

## CHEMICAL CHARACTERISTICS AND ORIGIN OF ORDOVICIAN K-BENTONITES ALONG THE CINCINNATI ARCH: A REPLY

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

Schultz (1982) raised six points concerning some of the conclusions and methods used to arrive at them in a recent paper by Huff and Türkmenoğlu (1981). They are:

1. Na and Ca are not insignificant in the calculation of structural formulae and should be included.
2. If some or all of the Ca is due to carbonate contamination, some or all of the Mg may also be due to carbonate contamination.
3. A balanced structural formula without Na and Ca is inaccurate. Further, the octahedral charges in Table 3 do not sum to the values given. Consequently, the total charge on sample KB-28A, for example, is  $-0.54$ , not  $-0.58$ .
4. If corrections for probable quartz and feldspar impurities are made, the tetrahedral charge is actually greater than the octahedral charge.
5. Greater emphasis should be placed on time as well as temperature in the conversion of smectite to illite.
6. The terms "rectorite-like" and "alleverdite-like" should not be used for the type of mixed-layering described.

These comments are discussed in the order listed.

1. We do not disagree that Na and Ca are present and that the values reported in Table 2 of the original paper must represent, to some extent, the cation population of the approximately 20% of the layers that are expandable. The decision not to include them in the calculation of structural formulae was based upon two considerations: (1) Na and Ca variation do not correlate well with the proportions of expandable layers, and (2) the inclusion or exclusion of Na and Ca from the computation of structural formulae does not alter our conclusion that these clays have octahedral charges that are significantly greater than their tetrahedral charges.

In the first instance, Table 2 of the original paper shows that Na and Ca vary more than most of the other ions measured, especially K. Further, a good correlation does not exist between the Na-Ca variation and the proportions of expandable layers. One would expect a better correlation if Na and Ca were located entirely in exchange positions. Two explanations are possible. Either the analyses are in error or the samples are contaminated. Repeated analyses by both wavelength-dispersive X-ray fluorescence and atomic absorption spectroscopy convinced us that the numbers were not accidents—that they are real values within the limits of analytical error. Thus, the second possibility was accepted, namely, that carbonate contamination and pretreatment with  $\text{Na}_2\text{CO}_3$  were responsible for the variations. Confirmation of this assumption would obviously rest upon reanalyzing the samples after carbonate removal and without Na-saturation, but we have not done this.

On the other hand, exclusion of Na and Ca from the computation of the structural formulae does not affect our conclusion that these clays have octahedral charges that are significantly higher than their tetrahedral charges. If, for example, the data for sample KB-28A are recalculated with Na and Ca included, the tetrahedral charge becomes  $-0.22$  instead of  $-0.20$ , and the octahedral charge is  $-0.47$  instead of  $-0.38$ . Without Na and Ca, the tet/oct charge ratio is  $0.53$  and, with them, it is  $0.47$ , a difference that is not significant enough to invalidate our principal conclusions. Further, we found that including Na and Ca in all computations resulted in total layer charges of about  $0.8$ – $0.9$ . Such values are to be expected for pure or nearly pure illites, but are too high for interstratified illite/smectites (I/S) having 20% expandable layers. We con-

cluded, therefore, that some portion of the Na-Ca content is excessive, but the exact amount could not be determined from the available data. Excluding these data from the computation of structural formulae does not seem inappropriate here, because these data are listed in Table 2 and, further, because we carefully and specifically stated in the text what we did and why.

2. Concerning the possibility of Mg contamination, we stated in the original paper that it is likely that not all of the Ca is due to contamination, but we did not know precisely how much. For the moment, assume that all of it is due to contamination. The dolomitic component of the High Bridge Group is about 15%  $\text{MgCO}_3$  (Dever, 1974). If we consider Ca/Mg variation on a strictly proportional basis, the maximum CaO in our samples is 1.0%, 15% of which is 0.15%. Thus, 0.15% of the total MgO (mean = 5.1%) = 0.008% MgO due to contamination, well within the range of analytical precision. We do not believe such an amount of contamination constitutes a serious problem.

3. The effect of excluding Na and Ca from structural formula calculations can be seen by recalculating, for example, the analysis of sample KB-28A in its entirety. Based on measured, not calculated, values of  $\text{K}_2\text{O}$ , the formula is  $(\text{Si}_{3.78}\text{Al}_{0.22})(\text{Al}_{1.37}\text{Fe}^{+3}_{0.16}\text{Mg}_{0.48})\text{O}_{10}(\text{OH})_2\text{K}_{0.58}\text{Na}_{0.09}\text{Ca}_{0.01}$ . The changes from those listed in Table 3 of our original paper are essentially in the second decimal place and are not significant enough to warrant changes in our principal conclusions. It must be kept in mind that the assignment of ions to sites in well-ordered minerals having well-established stoichiometries is not itself a straightforward process, and, when a two-phase mixture, such as illite-smectite is considered, the operation is fraught with assumptions. We have no problem in accepting the above structural formula as a fair description of our K-bentonites. For one thing, Hower and Mowatt (1966) report chemical data for the High Bridge, Kentucky, metabentonite, which comes from the same area and stratigraphic horizon as some of our samples. In their Table 2 (p. 834) and Table 4 (p. 840), the oxide values and their assigned portions in tetrahedral and octahedral positions agree quite closely with our sample KB-28A. Furthermore, the total octahedral cation population of sample KB-28A, as computed above, sums to 2.01, a value quite close to the theoretical half-cell occupancy. But, again, when Na and Ca are included in formula computations for some of our other samples, particularly those listed as containing appreciable CaO, the agreement is less consistent. The formulae become consistent only when one assumes that some portion of the Ca and Na is in excess due to contamination.

In calling attention to what he considers a miscalculation of octahedral layer charges in Table 3, Schultz is apparently suggesting that the distribution of layer charges should be reported on the equivalent basis of the theoretical layer occupancy of 2.00 rather than as actual values calculated from analytical data. We think it is unnecessary and even unwise to do this. A search of the literature reveals that octahedral cation populations tend to cluster statistically around 2.00 but may vary from it just as summations of chemical analyses seldom equal exactly 100.00%. Weaver and Pollard (1973), for example, reported structural formulae and statistical parameters for 29 illites (Chap. 2, Tables V, VI). The sum of octahedrally coordinated ions averaged 2.07, with values ranging from 1.85 to 2.24 (p. 7). Further, they stated (p. 7), "If the divalent cations in excess of 2.00 in the octahedral sheet are assigned to

the interlayer position, the layer charge increases as does the total number of interlayer cations. . . . Thus, if we do indeed assume ideal site population, for which there is no firm evidence in I/S clays, even higher layer charges could be calculated. In other words, recalculating layer charges on the basis of the theoretical layer population introduces another level of assumptions into a process which is already tenuous at best; we are reluctant to do so. It could be argued further that some of the Mg assigned to the octahedral layer might not belong in the interlayer position and that Ti should not even be included in the formula calculations. The arbitrary allocation of even small quantities of these cations will cause some variation in the layer charge computation.

4. We selected the <0.1- $\mu\text{m}$  size fraction for chemical analysis precisely for the reason Schultz raises, namely, the possibility of other mineral phases contributing to the analytical results. Other studies (e.g., Hower *et al.*, 1976) indicate that particle separation and concentration of the <0.1- $\mu\text{m}$  fraction is sufficient to reduce significant contamination by quartz, feldspar, and various sulfides below the limit of detection by X-ray powder diffraction. We believe that Figure 3 of our original paper indicates that for the most part such serious problems have been eliminated.

The report by Cole and Hosking (1957) cited by Schultz concerns the same material studied by Hower and Mowatt (1966) who, however, were careful to select only the <0.5- $\mu\text{m}$  fraction for analysis. If the Cole and Hosking data are recalculated to half-cell values and compared with those in Hower and Mowatt's study, the results are as follows:

	Cole and Hosking (1957)	Hower and Mowatt (1966)
IV { Si	3.72	3.84
Al	0.28	0.16
VI { Al	1.49	1.43
	Fe	0.06
	Mg	0.44
	Ti	0.01
K	0.63	0.47
Ca	0.04	0.09 (reported as X <sup>+</sup> )
Na	0.02	—

Hower and Mowatt reported a tetrahedral charge of  $-0.16$  and an octahedral charge of  $-0.43$  (misprinted as  $-0.34$  in their paper). These values are very much in line with ours and reinforce our confidence in the general accuracy of our data.

In private communications with Dr. Schultz, we called his attention to both the Hower and Mowatt (1966) report, as well as his own data on the Pierre Shale (Schultz, 1978). Specifically, Schultz's sample #159835 listed in Table 3 on page 14 of the 1978 report was described as a mixed-layer illite/smectite having 80% illite layers, a total layer charge of  $-0.73$ , a tetrahedral charge of  $-0.29$ , and, by subtraction, an octahedral charge of  $-0.44$ . Schultz (private communication) discounted both examples as unsuitable for comparison with our samples, because the K content of the Hower and Mowatt sample is too low, and because the  $\text{Al}_2\text{O}_3$  value reported for his sample is probably incorrect. However, these comparisons should not be easily dismissed. The octahedral charge of Hower and Mowatt's sample is twice as large as the tetrahedral charge, more than enough to offset an approximate 12% difference in fixed K and expandable layers. Schultz's sample seems to be consistent with the fourteen other samples re-

ported in his Table 3 and, in fact, serves as an important data point in his further examination of the data in his Figure 11. Thus, the scarcity of published examples of what we are describing should not, in itself, serve as an argument against the validity of our data.

5. We agree completely that time, as well as temperature, affect the rate of alteration of smectite to illite and had hoped that, by cautioning others against dependence on the I/S ratio as the sole indicator of paleogeothermometry, we might draw attention to this fact. We also intended our paper to suggest that original ash composition and early burial pore-water chemistry, especially K-activity, must affect, perhaps considerably, layer silicate composition and interstratification during burial diagenesis.

6. The names "rectorite" and "allevardite" were used in our original paper in the sense described by Eberl (1978, p. 327–328) in which he used "K-rectorite," "Na-rectorite," and "allevardite" (previously used to describe both Na- and K-rectorite) for ordered mixed-layer mica/smectite. The term "rectorite-type" refers to a regular alternation of illite and smectite layers with additional illite layers randomly distributed among the ordered packets. The recent report by Bailey (1981) should help clarify usage of interstratification terminology in the literature.

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