

A MIXED-LAYER CLAY MINERAL ASSOCIATED WITH AN EVAPORITE

by

R. E. GRIM

University of Illinois, Urbana, Illinois

JOHN B. DROSTE

Indiana University, Bloomington, Indiana

AND

W. F. BRADLEY

Illinois Geological Survey, Urbana, Illinois

ABSTRACT

Clay partings in the ore beds in a New Mexico evaporite section include a range of mixed-layer clay mineral sequences of the corrensite type. Specimens range from nearly regular alternations to sequences which depart from regularity to moderate degrees. The ore bodies consist of halite, polyhalite, sylvite, magnesite, dolomite, carnallite, and iron oxides.

Observed x-ray diffraction effects from representative specimens are compared with synthesized effects for montmorillonite- or vermiculite-chlorite layer sequences.

It is concluded that the segregation of the abundant Mg interlayer content into specific, regularly spaced interlayers represents the equilibrium relationship between a montmorillonite-chlorite or vermiculite-chlorite mixed assemblage and a mildly acid, Mg^{2+} , Na^+ , and K^+ -rich environment.

Occurrences of the regularly alternating corrensite (Lippman, 1954; Bradley and Weaver, 1956) type of chloritic clay mineral, and of more or less nearly regularly alternating assemblages are being reported with increasing frequency. The present occurrence is worthy of note because of its rather clearly defined geochemical environment. The clays constitute thin partings in the no. 2 and no. 4 potash ore beds of the Permian Salado formation of the workings of the U.S. Potash Co. at Carlsbad, New Mexico.¹ These levels correspond respectively to the seventh ore zone and the first ore zone of the U.S. Geological Survey stratigraphic designations. Evaporite minerals in the ore, identified by diffraction methods, include halite, polyhalite, sylvite, magnesite, dolomite, and carnallite. The partings are brown, green, gray and red. They clearly represent material that accumulated in, and has remained

¹ Permission by the U.S. Potash Co. to study the deposit is gratefully acknowledged, as is the support of the National Science Foundation in the work of one of us (J.B.D.).

in, an environment of high Na, K and Mg activity from Permian time to the present.

Oriented aggregates of clay fractions finer than $1\ \mu$ or finer than $2\ \mu$ (depending on the abundance) were prepared, following hand picking, by washing that minimum number of times which permitted dispersion of the clay.

The samples from one particular parting, about 1 in. thick at the top of the no. 2 ore bed (numbered USK 1 in Fig. 1) afforded diffractometer traces suitable for detailed examination. The natural and ethylene glycol complexed states are illustrated in Fig. 1. Several sharp weak diffraction effects (not responsive to glycol) from accessory chlorite and illite flakes modify the composite track at the positions noted. The remaining major scattering features are observed to result from an ostensibly mixed system. Reciprocal spacings for the major maxima for the natural state are listed in Table 1.

TABLE 1.—USK 1

Ordinal No. of Feature	Measured <i>d</i>	Reciprocal Spacing $100/nd$	Departure from Regular Increment	
1	30	3.33		-.12
2	14.48	3.452	+.002	
3	9.5	3.50		+.05*
4	7.22	3.46	+.01*	
5	5.67	3.53		+.08
6	4.83	3.449	-.001	
7	4.22	3.38		-.07
8	3.59	3.48	+.03*	
9	3.33	3.33		-.12*

* Precision limited by superposed accessory mineral reflections.

Even-numbered maxima appear in essentially integral sequence, for which the average departure cited is considered to be a measure of the precision of the observations. The odd-numbered maxima depart from the exactly integral positions by one order of magnitude more than do the even numbered, and the manner of the departures is found to be interpretable.

To arrive at a model which can afford both a rational and an irrational sequence along one given reciprocal direction it is necessary to have recourse to some mechanism other than the Hendricks and Teller type analysis of scattering effects from systems involving two or more phase angles. General resemblance of the diagram (Fig. 1, natural) to that of the regular corrensite suggests that any difference from the corrensite sequence must be trivial. It was therefore decided to seek "brucite" dispositions in a vermiculite matrix which would account for the observed diagrams.

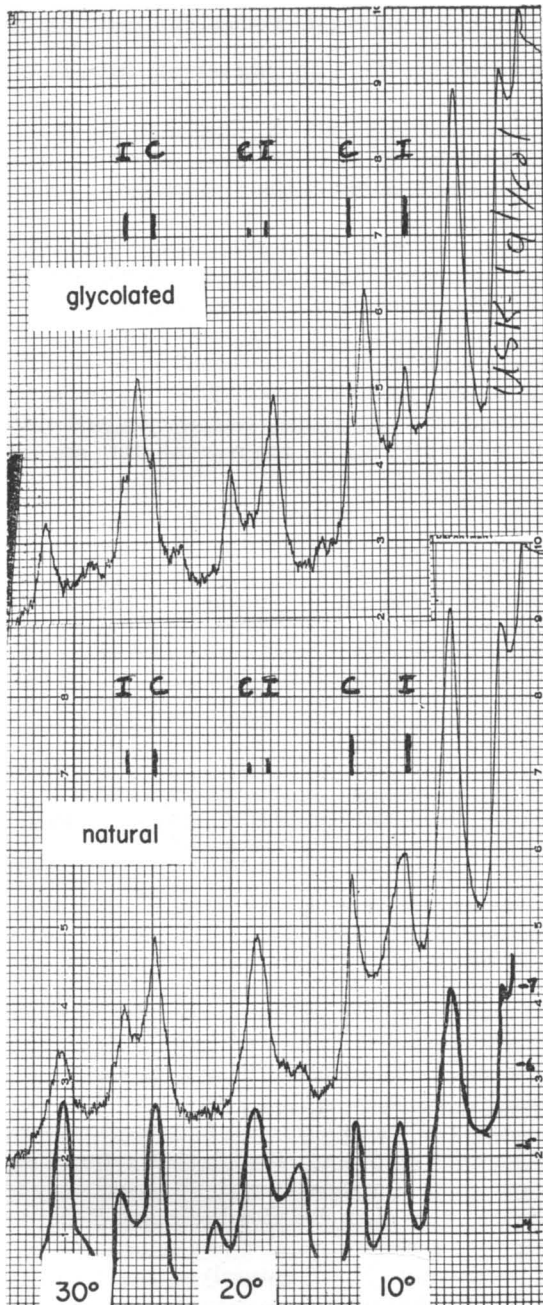


FIGURE 1.—X-Ray diffractometer traces of oriented $< 2\mu$ corrensite-type clay (sample USK-1) from the U.S. Potash Co. Workings. Upper, glycolated; middle, natural; lower, synthesized diffraction pattern. The positions of weak accessory chlorite and illite diffraction features are marked, respectively, C and I.

Figure 2*a* illustrates the shape of the Fourier transform for a limited number of vermiculite layers in a given packet. High amplitude spurious modulations characteristic of short summations were smoothed out by averaging amplitude per layer for summations of from 6 to 10 layer units. The curve is reasonably realistic for diffraction to be expected from vermiculite packets 100 to 300 Å thick. The curves *b* and *c* of Fig. 2 illustrate the modulation which would be imposed on the vermiculite transform if scattering power of layers of Mg were added as interlayer matter to alternate vermiculite units

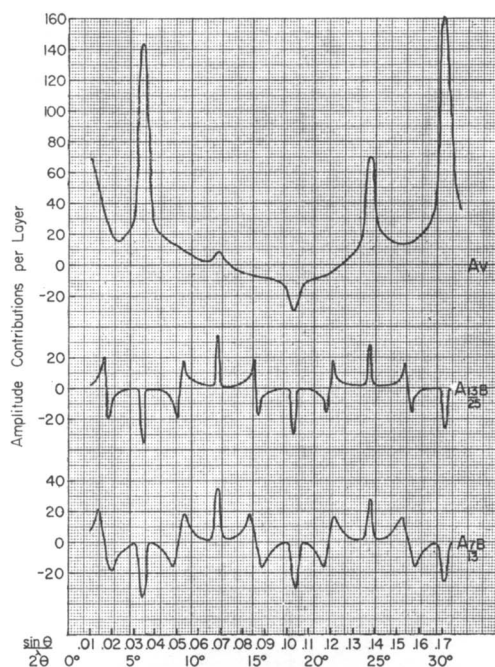


FIGURE 2.—(a) Diagrammatic transform of a thin packet of vermiculite layers. (b) and (c) Modulating functions for Mg scattering power in symmetrical alternation in 13 of 25 layers and 7 of 13 layers respectively.

(essentially endowing such layers with the properties of a chlorite), but with the provision that two magnesian layers occur adjacent about an arbitrary origin. The modulation 2*b* is for 13 magnesian layers and 12 vermiculite in a packet of 25, and 2*c* is for 7 magnesian and 6 vermiculite in a packet of 13. A calculated curve of diffraction power for an alternating sequence of chlorite layers and vermiculite layers, with chlorite the more abundant, is then available by addition of a selected modulator to the 2*a* transform, squaring the sum and applying Lorentz and polarization factors. The same

operation but with the "odd order" modulation inverted would cover the cases where vermiculite is the more abundant species.

The synthesized plot of $\log I$, calculated for the summation

$$(A_v + A_{13/25}\text{Mg})^2 \frac{1 + \cos 2\theta}{\sin 2\theta \cos \theta},$$

is reproduced to scale below the actual logarithmic recording spectrometer track for the USK 1 specimen. Gaps left in the curve are at positions where the compound amplitude sums cross zero. It is improbable that any aggregation of small crystals ever actually scatters none of the characteristic radiation incident on it to a given finite angle. The obvious decline of observed intensities with increasing angle is due to the extreme thinness of the prepared slide. Attenuation is proportional to the diffracting angle. It is concluded that the model of two adjacent chlorite layers in an alternating chlorite-vermiculite packet adequately describes the USK 1 specimen.

It seems only reasonable that the opposite arrangement, with vermiculite the more frequent component, should also be encountered among the specimens examined, but no illustration equally conclusive emerged. One probable instance is shown in Fig. 3 and tabulated in Table 2, but of the critical "odd

TABLE 2.—USK 6 < 1 μ

Ordinal No. of Feature	Measured d	100/ nd	Departure from Regular Increment	
1				
2	14.7	3.40	-.01	
3	9.6	3.47		+.06
4	7.37	3.39	-.02	
5	5.75	3.48		+.07
6	4.84	3.43	+.02	
7				
8	3.62	3.45	.04*	
9	3.15	3.56		+.15
10	2.93	3.41	.00	

* Precision limited by superposed accessory mineral reflection.

order" features only three are clearly observed, and one of them is of doubtful sign. The first low-angle maximum of the previous case is here reduced to an inflection and is not available for precise measurement. The low-angle inflection indicates that, if it does in fact arise from pairs of swellable layers adjacent, they occur rather frequently in the sequence, such as one pair in each five or six pairs.

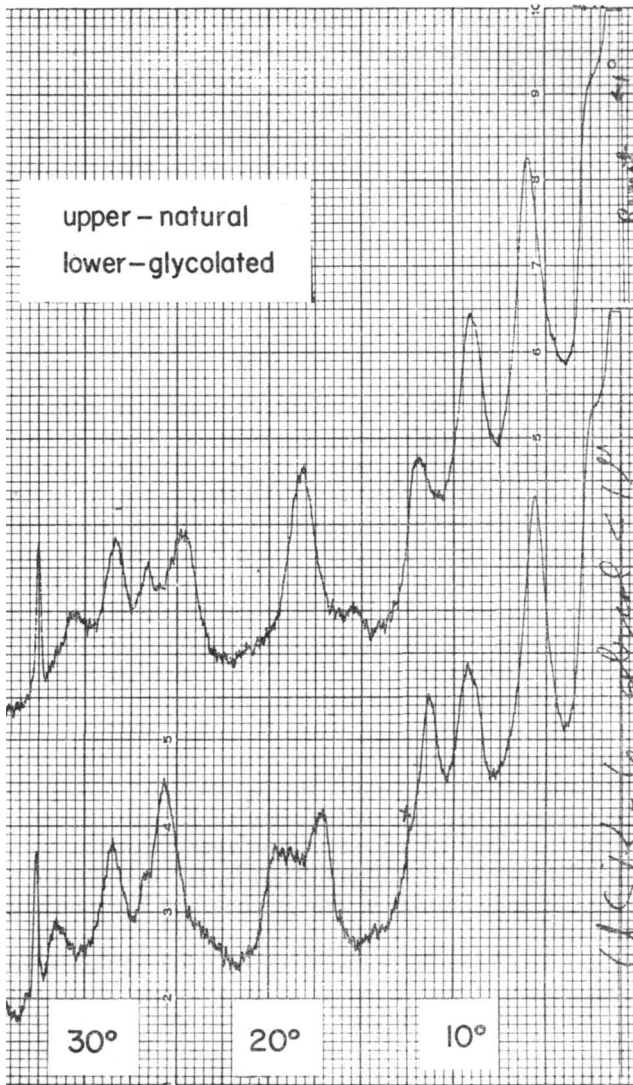
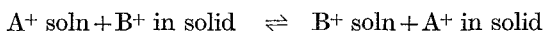


FIGURE 3.—X-Ray diffractometer traces of oriented 1μ clay (sample USK-6) from a less regularly alternating example than that of Fig. 1. Upper, natural; lower, glycolated.

It seems highly unlikely that so nearly monomineralic detrital chlorite could ever have been introduced into an evaporite environment, to serve as parent for these specimens, but intermittent influxes of montmorillonite minerals and similarly constituted degradation products are easily conceived. Such sedimented solid would presumably then be constrained to come to heterogeneous equilibrium with the highly saline basin solution. Under such equilibrium condition activity ratios of each pair of ion species in solution demand an activity ratio in any given solid phase that probably has some relation to relative population in the solid. If a reaction be written:



then

$$\left(\frac{a_{A^+}}{a_{B^+}}\right) \text{ in solid} = k \left(\frac{a_{A^+}}{a_{B^+}}\right) \text{ soln.}$$

The nature of activity, or of its relation to numbers of any one species in a solid is not a clearly understood phenomenon. There is probably more hope in a few specific assumptions bearing on the present material than in attempted generalities. Among the layer silicates it has long been apparent that convenience of fit and arrangement in interlayer space bears on the activities of interlayer ions. The Mg^{2+} "ion" activity is a much smaller fraction of the population of Mg^{2+} in chlorite and a smaller fraction in vermiculite than in montmorillonites. The same is true of the active fraction of K^+ in mica compared with K^+ in montmorillonite. Presumably the reverse holds for Ca^{2+} in chlorites or micas, for Ca^{2+} content is inconsequential in those minerals but is abundant in montmorillonites.

These impressions are equally reasonable when considered in the light that octahedral coordinations of oxygen about Mg^{2+} , which requires about 5 Å of interlayer space, would permit easy egress of K^+ from preponderately magnesian interlayers; and the articulation of K^+ into the silicate layers, which requires less than 1 Å effective interlayer clearance, would exclude Mg-octahedra from those interlayers. That is, K^+ is endowed with a high activity in Mg-rich solid interlayer arrangement, and Mg^{2+} with high activity in the K-rich solid.

Experimental data have been made available for equilibria involving the K^+/H^+ ion pair (Garrels and Howard, 1959) with muscovite and for many cation pairs with montmorillonite (Schachtschabel, 1940). The Mg^{2+}/H^+ pair does not seem to have been studied, but their relations can be approximated in a rough way from brucite and basic magnesium salt solubilities.

Approximate Mg^{2+} solubility limits may be taken as a line through the Mg-basic salt solubility area and the brucite solubility position in Fig. 4. Such a line crosses the field about one-half to one log unit lower than Garrels and Howard's (1959) experimental determinations for the K^+/H^+ pair above ground muscovite. That is, at a given pH, the Mg^{2+} concentration in solution necessary to drive Mg^{2+} into the solid may be as little as one-tenth of the

K^+ concentration necessary to drive K^+ into the solid. The actual composition of sea water seems to be essentially at the level of equilibrium with Mg layer silicates.

Observed occurrences of alteration of phlogopite to vermiculite are consistent with the above inferred relations, and observed subaerial alteration of chlorite to vermiculite indicates the relatively more acid (or less basic) character of vermiculite with respect to chlorite.

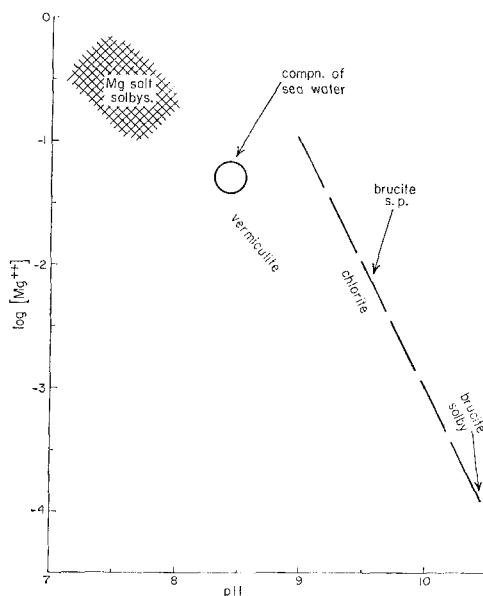


FIGURE 4.—Approximate relative locations of inferred stability fields of basic magnesium solids with respect to Mg^{2+} and H^+ concentrations in solution, and to the $Mg(OH)_2$ solubility product.

Heterogeneous equilibrium at moderate pH in the liquid phase apparently requires the presence of both chlorite and vermiculite in the solid. In view of the success of the important Pauling principle that a complex solid structure tends to become electrostatically neutral in the smallest practical volume, it seems only natural that its extension to neutrality in the acid-base sense is equally valid. For the articulated layer structures, best economy of space is achieved by regularly alternating intergrowth of the two species of layers.

The perhaps over-extended attention devoted to this one given occurrence is presented to illustrate the confidence that establishment of physical-chemical environments of clay mineral assemblages is feasible.

REFERENCES

- Bradley, W. F. and Weaver, C. E. (1956) A regularly interstratified chlorite-vermiculite clay mineral: *Amer. Min.*, v. 41, pp. 497-504.
- Garrels, R. M. and Howard, Peter (1959) Reactions of feldspar and mica with water at low temperature and pressure: in *Clays and Clay Minerals*, 6th Conf., Pergamon Press, New York, pp. 68-88.
- Lippman, Friedrich (1954) Über einen Keuperton von Zaisersweiher bei Maulbronn: *Heidelberg Beitr. Min.*, v. 4, pp. 130-134.
- Schachtschabel, P. (1940) Untersuchungen über die Sorption der Tonminerale und organischen Bodenkolloide: *Kolloid-Beihfte*, v. 51, pp. 199-276.