

## CHEMICAL CHARACTERISTICS AND ORIGIN OF ORDOVICIAN K-BENTONITES ALONG THE CINCINNATI ARCH: A DISCUSSION<sup>1</sup>

**Key Words**—Bentonite, Chemical composition, Illite/smectite, K-bentonite, Rectorite.

In a recent issue of this journal, Huff and Türkmenoğlu (1981) concluded that montmorillonite layers alter to illite layers in mixed-layer illite/smectite (I/S) having 18 to 27% smectite layers and having rectorite-type ordering. K-fixation was inferred to be controlled largely by substitution of octahedral Mg for Al, a conclusion of major significance because almost all similarly interlayered clay described in the literature (Weaver and Pollard, 1973, among many others) has mostly substitution of tetrahedral Al for Si. Their calculation of structural formulae from which layer-charge distributions were inferred involves the assumptions that K is the only significant interlayer cation and that Na and Ca detected in chemical analyses of the clays can be ignored for two reasons: (1) the amounts are small and most likely do not represent structural site occupancy, and (2) Ca is a likely contaminant because the metabentonite beds occur in a massive carbonate section. They further justified these assumptions by the close agreement between calculated interlayer and total layer charges.

I find these assumptions unwarranted. First, the amounts of Na<sub>2</sub>O and CaO, as much as 1.9% and 1.0%, respectively (see their Table 2), are not small; the approximately 20% expanding layers must contain some exchangeable cations, predominantly Na because of the Na<sub>2</sub>CO<sub>3</sub> pretreatment, or the layers would not expand. This Na is as essential a constituent of the structural formula as is any other cation in or between the clay layers regardless of whether or not the site occupied by the Na is considered to be "structural," and its omission gives an incorrect picture of the structural distribution of cations. Second, if Ca represents a carbonate impurity in such a dolomitic section (see their Stratigraphy section, p. 114), the impurity also brings into question the amount of Mg assigned to the clay. Third, the nature of the structural formula is such that, within the limits of rounding, the layer charges must balance. Exclusion of Na, or even part of the K or of other cations, from the calculation will generally give a balanced formula, unless one cation exceeds the maximum possible occupancy of a layer; but if the exclusion is inappropriate, then the entire formula is incorrect, including distribution and amounts of cations and of the charges of the octahedral, tetrahedral, and interlayer parts of the structure.

None of the octahedral layer charges for Al, Fe, Mg, and Ti in their Table 3 add up to the net negative layer charges given. For example, for sample KB-28A, 0.49 Mg results in a -0.49 charge, but the excess of 0.05 cations over the ideal 2.00 balances +0.15 of the negative charge, for a net charge of -0.34, not -0.38, and a total layer charge of -0.54, not -0.58. The total layer charge, with the exception of sample KB-7C, seems to have been set equal to the calculated interlayer K and the octahedral charge adjusted accordingly. In this case, the many samples on their Figure 4 that do not plot exactly on the line for equal amounts of fixed K<sup>+</sup> and total charge seems surprising.

Several examples from the literature may seem to corroborate the high proportion of octahedral layer charge reported by Huff and Türkmenoğlu, but all involve problems. Cole and Hosking (1957, p. 263, Table X, 2, sample 13) reported a structural formula for a High Bridge, Kentucky, metabentonite of

$K_{1.26}Na_{0.03}Ca_{0.08}(Al_{2.98}Fe_{0.11}Ti_{0.02}Mg_{0.87})_{3.98}(Al_{0.56}Si_{7.44})O_{20}(OH)_4$ . The formula is calculated directly from the chemical analysis in API Report No. 7, reproduced here in column A of Table 1; no structural formula was given in the API report, but Cole and Hosking's formula is essentially the same as the one calculated by the writer. However, in API Report No. 5 (Kerr *et al.*, 1950b) on p. 41, line 5, the High Bridge sample is reported to contain 5% quartz and 3% plagioclase, but on line 7 a potassium feldspar is indicated. My High Bridge sample from Ward's Natural Science Establishment (Metabentonite #42) contains quartz and K-feldspar in about these amounts, and Huff and Türkmenoğlu (1981) mention K-feldspar but not plagioclase, so the "plagioclase" in the API report is probably a misnomer. If corrected for 5% quartz and 3% K-feldspar, the API chemical analysis calculates to the structural formula in column B of Table 1, in which the proportions of charge in the octahedral and tetrahedral layers are reversed. Hower and Mowatt (1966) give a chemical analysis and structural formula for High Bridge K-bentonite, shown here in column C of Table

Table 1. Chemical compositions reported for High Bridge, Kentucky, metabentonite and structural formulae.<sup>1</sup>

	A (wt. %)	B (wt. %)	C (wt. %)
SiO <sub>2</sub>	53.43	46.88	56.9
Al <sub>2</sub> O <sub>3</sub>	21.59	21.05	20.0
Fe <sub>2</sub> O <sub>3</sub>	1.04	1.04	1.13
MgO	4.17	4.17	5.5
CaO	0.53	0.53	0.08
Na <sub>2</sub> O	0.11	0.11	Trace
K <sub>2</sub> O	7.00	6.49	5.41
TiO <sub>2</sub>	0.28	0.28	0.18
Full-cell structural formula			
IV			
Si	7.44	7.16	7.72
Al	0.56	0.84	0.28
Charge	-0.56	-0.84	-0.28
VI			
Al	2.98	2.99	2.90
Fe <sup>+3</sup>	0.11	0.12	0.11
Mg	0.86	0.95	1.11
Ti	0.03	0.03	0.01
Sum	3.98	4.09	4.13
Charge	-0.89	-0.65	-0.71
Total layer charge	-1.45	-1.49	-0.99
Interlayer			
K	1.25	1.28	0.94
Na	0.03	0.04	0.00
Ca	0.08	0.08	0.02
Charge	+1.44	+1.48	+0.98

A, Kerr *et al.*, 1950a, p. 56; B, analysis A corrected for 5% quartz and 3% K-feldspar; C, Hower and Mowatt, 1966.

<sup>1</sup> Calculated by the writer.

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1, that showed a low tetrahedral charge similar to those of Huff and Türkmenoğlu. However, Hower and Mowatt also reported considerably less interlayer K (0.47/half cell) and more expanding layers (33%) than any of Huff and Türkmenoğlu's analyses, so the samples are not exactly comparable, and amounts of CaO and Na<sub>2</sub>O (Table 1, column C) seem much too low for 33% expandable layers. The writer (Schultz, 1978, Table 3, sample 159835) reported one interstratified illite/smectite (I/S) sample from an equivalent of the Pierre Shale with an estimated 20% expandability that was calculated to have only about 40% tetrahedral layer charge, but this sample is so out of line with other illite/smectites from the Pierre that the reported Al<sub>2</sub>O<sub>3</sub> is probably appreciably low. For these reasons—inappropriate basic assumptions on calculation of structural formulas, failure to correct for impurities, and/or possible inaccuracies in chemical analyses, I doubt the existence of illite or highly illitic mixed-layer clay in which the octahedral layer charge is much greater than the tetrahedral layer charge.

Huff and Türkmenoğlu (1981) suggested that 80°C is an insufficiently high temperature to generate the High Bridge K-bentonites, as compared to a minimum of 100°C for similar clays in Tertiary sediments of the Gulf Coast, but Hoffman and Hower (1979) showed that time as well as temperature affect the rate of alteration of smectite to illite. Although the authors noted in their introduction (p. 113) that time may play a role, they give no consideration in their discussion to the much greater time available to alter the Ordovician than the Tertiary sediments.

A final comment not directed specifically at Huff and Türkmenoğlu's paper concerns the common practice, originated by Reynolds and Hower (1970) and followed by Huff and Türkmenoğlu, of referring to I/S or I/M ordered interlayering as rectorite- or allevardite-like. Rectorite and allevardite both are regular 1:1 (equally abundant) interlayers of expanding and nonexpanding layers (Brown and Weir, 1963). In contrast, I/S interlayering typically has unequal proportions of illite and smectite layers; a less abundant layer tends not to be adjacent to similar layers, and I/S packets are randomly interlayered with the excess of the more abundant layers. In nature good I/S interlayering commonly occurs in the illite-smectite transformation, only if illite makes up about 60–80% of the layers and tends not to be regular when the proportions are near the 50:50 ratio of allevardite or rectorite; this difference suggests some genetic difference between the two types of regularity rather than a similarity implied by "rectorite-like." Because of the nonequal proportions and genetic implications, I think that the phrases allevardite- or rectorite-like should not be used for I/S ordering of Reynolds and Hower; that IS without the slash should be used in order to avoid the cumbersome I/S/I1

designation that would logically follow for ISII Kalkberg-type ordering; and that I/S should be used to imply neither ordering nor lack thereof. An attractive alternative is the use of Reichweite numbers (Jadgodzinski, 1949) to designate the number of layers over which ordering extends ( $R = 0$  for random,  $R = 1$  for IS, etc.); they are simple, short, easily express partial ordering, and have no genetic implications.

U.S. Geological Survey  
Federal Center, MS 918  
Denver, Colorado 80225

LEONARD G. SCHULTZ

#### REFERENCES

- Brown, G. and Weir, A. H. (1963) The identity of rectorite and allevardite: in *Proc. Int. Clay Conf., Stockholm, 1963*, 1, I. Th. Rosenquist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 27–35.
- Cole, W. F. and Hosking, J. S. (1957) Clay mineral mixtures and interstratified minerals: in *The Differential Thermal Investigation of Clays*, R. C. Mackenzie, ed., Mineralogical Society, London, 248–274.
- Hoffman, Janet and Hower, John (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana: in *Aspects of Diagenesis*, P. A. Scholle and P. R. Schluger, eds., *SEPM Spec. Publ.* 26, 55–79.
- Hower, John and Mowatt, T. C. (1966) The mineralogy of illites and mixed-layer illite/montmorillonites: *Amer. Mineral.* 51, 825–854.
- Huff, W. D. and Türkmenoğlu, A. G. (1981) Chemical characteristics and origin of Ordovician K-bentonites along the Cincinnati arch: *Clays & Clay Minerals* 29, 113–123.
- Jadgodzinski, H. (1949) Eindimensionale Ferlordnung in Berechnung des Fehlorderungsgrades aus der Röntgenintensitäten: *Acta Crystallogr.* 2, 201–207.
- Kerr, P. K., Hamilton, P. K., and Pill, R. J. (1950a) Analytical data on reference clay minerals: *API Proj. 49, Report No. 7*, 160 pp.
- Kerr, P. F., Main, M. S., and Hamilton, P. K. (1950b) Occurrence and microscopic examination of reference clay mineral specimens: *API Proj. 49, Report No. 5*, 58 pp.
- Reynolds, R. A., Jr. and Hower, John (1970) The nature of interlayering in mixed layer illite-montmorillonites: *Clays & Clay Minerals* 18, 25–36.
- Schultz, L. G. (1978) Mixed-layer clay in the Pierre Shale and equivalent rocks, northern Great Plains Region: *U.S. Geol. Surv. Prof. Pap.* 1064-A, 28 pp.
- Weaver, C. E. and Pollard, L. D. (1973) *The Chemistry of Clay Minerals*: Elsevier, Amsterdam, 213 pp.

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