

An alternative approach to assess the true nature of 2:1 mixed-layer silicates in diagenetic and weathering environments

H. Vali
S.K. Sears
R. Hesse
R.F. Martin

*Department of Earth and Planetary Sciences, McGill University,
3450 University Street, Montreal, Quebec, Canada H3A 2A7*

Introduction

Questions concerning the definition and classification of 2:1 layer silicates and related I/S mixed-layer minerals evidently remain unresolved in light of conflicting results from analytical (e.g. Środoń *et al.*, 1992) and thermodynamic (e.g. Ransom and Helgeson 1993) studies. Critical problems inherent in the analytical approach arise from analytical errors and sample heterogeneity and impurity (even in the finest clay-size fractions), which prevent the determination of the true structure and chemical composition of individual clay mineral phases.

The current definition of 2:1 mixed-layer structures (I/S) is based principally on XRD and to some extent thickness measurements of fundamental particles in TEM (Nadeau *et al.*, 1984; Środoń *et al.*, 1992). However, Ransom and Helgeson (1989) have stressed that any classification scheme must be based strictly on mineralogical and chemical criteria. Expandability behavior, as measured by XRD after ethylene glycol solvation, should not be taken as *de facto* evidence for the presence of a smectite-group phase in mixed-layer 2:1 layer silicates (I/S) because of inherent ambiguities in the interpretation of the results.

An alternative approach, and one that does provide reliable chemical and structural data, involves the treatment of clay-mineral samples with *n*-alkylammonium ions (Vali and Hesse 1990), followed by imaging and analysis of selected areas using analytical HRTEM. This approach leads to an improved characterization of individual clay-mineral components, and thus to a more reliable classification of 2:1 mixed-layer phases.

Materials and methods

We selected clay mineral samples from different environments: 1) Zempleni, Hungary (hydrothermal), 2) Reindeer D-27 and Kumak E-

58 oil wells in the Beaufort-Mackenzie area, Northwest Territories, Canada, and 3) SMJ9 from the Ae soil horizon, New Brunswick, Canada, and E4, from the Ae soil horizon, Aylesford Lake, Nova Scotia, Canada. In addition, muscovite from Wacker Chemie, Germany was used as a reference sample.

Sodium-saturated and size-fractionated (<0.05 μm to <2 μm) dispersions were used for TEM/AEM, XRD, *n*-alkylammonium-ion exchange and freeze etching investigations. Sample preparation and analytical conditions are described by Vali *et al.* (1991, 1993, 1994).

Results

The layer structure, chemical composition, stacking order and surface morphology of individual samples from different environments are distinct. The hydrothermal sample from Zempleni, treated with octadecylammonium ions ($n_C = 18$), shows an $R = 3$ structure with packets consisting of three to six 2:1 layers having nonexpandable interlayers that are stacked in an apparently coherent sequence. Some of these packets (~20%) show uniform expansion (2.5 nm spacing). A small proportion (10%) of packets consist of a few layers that appear disorganized and bent.

Progressive illitization with depth is observed in diagenetic samples from the Beaufort-Mackenzie area. At shallow depths, single units of 2:1 layer silicates represent a smectite-group phase; they are curved and of short length, and do not seem to form coherent sequences. At the same depths, discrete packets of illite, between three and ten layers thick, are present as isolated particles. At greater depths of burial (>3050 m), packets of illite appear as isolated particles or as apparently more coherent sequences with a $R > 1$ structure, together with a $R = 1$ ordered structure. Smectite-like particles are not present at these depths.

In the weathering environment, the thickness of particles in soil samples is greater than in hydrothermal and diagenetic samples, as is the degree of order of the apparently coherent sequences. The soil samples are characterized by random mixed-layer structures having expandable and nonexpandable interlayers, R = 1 ordered structures, and uniformly expanded sequences consisting of nonpolar layers typical of vermiculite and weathered micaceous minerals.

Different responses of the interlayers to *n*-alkylammonium-ion exchange and relatively high values of interlayer spacing (2.5-3.0 nm) in the expandable components indicates: a) an interlayer charge-density greater than 0.6 per $O_{10}(OH)_2$ (Vali and Hesse 1990), b) a variation in extent of isomorphous substitution within the T-O-T (tetrahedra-octahedra-tetrahedra) part of the 2:1 layer silicates, and c) coexistence of different types of expandable components associated with different type of stacking order. Note that neither variation in the charge density nor the occurrence of different types of expandable components can be detected by ethylene-glycol solvation in XRD.

An attempt was also made to assess the relationship between the degree of expandability caused by reaction with *n*-alkylammonium ions and the extent of Al-for-Si isomorphous substitution within the T-O-T sequences of the samples characterized above. The particles consisting predominantly of nonexpandable packets reveal high K and Al contents, whereas the particles in which the interlayer has become expanded with *n*-alkylammonium ions have a lower concentration of K and Al. There is an extensive variation in chemical composition among the particles within the same sample, as well as in the samples from different environments. Muscovite, which shows no expansion upon treatment with *n*-alkylammonium ions, has the highest Al_2O_3/SiO_2 ratio and K_2O content. The amount of K_2O and the ratio of Al_2O_3 to SiO_2 decrease with increasing proportion of expandable interlayers. Generally, the Al_2O_3/SiO_2 ratio of the expandable component is higher than that of low-charge smectite-group minerals, which suggests that the expandable component may be vermiculite-like or a high-charge smectite.

Freeze-etched replicas of these samples reveal the occurrence of different types of particles having characteristic surface morphology and crystal shape within individual samples. This array may correspond to the various layer structures observed in ultrathin sections. Distinct morphological differences exist among the samples from different environments. As an example, in diagenetic samples, smectite-group minerals from

shallow depths appear as thin anhedral or irregularly shaped particles (detrital) whereas illitic material at greater depths shows thicker crystals having an irregular shape (detrital), or is present as euhedral laths and pseudo-hexagonal plates (neoformed). These observations have significant implications for our understanding of diagenetic processes and radiometric dating.

Discussion

The analytical approach applied in this study leads us, 1) to distinguish among different types of expandable and nonexpandable components, 2) to document variations in density of interlayer charge of the expandable components, which are not detectable by XRD, 3) to distinguish among different types of illite (expandable and nonexpandable), which do not respond differently to ethylene glycol treatment, 4) to distinguish between fundamental particles and short-range ordered structures, 5) to relate the ordering of the T-O-T layers and chemical composition, as measured directly by TEM (XRD study of oriented samples gives information on the interlayer spacing only), and 6) to characterize all types of particles present (not only the coherent sequences, as given by XRD).

The status of 'illite-smectite' mixed-layer attributed to these materials is found to reflect the composition and arrangement of polar and nonpolar 2:1 layer silicates. The nature of the 2:1 mixed-layer silicate thus cannot be ascribed to a mixture of illite and smectite layers. The extensive chemical variability among members of the clay-mineral group usually is attributed to the occurrence of solid solution. The variability in 2:1 mixed-layer silicates studied also could be due to: 1) presence of compositionally distinct domains in the structure, 2) a mixture of two or more distinct phases or 3) intergrowth of two types of structure. A clear distinction between a monomineralic solid-solution phase and a mixture of coexisting end-members based on chemical composition or even conventional XRD and HRTEM techniques is of crucial importance. The data presented in the literature concerning the nature of the smectite-group phase and related I/S mixed layers do not necessarily reflect the true nature of the individual clay-mineral phases.

References

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- Ransom, B. and Helgeson, H.C. (1989) *Clays Clay Min.*, 37, 189-91.