

EXPERIMENTALLY INDUCED VARIATION AND THE ENVIRONMENTAL SIGNIFICANCE OF CORRENSITE

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ABSTRACT. — Clay minerals of the corrensite type present some particular problems in the identification of the interstratified components. Choice of a reflection or combination or reflections from which unit basal spacings are calculated, choice of method of heat application, and history of the specimen before analysis may each induce large variations in the X-ray properties of corrensite.

The ubiquitous association of sedimentary corrensite with saline environmental indicators and the absence of corrensite in the sediment loads of modern streams implies that sedimentary corrensite is always a diagenetic product of saline conditions.

The first descriptions of a corrensite-like clay mineral were made by Stephen and MacEwan (1951) and Honeyborne (1951), both from the Keuper Marl of Great Britain. The term *corrensite* was first used by Lippman (1954) to describe a similar interstratified clay mineral from the Keuper Sandstone of Germany and later extended to a fourth occurrence from the Buntsandstein (Lippmann, 1956). In the following several years new occurrences multiplied (Earley, Brindley, McVeagh, and Vanden Heuvel, 1956; Bradley and Weaver, 1956; Martin Vivaldi and MacEwan, 1957; Sudo, 1959; Grim, Droste, and Bradley, 1960; Braitsch, 1960; Peterson, 1961, 1962; Millot, Lucas, and Wey, 1963). The term *corrensite* is now well entrenched in the literature of

general geology and new discoveries of its occurrence no longer constitute major finds.

It has long been known that the described corrensite specimens do not behave identically under experimental treatment. These variations were ascribed to differences in layer composition, and it was proposed that *corrensite* actually is a group of minerals composed of the several possible combinations of chlorite, swelling chlorite, vermiculite, and smectites. Because of this interpretation Martin Vivaldi and MacEwan (1960), Frank-Kamenetsky (1960) and MacEwan, Ruiz Amil, and Brown (1961) urged that the term *corrensite* be restricted to Lippman's original and "type" corrensite and that the remainder of these combinations receive new names. Unfortunately, the identity of the layer components in the original material has never been satisfactorily determined. Furthermore, Lippman's second occurrence certainly differed from his first, and, although the first ought to have priority, it is common to see the term *corrensite* used for the second variety even among those who advocate restricted usage of the term. Herein the term *corrensite* is used in its broadest sense, i.e., to include those clay minerals consisting of the regu-

lar interstratification of an expandable combination of 14 angstrom clay minerals.

In spite of awareness of the inherent variability of corrensite, identification of the component layers has proven to be difficult. An experimental scheme to distinguish among the possible layer constituents was first proposed by Martin Vivaldi and MacEwan (1906), and has gained general use among geologists who do not wish to go into detailed structural analyses. However, difficulties have often arisen with such schemes when replicate analyses are made on single specimens. Such variation can be attributed only to variations in experimental procedure. Recent studies on a series of corrensite specimens from the Sespe Formation of California are used here to illustrate these experimentally induced variation.

SAMPLE MATERIAL

Specimens containing corrensite were collected from four outcrop localities of the Sespe Formation, a mid-Tertiary non-marine redbed unit which outcrops in southern California in the general vicinity of Los Angeles. The four localities are Old San Marcos Pass northwest of the city of Santa Barbara, Sycamore Canyon north of Santa Barbara, Casita Pass northwest of Ventura, and Agua Dulce Canyon 3 miles northeast of Lang (Flemal, 1966). At each locality the corrensite occurs only in gypsiferous strata or in strata associated with gypsum-bearing beds, and is generally associated with minor amounts of chlorite and illite. Smectite is the dominant

clay mineral in the large portion of the Sespe Formation that does not contain corrensite, but it was not identified as a separate species in any of the corrensite-bearing strata.

SAMPLE PREPARATION

Preparation of the samples for X-ray analysis was achieved in the following steps:

1) 0.5 to 2.0 grams of material were lightly ground in a mortar and sieved to less than 0.88 mm in diameter. Six ml of distilled water and 4 drops of concentrated sodium hexametaphosphate were added to the powder.

2) The samples were agitated in an ultrasonic vibrator for one hour to effect disaggregation. Each sample was then mixed and allowed to settle for 3½ hours, after which the liquid portion was decanted and placed on round cover slips to air-dry.

3) Four X-ray slides were made from each decant. A single slide was used for both untreated X-ray and glycolated X-ray runs. A second slide from the same decant was used for heat experiments. The two remaining slides were used to check results obtained from the first two.

4) For glycolation, each slide was placed in a covered box containing an open well of ethylene glycol. Complete glycolation was usually achieved at room temperature within one week. For some slides, the box was held in an oven heated at 35 degrees C. This procedure usually affected glycolation within 24 hours, but tended to cause minor warping of the thin clay film.

5) Heat treatment experiments,

TABLE 1.—Basal reflection properties of four untreated samples of corrensite from a single microscopically uniform hand specimen. Measurements in angstroms.

Reflection	Intensity	Samples				Average	Calculated Unit Basal Spacing	Deviation from Average	Deviation from Calc. 002
		(1)	(2)	(3)	(4)				
001.....	s	28.5	28.5	28.5	28.5	28.5	+0.9	+1.2	
002.....	vs	13.7	13.7	13.6	13.6	13.65	-0.3	0.	
003.....	s	9.0	8.93	8.93	8.93	8.94	-0.74	-0.48	
004+chlorite?	m	7.15	7.13	7.13	7.13	7.14	+1.00	+1.26	
005?	mb	5.34	5.37	5.30	5.29	5.33	-0.91	-0.65	
006.....	w	4.77	4.77	4.74	4.77	4.76	+1.00	+1.26	
007.....	vw	**	3.78	3.78	3.78	3.78	-1.10	-0.84	
008+chlorite?	w	3.565	3.55	3.55	3.54	3.55	+0.84	+0.90	
009.....	w	2.97	2.97	2.96	2.95	2.96	-0.92	-0.66	
						27.56			
						Average			

** = reflection absent.

strom pair, one of which is expandible to 17 angstroms. However, if only the measured (001) values are used, the glycolated samples at an average of 33 angstroms suggest that both members of the pair are expandible to nearly 17 angstroms. If the latter may be attributed to measurement error, according to the Martin Vivaldi and MacEwan scheme, the 14-14 pair would be normal chlorite with either smectite or swelling chlorite. Attempted distinction between the swelling chlorite and smectite would normally be made by heat treatment (Martin Vivaldi and MacEwan, 1960, p. 178). However, in the case of the Sespe corrensite, for which differing methods of heat treatment were applied, the results are not diagnostic.

Four methods of heat treatment were applied to the Sespe corrensite. The first two consisted simply of placing a prepared slide directly on a hot plate for one hour. The hot plate was either cold and allowed to heat gradually to 450 degrees C. (method #1), or already heated to and held at 450 degrees C. (method #2). Conflicting results were obtained: in method #1 the resultant trace showed an irregular series of reflections, the largest of which was at 13.7 angstrom; the method #2 trace showed no peaks at all, indicating that the interlayered water was expelled from the corrensite structure so fast that the disruption destroyed any regularity of layering.

The second two heating methods were developed to allow sequential X-raying in such a manner as to permit tracing the changes induced by the heating. Method #3 consisted of placing a sample in a closed crucible

which was held at approximately 450 degrees C. during the experiment. At intervals beginning at 1.5 minutes the specimen was removed from the crucible and X-rayed over the range of the first four basal reflections. The results (figure 1 and table 3) show a gradual decrease in intensity and spacing of the peaks, particularly the (001) and (003) reflections which decreased in spacing 0.9 and 1.00 angstroms respectively before they were lost. A similar decrease but of lesser magnitude occurred in the (002) reflection which fell from 13.6 to 13.2 angstroms after 45 hours of heating.

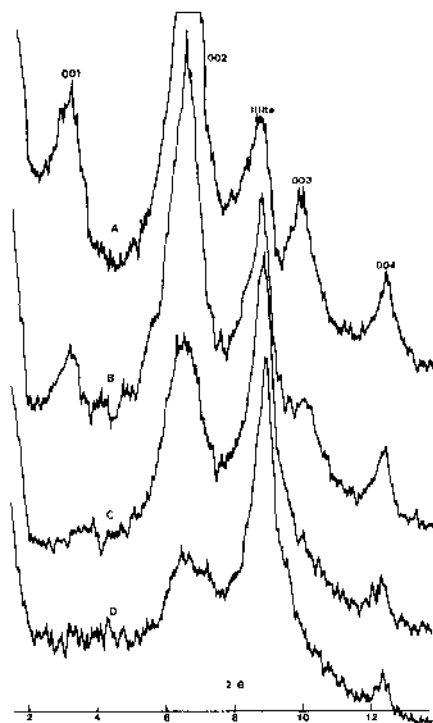


FIGURE 1. Sample x-ray diffraction traces of corrensite-illite clay mixture. Heat treatment method #3 (see text). A. Unheated. B. 9.5 minutes. C. 2.0 hours. D. 45.0 hours.

TABLE 3.—Results of sequential heating experiment on *corrensile*, method #3 as described in text. Intensity (I) measured as peak height above an arbitrary baseline.

Temperature	Time	001		002		111ire		003		004	
		Å	I	Å	I	Å	I	Å	I	Å	I
25 C.	0	29.4	3.9	13.6	8.9	10.2	3.5	8.93	2.5	7.13	1.2
450 C.	1.5m	28.5	3.4	13.6	7.4	10.2	4.0	8.88	2.0	7.16	1.4
450 C.	4.5m	28.0	2.7	13.7	6.9	10.2	4.4	8.84	1.8	7.13	0.8
450 C.	9.5m	28.5	2.2	13.7	6.9	10.1	4.5	8.84	1.7	7.13	0.8
450 C.	24.5m	28.5	2.0	13.8	6.7	10.2	4.8	8.84	1.5	7.16	0.8
450 C.	54.5m	28.5	1.7	13.8	5.3	10.1	5.3	1.5	7.19	0.5
450 C.	2.0h	13.7	4.2	10.1	5.5	7.22	0.5
450 C.	8.0h	28.5?	1.6	13.8	4.6	10.1	5.8	7.19	0.6
450 C.	20.5h	13.3	2.8	10.0	6.1	8.67	1.1	7.13	0.5
450 C.	25.0h	13.2	2.6	10.1	6.0	8.34	0.7	7.16	0.5
450 C.	30.5h	13.2	2.5	10.0	5.2	7.96?	7.13	0.4
450 C.	45.0h	13.2	2.1	10.0	5.4	7.16	0.4

Method #4 consisted of placing a slide prepared identically to the one used in method #3 in an oven which was allowed to heat up gradually from room temperature to 180 degrees C. The results are presented in figure 2 and table 4. There are several significant differences between these results and those produced by method #3. In general the peaks showed the same decrease in intensity, with the (001) reflection disappearing after 27.5 hours of heating. The (003) reflection, which was undetectable during the latter part of the method #3 treatment, first showed a decrease in intensity accompanied by broadening of the peak, and then an increase in intensity and sharpening of the reflection. Even more intriguing is the greater collapse of the unit basal spacing which fell to 24.8 angstroms (2×12.4), versus to 26.4 angstroms (2×13.2) for method #3.

Few of these peculiarities produced by differing heat treatments have been discussed in the literature. The gradual loss of the (001) reflection in heating experiments, is not unusual, as is shown by Lippmann's (1956), Earley, Brindley, McVeagh and Vanden Heuval's (1956), and Sudo's (1959) data. Smith (1960, p. 285) suggests that his loss is due to undefined "structural irregularities," but the phenomenon still remains largely unexplained. One method by which this loss might be achieved is by having the heat produce an homogenizing effect on the individual layers of the corrensite. This could be done by driving out water layers that occur between every second layer of otherwise similar inter-layered components. Such a phe-

nomenon would occur if the inter-layered components were swelling chlorite and normal chlorite. This explanation, however, is not entirely adequate since the higher order odd reflections persist, even though the (001) reflection disappears.

The type of variable intensity shown by the (003) reflection in method #4 is explained by uneven loss of water from the structure, which caused a temporary disordering of the reflection. But why this should be more pronounced in one method than in the other is unexplained. Also, why the two methods produced different basal spacings is undetermined. If either of these two phenomena were due to the degree of dehydration alone, the results of the last two heat methods would likely have been reversed, since the third method involved greater temperature than did the fourth.

If only the results of the first or third heating methods were available, the conclusion would be that the Sespe corrensite consists of two species which have 13-14 angstrom spacings when collapsed (i.e., normal chlorite and expandable chlorite). On the other hand, if only the results of method #4 were available, the suggestion would be that a 14-10 angstrom collapsed pair was present (normal chlorite and smectite). Clearly, the choice will depend on the treatment procedures.

The behavior of the 10.1 angstrom reflection in the heated samples (figures 1 and 2) does give some suggestion for a 14-10 angstrom collapsed pair, in as much as the increase in its intensity may be more than can be expected for simple or-

TABLE 4.—Results of sequential heating experiment on corrensite, method #4 as described in text. Intensity (I) measured as peak height above an arbitrary baseline.

Temperature	Time	001		002		Illite		003		004	
		Å	I	Å	I	Å	I	Å	I	Å	I
25 C	0	29.4	3.9	13.6	8.9	10.2	3.5	8.93	2.5	7.13	1.2
100 C	20.0m	29.9	3.7	13.6	8.1	10.2	3.6	8.93	2.5	7.13	1.6
150 C	2.0h	28.5	2.5	13.6	5.9	10.2	4.3	8.75	1.8	7.19	1.8
180 C	8.0h	26.8	1.4	13.6	6.3	10.2	4.6	8.75	1.6	7.19	1.1
180 C	18.0h	1.5	12.8	4.8	10.1	5.5	9.11	1.9	7.19	1.1
180 C	23.0h	26.0?	1.8	12.6	3.8	10.1	5.2	8.14	1.8	7.13	1.0
180 C	27.5h	12.6	3.7	10.1	4.9	8.18	1.7	7.13	0.8
180 C	43.0h	12.4	3.4	10.1	4.5	8.18	1.5	7.19	0.7

dering of an illite (001) reflection. However, this is not conclusive proof.

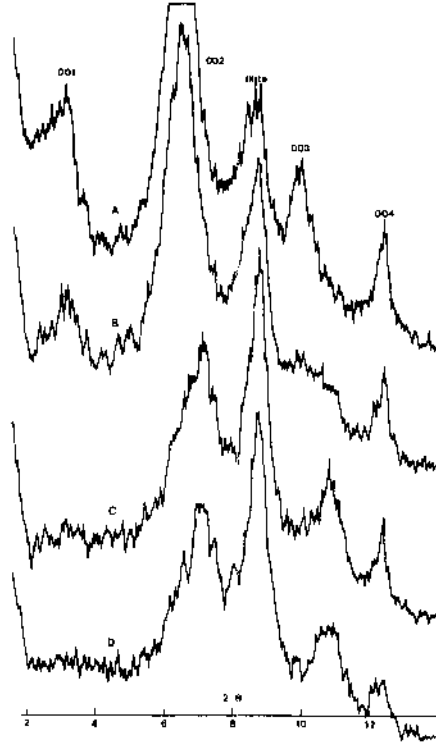


FIGURE 2. Sample x-ray diffraction traces of corrensite-illite clay mixture. Heat treatment method #4 (see text). A. 20.0 minutes. B. 8.0 hours. C. 23.0 hours. D. 43.0 hours.

Prolonged drying of a specimen before analysis also introduces a complicating factor. The original experiments on the Sespe corrensite were run in 1966. The specimens were at that time fresh from the field where they had been collected at some distance back from the outcrop face. In 1968 one of the same specimens used earlier was again analyzed in exact repetition of the earlier procedures. The results were similar

with the exception that all of the corrensite reflections were remarkably reduced in intensity, similar to those of a heated specimen. In the intervening two years the specimen had been stored at normal room temperatures without humidity control. The corrensite had dehydrated, apparently irreversibly, since soaking of corrensite in water for one month did not restore the original condition. Caution is therefore called for in dealing with corrensite samples which may have been altered in nature at the outcrop before being collected, or while sitting in a laboratory.

SUMMARY

It remains difficult to identify the component species in the mineral corrensite by any simple identification scheme. It is natural to expect that a mineral such as corrensite which has a high potentiality for chemical and structural variation does indeed exhibit these variations in nature. However, many of the observable properties of this mineral may in fact be the result of experimental rather than natural variations. Of particular importance is the duration and temperature of heating, and the conditions to which the sample was exposed before analysis.

ENVIRONMENTAL IMPLICATIONS OF SEDIMENTARY CORRENSITE

Minerals of the corrensite type have been identified in two environments: sedimentary and replacement, the latter probably hydrothermal. Table 5 lists the published occurrences of corrensite in relatively undisturbed sedimentary rocks. Sig-

nificantly, in each case the corrensite is associated with strata of known or suspected saline depositional environments. Furthermore Peterson (1962, p. 18) observed that corrensite is never found in sediment loads of modern streams. The observation made here that the corrensite structure is destroyed through long periods of exposure to air probably accounts for this observation. Accordingly, sedimentary corrensite is probably always diagenetic.

The ubiquitous association of corrensite with salines implies that either the salines themselves or the saline environment is necessary for the corrensite to develop. This suggests further that corrensite is an indicator of a warm dry climate, at least to the degree that a saline environment is indicative of these conditions.

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TABLE 5.—Known occurrences and association of sedimentary *corrensite*.

Strata	Location	Age	Association	Reference
1) Keuper Marl.....	England.....	Trias.....	Red beds.....	Stephen and MacEwan, 1951; Honey- bourne, 1951
2) Keuper.....	Germany.....	Trias.....	Gypsum, red beds, dolomite, evapo- rites.....	Lippmann, 1954; Eche, 1961
3) Buntsandstein.....	Germany.....	Trias.....	Gypsum, rock salt, red beds.....	Lippmann, 1956
4) Yates Formation.....	West Texas.....	Permian.....	Dolomite, evaporites.....	Farley <i>et al</i> , 1956
5) Brazier Lm.....	Colorado.....	Miss.....	Limestone.....	Bradley and Weaver, 1956
6) Keuper.....	France, Spain.....	Trias.....	Gypsum, anhydrite, limestone, dolo- mite, red beds.....	Martin Vivaldi and MacEwan, 1957
7) Salado Formation.....	New Mexico.....	Permian.....	Potash Beds.....	Grim, Droste, and Bradley, 1960
8) Straßfurt Salz.....	Germany.....	Permian.....	Evaporites.....	Bratsch, 1960
9) Chesterian.....	Tennessee.....	Miss.....	Limestone, dolomite, evaporites, red beds.....	Peterson, 1961; 1962
10) Jura Basin.....	France.....	Trias.....	Gypsum, limestone, salt.....	Millet <i>et al</i> , 1963
11) Sespe Formation.....	California.....	Oligo.....	Red beds, gypsum, borates, limestone.....	This report

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