Interstratified Clays as Fundamental Particles

Abstract. *Materials representing common interstratified clay minerals are shown to be composed of aggregates of fundamental particles. Transmission electron microscopy and x-ray diffraction demonstrate that the x-ray diffraction characteristics of a wide range of interstratification can be modeled experimentally by utilizing materials containing only three types of particles. The data have been incorporated into a new model that regards interstratified clay minerals as populations of fundamental particles whose x-ray diffraction patterns result from interparticle diffraction.*

Although interstratified clays, which are common in soils (*1*) and sediments (*2*), have been widely studied by x-ray diffraction (XRD), their actual physical nature remains uncertain. Conventional theory regards these minerals as made up of fixed sequences of silicate layers within relatively large crystallites, the layer sequence being designated as regular or random according to the repetition of the different layer types within the crystallite.

The regular varieties are commonly given a distinct mineral name, such as K-rectorite for interstratified illite-smectite (I-S) and corrensite for interstratified chlorite-smectite (C-S) (*3*). Calculated profiles for interstratified clays often assume crystallites of 7 to 13 layers in thickness (*4*); such profiles agree very closely with diffraction patterns obtained experimentally from natural clay material, thus seeming to validate the above assumption.

Here we demonstrate that for specially prepared samples yielding XRD patterns identical to those of interstratified clays, the sequence of layers is not fixed within relatively large crystallites. Moreover, our results indicate that the layer sequence results from a random arrangement of a population of much thinner fundamental particles and that smectite behavior, which is extremely common in interstratified clays, arises from adsorption of water or organic molecules at the interfaces of these fundamental particles.

The clay materials investigated include two smectites, the Wyoming montmorillonite (Wards montmorillonite 25, Upton, Wyoming) and a saponite from the Panamint Valley, Ballarat, California (*5*) (here designated as Wm and Bs, respectively), and two regularly interstratified clays, a K-rectorite bentonite from Canon City, Colorado (*6*), and a corrensite from Hillhouse Quarry, Ayrshire, Scotland (*7*) (here designated Cb and Hc, respectively). The dioctahedral samples, Wm and Cb, were saturated with 1*M* NaCl, and the trioctahedral samples, Bs and Hc, were saturated with 1*M* LiCl. The suspensions were washed free of chloride ions, the final washings being achieved by dialysis to ensure quantitative retention of the dispersed materials. Suspensions containing particles with an equivalent spherical diameter less than 0.1 μm were obtained by centrifugation. The concentration of clay in the suspensions was determined by oven drying 4 ml of each suspension and weighing the residue. Portions of the suspensions were dried on glass slides to form sedimented aggregates, and then the aggregates were solvated with ethylene glycol vapor before XRD. Mixtures of Wm with Cb and of Bs with Hc, in 1:2 ratios by weight, were prepared in suspension and examined by XRD in the

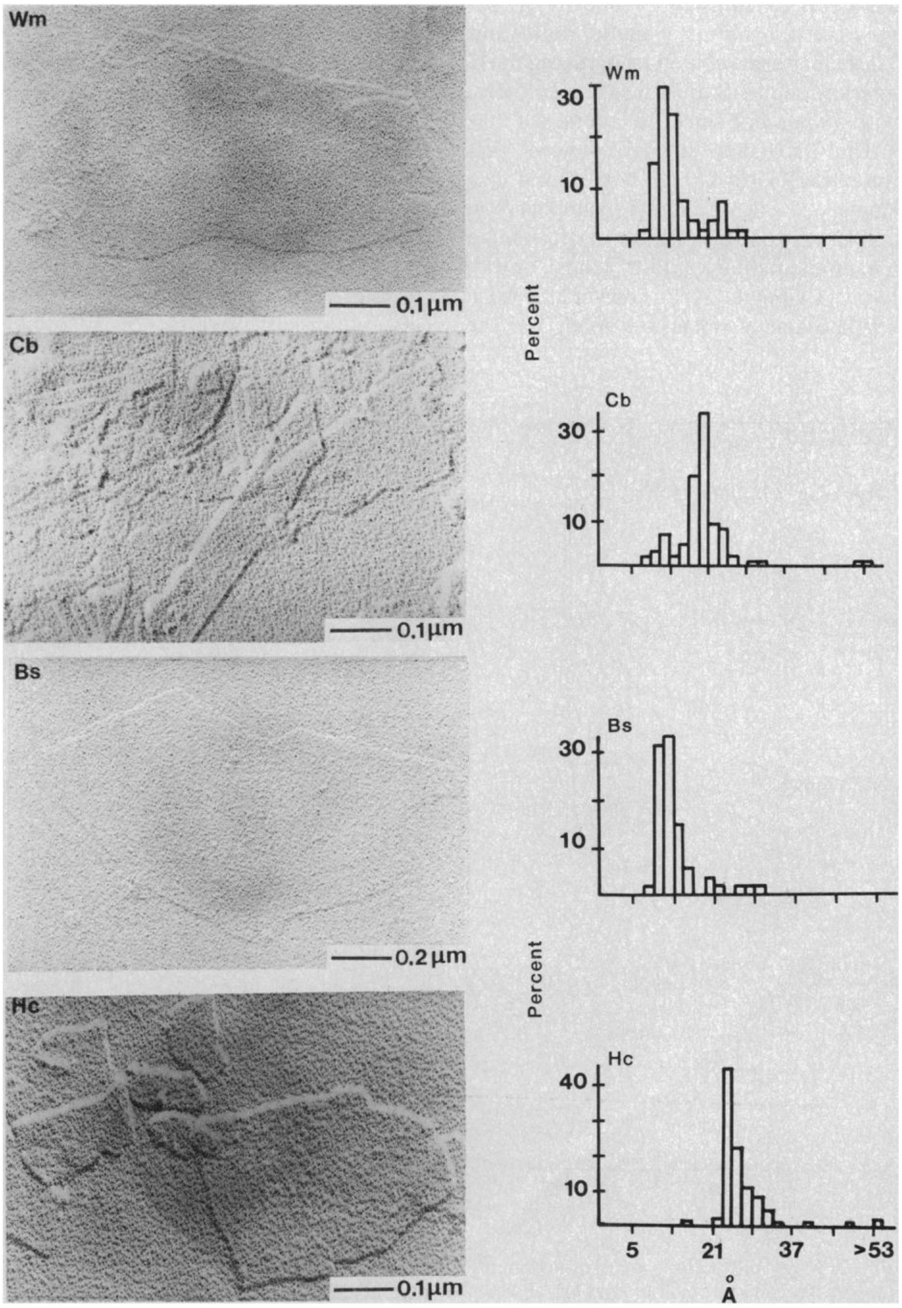

Fig. 1. Transmission electron micrographs of platinum-shadowed particles dried from dilute clay suspension. Sample designation is the same as in text. Particle thickness distributions from measurements of 52 to 85 particles per sample are also shown. Histograms are in 2-Å intervals.

same manner. In addition, diluted suspensions of the four samples were dried on mica sheets and prepared for transmission electron microscopy (TEM) by platinum shadowing (*8, 9*). The shadowing angle and directions were recorded so that the thickness of the particles could be measured within 3 to 4 Å.

The TEM data from the clays show a predominance of particles 10 Å thick in the smectites, 20 Å thick in Cb, and 24 Å thick in Hc. Measurements of 52 to 85 particles per sample show that these thicknesses are representative of the sample (Fig. 1). The XRD patterns for samples Wm and Bs are typical of dioctahedral and trioctahedral smectites and show spacings of 16.9 and 16.7 Å, respectively, after ethylene glycol solvation (Fig. 2). Samples Cb and Hc show a rational series of orders based upon fundamental spacings of 27 and 31 Å, respectively, again after glycol solvation. These patterns correspond to regularly interstratified I-S and C-S, respectively, with 50 percent smectite layers.

The TEM data strongly suggest that the particles 10 Å thick correspond to a single 2:1 silicate layer in samples Wm and Bs; the particles 20 Å thick in sample Cb, to elementary "illite" consisting of two 2:1 silicate layers coordinated by a single plane of potassium ions; and the particles 24 Å thick in sample Hc, to elementary "chlorite" consisting of two 2:1 silicate layers coordinated by a single brucite sheet. Given that these samples are dominated by very thin particles, it is remarkable that they should exhibit such intense basal reflections.

Rigid application of XRD theory to the TEM data would predict that these samples would produce little, if any, Bragg reflections from the basal planes. Moreover, use of the Scherrer equation (*10, 11*), which relates the number of coherent diffracting layers, *n*, to XRD peak breadth, predicts $n = 9$ for the smectite samples, corresponding to particles 90 Å in thickness and $n = 5$ to 7 for sample Hc, corresponding to particles 70 to 100 Å thick. This anomaly can be resolved by postulating that sedimented aggregates of these elementary particles exhibit an interparticle diffraction phenomenon.

When these materials are dried on to a flat surface from suspension, the layer sequence in the sedimented aggregate examined by XRD is determined by the types and proportions of the particles present. Because the effective number of coherently diffracting silicate layers is greater than the number of layers per particle, the interfaces between the particles, which are capable of adsorbing water and organic molecules, are perceived by XRD as smectitic interlayers. Thus, an aggregate composed of elementary "illite" particles appears to be a regular alternating sequence of illite and smectite layers through XRD. Incompatible identification of similar clay materials by TEM and XRD has been noted previously (*9, 12–14*). Indeed, one such study speculates that the apparent interstratified nature of an authigenic illite is the product of interparticle diffraction (*9*).

The concept of interparticle diffraction is strongly supported by experiments in which XRD patterns of sedimented aggregates of mixed suspensions cannot be interpreted in terms of a simple mixture of both components (*15*). In fact, the XRD patterns (Fig. 2) of the mixtures of Wm and Cb and Bs and Hc, are identical to those of randomly interstratified I-S and C-S samples with 60 to 75 percent smectite layers (*4, 16*) indicating that the entire layer sequence examined by XRD has been rearranged.

The proportions of the components in the layer sequences depend on the proportions and types of particles in the mixed suspension. We have experimentally produced a wide range of materials that yield XRD patterns typical of natural interstratified clay minerals simply by making mixtures using the three types of elementary particles in various combinations and proportions. In addition, we have produced unusual associations such as randomly interstratified trioctahedral chlorite and dioctahedral smectite and three component illite-chlorite-smectite interstratified systems.

This interpretation of the data suggests that naturally occurring I-S and C-S clays may be physical mixtures of thin particles. Where interstratified minerals are identified by XRD in samples with large particles (0.2 to 4.0 μm, for example), this may result from an interparticle, intra-aggregate diffraction phenomenon. Data from TEM show that larger particles are almost always aggregates of smaller particles and that they invariably yield rotational turbostratic electron diffraction patterns rather than single crystal patterns. Furthermore, many particles, including those of the elementary illite in sample Cb, exhibit morphologies that suggest they are individual crystals rather than crystal fragments. True interstratification, where there is crystallographic continuity between the various components, may, therefore, exist only in weathering products like hydrobiotite (*17*), where large layer sequences are inherited from macroscopic crystals.

The concept of interstratified clays as

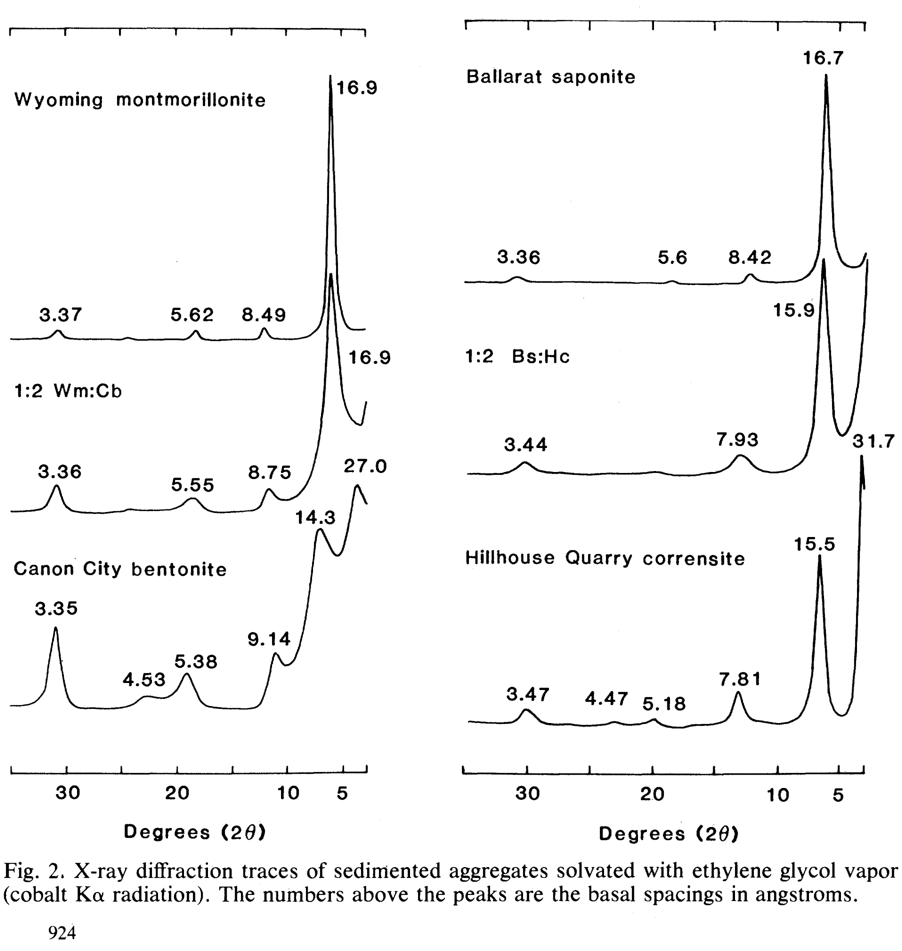

Fig. 2. X-ray diffraction traces of sedimented aggregates solvated with ethylene glycol vapor (cobalt Kα radiation). The numbers above the peaks are the basal spacings in angstroms.

fundamental particles may bear upon a variety of geological problems. For example, the diagenetic conversion of smectite to illite is an important geochemical reaction commonly observed in sediments with increasing depth, or inferred depth, of burial (*18–21*). In the currently accepted transformation mechanism, smectite layers are converted to illite layers by substituting aluminum for silicon and sorbing potassium ions within fixed layer sequences to produce an I-S series of increasing illite content (*22*). The sequence is randomly interstratified until there is more than 50 percent illite layers, at which point, for some unexplained reason, the interstratification sequence becomes regularly arranged.

Using our concept of interstratified clays, randomly interstratified I-S would be composed primarily of populations of elementary illite and smectite particles. During diagenesis, smectite particles become unstable and dissolve, while illite particles are formed. When smectite particles are no longer present the population becomes one of elementary illite particles and, possibly, other thicker illite particles which, when examined by XRD, appear to be regularly interstratified I-S with 50 percent or more illite layers.

As diagenesis continues, the thickness of the fundamental illite particles increases within the population. When the particles become sufficiently thick to produce diffraction maxima with a 10-Å series the clay material is identified by XRD as conventional illite.

We have shown that diagenetic illite with no detectable expanding component is made up of particles 20 to 160 Å thick, with the average being 70 Å (*15*). Thus, the diagenetic conversion of smectite to illite may actually be a recrystallization phenomenon where smectite dissolution and illite precipitation occurs within a population of extremely small phyllosilicate crystals.

Our interpretation also suggests a solution to the currently enigmatic thermodynamic status of interstratified clays (*23, 24*). Although randomly interstratified, I-S would be regarded as two phases, smectite and illite, regularly interstratified I-S could be regarded as a single phase, that is illite 20 to 50 Å thick.

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5. Sample collected by J. L. Post, California State University, Sacramento.
6. This sample is analogous to sample MB670 in figure 8 of Nadeau and Reynolds (*20*).
7. Sample collected by V. C. Farmer, from a fracture in a doleritic sill.
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6 March 1984; accepted 6 June 1984

Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling

Abstract. *Computer modeling of 611 high-quality analyses of normal ground waters from diverse geographic areas reveals that aqueous oxidation-reduction reactions are generally not at equilibrium. Multiple redox couples present in individual samples yield computed Nernstian Eh (redox potential) values spanning as much as 1000 millivolts. The computed Eh values do not agree with each other, nor do they agree with the single "master" value measured in the field with a platinum electrode. Because of internal disequilibrium, the use of any measured Eh value as input to equilibrium hydrogeochemical computer models will generally yield misleading results for normal ground waters.*

The concept of oxidation-reduction potential (Eh) is used extensively in many scientific fields. However, some investigators have recognized problems associated with the measurement and interpretation of Eh (*1–4*).

Of the thousands of Eh measurements reported for natural waters, only a few have been successfully interpreted on a quantitative, Nernstian basis. Some Eh measurements have been related to the reversible Fe^{2+}/Fe^{3+} couple in acid mine drainage waters (*5*) and to various dissolved sulfur couples (*6*). In laboratory studies, relatively concentrated solutions of manganous ion saturated with respect to Mn(IV) precipitates yield Eh values in agreement with the Nernst equation (*7*). However, most natural waters have low concentrations of redox elements and are poorly poised, with exchange currents too low to establish a Nernstian Eh during potentiometric measurements.

Most investigators of Eh have emphasized techniques of measurement of Eh, but the most serious problem in applying the concept of Eh to natural low-temperature aqueous systems is the lack of internal equilibrium (*1–4*). The redox potentials observed in natural waters are usually mixed potentials, which are impossible to relate to a single dominant redox couple in solution.

One can test the redox equilibrium in a single sample of water by analyzing for the dissolved species of multivalent elements, correcting the concentrations to activities, and calculating a theoretical Nernstian Eh for each analyzed couple. If all the computed Eh values agree, redox equilibrium probably obtains in the sample. Disagreement among the computed Eh values suggests that the system is at disequilibrium and that there is no single master Eh value.

Few investigators have examined natural water chemistry to determine the extent of redox equilibrium (*5, 8–10*). Papers by Stumm (*1*) and Morris and Stumm (*2*) are noteworthy for presenting arguments for the lack of redox equilibrium in natural waters. However, our results apparently represent the first comprehensive investigation of the degree of reversibility of oxidation-reduction reactions in a large number of ground waters.

A request was made to the National Water Data Exchange (NAWDEX) (*11*) for a search of the entire WATSTORE data base, which contains water data collected by the U.S. Geological Survey.