and early Cretaceous. More information must be compiled on hydrothermal corrensite occurrences.

The mineralogical data presented outlines the numerous problems in identifying true corrensites and in the accurate description and characterization of it. The literature data by which corrensite is now defined is contradictory, resulting understandably in misidentifications. Many corrensites, because of their complexity, have probably been identified improperly as chlorites. The preliminary interpretations given in this paper contribute somewhat toward a clearer understanding of corrensite. X-ray powder data show the probability of two species; a smectite that chemistry indicates is a saponite; and a swelling chlorite that is chemically in the vermiculite field. However, even if there are "only" two species, rather than four, they both cannot legitimately be known as "corrensite." Modern technology no longer permits the vagueness of former inexact measurements. These species can now be defined as precisely as their nature will allow.

Differential thermal analysis shows patterns unique to corrensites which can be further explored; the interlayer water molecules and the brucite layer hydroxyl ions can be identified. Thermal gravimetric analysis even more precisely defines the amount and location of water present. Infrared absorption analyses can establish the trioctahedral or dioctahedral nature of the clay layers. Further data on the nature of these layers is needed to understand the smectite species. Cation exchange work will be used to identify the presence and nature of interlayer cations which could explain the 14.3A to 17.5A variation in spacing exhibited by the swelling layer component. Detailed X-ray diffraction research using a precise goniometer that sees the superorder regions in greater and more accurate detail is necessary to resolve the seeming ambiguities in the presently documented lattice spacings. To establish the exact nature of the smectite species the Greene-Kelly test is also useful as it will complement existing X-ray and chemical data. Chemical digestions must be performed to determine the presence or absence of interlayer hydroxyls. Microprobe and comparable chemical analyses are needed. Additional SEM studies should delineate the trend in the habits already observed. Transmission electron microscopy can hopefully determine the configurations of the layers and their angstrom values. This briefly outlined schedule of analyses is planned by the author in an attempt to resolve the problems surrounding corrensite.

Corrensite can become valuable for the understanding of certain sedimentary environments. To utilize this potential exploration tool, corrensite the mineral species must be understood, officially described, and dependable, accurate, and consistent criteria established for its identification. Whether "corrensite" becomes the name of a group of mixed-layer clay species, each rigorously defined, or is allocated to a single mixed-layer phase, is the responsibility of the International Nomenclature Committee. The present literature confusion must be resolved and clear nomenclature instituted.

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