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COMMENTS ON THE CLASSIFICATION OF TRIOCTAHEDRAL 2:1 PHYLLOSILICATES

Key Words—Layer charge, Nomenclature, Saponite, Swelling, 2:1 phyllosilicate, Vermiculite.

In 1964, the International Committee of the Classification and Nomenclature of Clay Minerals (A.I.P.E.A.) proposed a scheme for the classification of the 2:1 phyllosilicates based mainly on layer-charge density and nature of interlayer material. In 1969, Méring and Pédro proposed an alternative method of classification based on the following four criteria: (1) the number of cations occupying the octahedral sheet (i.e., di- or trioctahedral sheet); (2) the location of cationic substitutions in the octahedral or tetrahedral sheets; (3) the anhydrous or hydrated character of the mineral, a property related to the mineral genesis; and (4) the amount of interlayer charge. According to Méring and Pédro (1969), minerals having layer charge per formula unit in the range 0.2–0.6 are characterized by a structure in which the cationic substitutions are distributed in a totally disordered manner. These minerals correspond to the smectite group. Minerals having layer charge equal to or greater than 0.6 are characterized in this classification by partially ordered cationic substitutions. These minerals constitute the vermiculite-mica group. The present report addresses the fourth point of this classification; more particularly, it discusses whether or not there is a cristallochemical justification for an abrupt division of trioctahedral minerals having tetrahedral substitutions at a layer charge level of 0.6.

MATERIALS AND METHODS

Six samples of natural vermiculites having a layer charge of 0.86 (a transformed Madagascar phlogopite), 0.82 (Santa-Olalla, Spain), 0.74 (Kenya), 0.65 (Malawi), 0.54 (Prayssac, France), and 0.53 (Benahavis, Spain) were studied, as well as a natural saponite having a layer charge of 0.45 (Kozakov, Czechoslovakia). All samples were saturated with six different cations (Li, Na, K, Ca, Mg, and Ba), and their swelling characteristics in water, ethylene glycol, and glycerol were studied. Only the following homogeneous swellings are considered (i.e., giving rise to rational 00*l* reflections): (1) six reflections for the two-organic layer complexes and the three-water layer hydrates; (2) five reflections for the one-organic layer complexes and the two-water layer hydrates; and (3) four reflections for the one-organic layer complexes and the one-water layer hydrates. The layer stacking sequences of samples as a function of relative humidity were determined by X-ray powder diffraction (XRD).

EXPERIMENTAL RESULTS

Swelling in liquids

Figure 1 gives basal spacings of air-dry trioctahedral 2:1 phyllosilicates having tetrahedral substitutions after immersion of the air-dry clay in water, ethylene glycol, and glycerol. For saponites and vermiculites, 48-hr contact with the different solvation liquids was necessary to be sure that their equilibrium state was reached. The liquid-clay paste was placed in a glass tube and examined by XRD. K-saturated minerals gave large and diffuse XRD reflections; they have not been included in a swelling study as a function of the layer-charge density.

Figure 1 shows that tetrahedrally charged minerals behaved in four different ways as a function of layer-charge density, depending upon the nature of the solvation liquid and the interlayer cation involved: (1) They formed a single solvation complex corresponding to an arrangement of double layers of molecules between the silicate layers. The thickness of this double-layer complex gradually decreased with an increase in charge density, as illustrated by the behavior of the Na- and Ca-saturated samples with water, and the Ca- and Ba-saturated samples with ethylene glycol. This behavior suggests a high flexibility in the role of charge density in the arrangement of solvation molecules in the interlayer space. (2) They formed two solvation complexes having n and n − 1 layers of molecules (n = 3 in water and n = 2 in ethylene glycol and glycerol). A discontinuity in the swelling for different values of the charge density was observed at about 0.5 for Mg and Ba in water, 0.7 for Ca and Ba in glycerol and for Mg in ethylene glycol, and 0.8 for Li and Na in ethylene glycol. (3) They formed three solvation complexes. Their swelling showed two discontinuities, as noted for the Li- and Na-saturated 2:1 phyllosilicates upon glycerol solvation. These materials formed a double-layer glycerol complex having a basal spacing of about 18.1 Å and two different single-layer complexes having basal spacings of about 14.3 and 12.2 Å. (4) In water Li-saturated minerals showed unlimited swelling up to a charge density of about 0.6 and a two-water hydrate for $x > 0.6$.

Swelling and layer stacking type as a function of relative humidity

The behavior of saponites and vermiculites as a function of relative humidity (RH) was followed by the

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basal spacings and layer stacking types of the materials. These two factors were well studied by de la Calle *et al.* (1978, 1985) and Suquet and Pézerat (1987). From the nature of the interlayer cation and the RH, these last authors determined 11 layer-stacking sequences: V_0 and 1*M* for the "zero layer" state; V_a, V_b, V_c, V_d, and V_e for the one-layer hydrate; and V_I, V_{III}, V_V, and V_{VII} for the two-layer hydrate. Each layer stacking sequence was characterized by the components along the 0x and 0y axes of the translation which defined the position of one layer with respect to the next layer. For a given RH, each cation induced an interlayer structure and a specific layer stacking type to fit this interlayer structure. The layer charge density and the bidimensional size of the particles modified the range of RH at which a specific structure existed.

With several cations (Figure 6 in Suquet and Pézerat, 1987), regardless of layer charge, saponites and vermiculites assumed the same layer-stacking sequence; e.g., (1) the V_{III} layer-stacking sequence between 55 and 100% RH with Na and between 47 and 100% RH with Ca; (2) the V_I layer stacking sequence between 12 and 60% RH with Mg; (3) the V_d layer stacking sequence between 2 and 40% RH with Ba; (4) the layer stacking sequence 1*M* between 0 and 2% RH with Li and Ba and between 0 and 35% RH with K; and (5) the layer stacking sequence V_0 between 0 and 2% RH with Na. Furthermore, some low-charge vermiculites behaved like saponite and not like high-charge vermiculite. Thus, Li-saponites and low-charge Li-vermiculites were disordered, whereas high-charge Li-vermiculites assumed the layer stacking type V_b. Between 20 and 40% RH, Na-saponites and low-charge Na-vermiculites assumed the V_a structure, whereas high-charge Na-vermiculites had the V_c structure. At about 40% RH, Ca-saponites and low-charge Ca-vermiculites were three-dimensionally ordered (V_{III}), but the high-charge vermiculites were only semi-ordered (V_V). Consequently, the layers of saponites and vermiculites do not appear to differ cristallographically, and no basis exists for saying that Si-Al substitutions may not be identically distributed in these two minerals.

DISCUSSION

The swelling properties of saponites and vermiculites showed no single discontinuity, but rather several discontinuities at layer charges per formula unit of about 0.5, 0.6, 0.7, and 0.8. The discontinuity was dependent on the nature of the interlayer cation (Li, Na, Mg, Ca, or Ba) and the solvation liquid (water, ethylene glycol, or glycerol), but not on the type of mineral (saponite vs. vermiculite). These values represent limits for the stability domains of some interlayer structures as functions of the charge density, the specific nature of the balancing cation, and the nature of the solvation liquid,

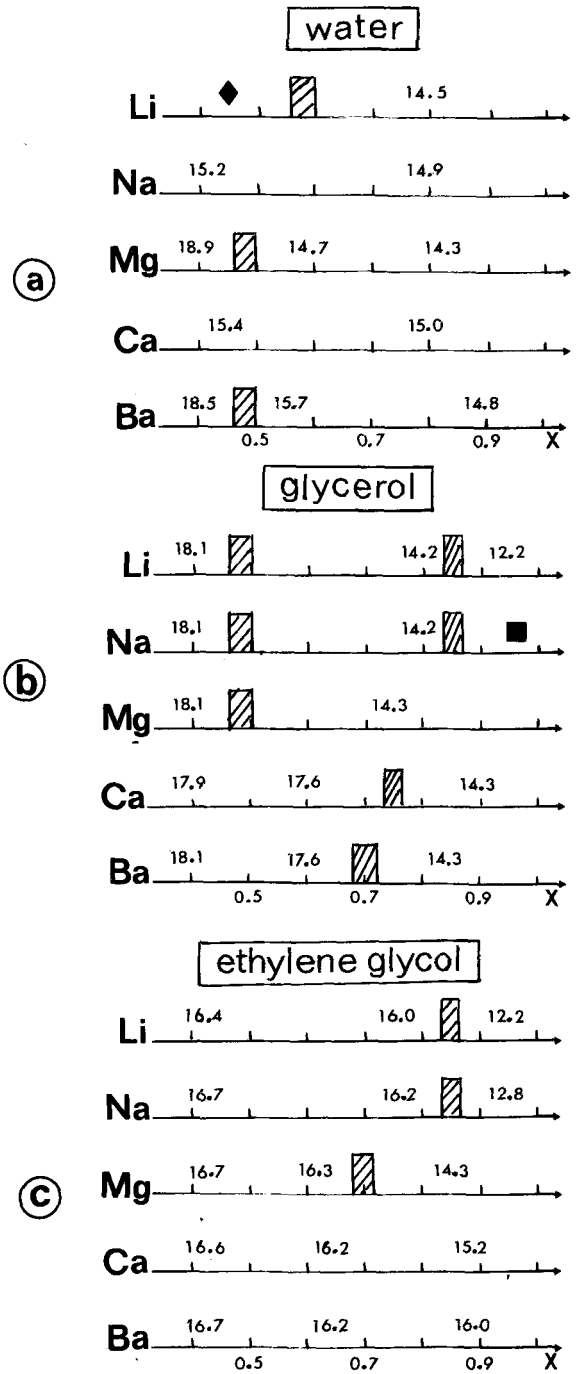


Figure 1. Mean values of basal spacings (Å) of (a) water, (b) glycerol, and (c) ethylene glycol solvation complexes of trioctahedral 2:1 phyllosilicates with the layer charge x per formula unit $(Si,Al)_4Mg_3O_{10}(OH)_2$. ■ = irregular layer sequence; dashed bar indicates discontinuity in swelling behavior; ◆ = unlimited swelling.

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but not as a function of a crystallochemical difference of the layers of saponites and vermiculites.

The criterion of the "order" or "disorder" of cationic substitutions, therefore, cannot be used to justify a separation between smectites and vermiculites. Méring and Pédro (1969) proposed this criterion on the basis of a correlation made between diffuse scattering linking certain Bragg reflections together and a postulated distribution of Al substitutions along chains in muscovite. This type of diffusion has since been observed in smectites and micas and is apparently produced by fluctuations of the position of the surface oxygen atoms around their equilibrium points (Kodama, 1977). Besson *et al.* (1974) based the "order vs. disorder" of cationic substitutions on the interpretation of honeycomb-shaped diffusion that is observed only in vermiculites and micas. They correlated this phenomenon with an ordered distribution of the interlayer cations and consequently to an ordered distribution of Si-Al tetrahedral substitutions in these minerals. Suquet and Pézerat (1987) explained that all types of extra spots between Bragg reflections, such as honeycomb-shaped diffusion, can be correlated with the distribution of the interlayer cations, which tend to locate as far as possible from each other. The resultant superstructure can be experimentally detected if the layer charge density and the charge corresponding to the superstructure are compatible.

Moreover, the presence or absence of a relationship between the distribution of the interlayer cations based on the repulsion forces and the distribution of the cationic substitutions in the tetrahedral sheets must be questioned. Herrero *et al.* (1985a, 1985b) showed by a ^{23}Si nuclear magnetic resonance study that in most synthetic and natural 2:1 phyllosilicates, tetrahedral Al is homogeneously dispersed so as to minimize electrostatic energy and to respect Loewenstein's rule. Bailey (1986) and Rule and Bailey (1987) found that in chlorites Ia and IIb, interlayer cations are ordered, but tetrahedral Al cations are completely disordered. Thus, Si-Al substitutions are not ordered in most smectites and micas. This result agrees with Bailey's conclusions (1984) that long-range ordering of tetrahedral cations is only favored by phengitic compositions, by the $3T$ stacking sequence, and by tetrahedral Si:Al ratios near 1:1. These conditions do not exist in the most common 2:1 phyllosilicates.

Finally, the swelling properties listed above for powders of trioctahedral 2:1 phyllosilicates having tetrahedral substitutions allow a distinction to be made between high-charge minerals termed vermiculites ($x > 0.7$) and low-charge minerals termed saponites ($x < 0.5$). For medium-charge samples, none of the results brought out in this study enables a clear distinction to be made between a saponite and a vermiculite. This paper shows the futility for consideration of any precise distinction between these two minerals, inasmuch as there is no crystal chemical difference in the layers to support a sharp division between smectite and vermiculite at $x = 0.6$. Such samples should be called smectite-vermiculite intermediates, and they should be characterized by a combination of swelling tests. It has been aptly remarked that information of this type would be more useful than merely allocating a given specimen to one or another of the groups (Brindley and Brown, 1980, and the references cited therein).

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