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PROBLEMS IN IDENTIFICATION OF MONTMORILLONITE AND BEIDELLITE

Key Words—Beidellite, Greene-Kelly test, Identification, Layer charge, Lithium, Montmorillonite, Swelling.

Hofmann and Klemen (1950) first indicated that the anomalous loss of expansion and cation-exchange capacity (CEC) of Li-montmorillonite after drying was due to the migration of Li^+ ions from the interlayer position to vacant octahedral sites, with a consequent neutralization of negative charge originating in the sheet due to cationic substitution. Calvet and Prost (1971) confirmed that the same Li^+ ions do indeed move to octahedral sites, but that more Li^+ ions migrate to hexagonal cavities. Greene-Kelly (1953, 1955) utilized the hypothesis of Hofmann and Klemen (1950) to differentiate montmorillonite and beidellite. The irreversible collapse of an expanding mineral to 9.5 Å after saturation with Li^+ and heating at 200°–300°C was the criterion for calling the mineral montmorillonite. On the other hand, expansion to 17.8 Å with glycerol after Li-treatment and drying was the criterion for characterizing the mineral as beidellite.

Since Greene-Kelly's work, several investigators have used this technique to identify montmorillonites and beidellite from soil environments (Ross and Mortland, 1966; Douglas, 1982) and geological deposits (Schultz, 1969). Other investigators have prepared Li^+-reduced, reduced-charge montmorillonites to study various surface and solvation properties as a function of layer charge (Calvet and Prost, 1971; Brindley and Ertem, 1971; Ertem, 1972; Clementz and Mortland, 1974; Clementz *et al.*, 1974; Maes *et al.*, 1979). The purposes of the present investigation were: (1) to evaluate the reversibility of expansion properties of clay minerals due to back migration of Li^+ ions (due to concentration gradient) from the octahedral sites, an especially important phenomenon if reduced-charge minerals must be kept in saturating medium for a relatively long period of time; and (2) to evaluate the validity of the Greene-Kelly test to nonideal montmorillonite-beidellite series; ideal montmorillonites or beidellites are rare in nature, and most montmorillonites and beidellites possess some tetrahedral and some octahedral charge, respectively.

EXPERIMENTAL

Bulk powder forms of two montmorillonites (SWy-1 and SAz-1), one beidellite (B 18/4), and the <0.2-μm fraction of one nontronite (NG-1) were used in this study. Sources and charge characteristics of the samples are given in Table 1. This table shows the relative amounts of charge in the octahedral and tetrahedral sheets of the samples obtained from the same general location, but not necessarily the exact samples used in the present study. All the samples apparently possess both tetrahedral and octahedral charge.

Oriented films of clays were characterized by X-ray powder diffraction after the following preparations: (1) Mg-saturation and glycerol solvation; (2) K-saturation followed by heat treatment at 300°C for 1 hr and glycerol solvation (Malla and Douglas, 1987), and (3) Li-saturation (Greene-Kelly, 1953), followed by heat treatment at 300°C for 24 hr in a platinum crucible. This last treatment eliminates the problem caused by heating the sample on a glass slide, as encountered by Bystrom Brusewitz (1976). Samples were then exposed for varying lengths of time to a maximum of 20 weeks to the following: (1) 15% glycerol by volume in 1 N Mg-acetate solution; (2) distilled water; and (3) n-alkylammonium chloride solutions at 65°C (Ruehlicke and Kohler, 1981).

The above treatments were analyzed on a Siemens X-ray diffraction system using CuKα radiation monochromatized by a Johanson crystal. Data were recorded on a Dapple Theta Plus computer system. The d-values reported were measured from d(001) reflections only.

The layer charge of all the samples before Li-saturation was estimated from monolayer to bilayer transition (Figure 1) by n-alkylammonium ion exchange (Lagaly and Weiss, 1969; Lagaly *et al.*, 1976; Malla and Douglas, 1987). For nontronite NG-1, however, the layer charge was also determined after saturation with Li^+ and heat treatment.

RESULTS

Layer charge and the solvation properties after Mg-, K-, and Li-saturation are summarized in Table 2. The magnitude of total layer charge per half unit cell ranged from 0.28 in sample SWy-1 to 0.41 in sample B 18/4. All the samples characteristically accommodated two layers of glycerol following Mg-saturation. Reexpansion with glycerol after K-saturation and heat treatment (column 4) is in agreement with the magnitude of layer charge, as predicted by Malla and Douglas (1987).

Samples SWy-1, SAz-1, and B 18/4 assumed a pyrophyllite-type structure as indicated by the 9.6-Å basal spacings after Li-saturation and heat treatment and

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Table 1. Characteristics of samples.

Sample	Location	Cationic substitution[2]		Data source
		Octahedral	Tetrahedral	
SAz-1[1] Montmorillonite	Apache County, Arizona	0.42 (86%)	0.07 (14%)	Grim and Güvan (1978)
SWy-1[1] Montmorillonite	Crook County, Wyoming	0.23 (69%)	0.10 (31%)	Senkayi *et al.* (1985)
B 18/4[3] Beidellite	Unterrupsroth, Federal Republic of Germany	0.32 (70%)	0.14 (30%)	Besson (1980)[4]
NG-1[1] Nontronite	Hohen Hagen, Federal Republic of Germany	0.10 (25%)	0.30 (75%)	Schneiderhohn (1965)

[1] Samples obtained from the Source Clay Repository of The Clay Minerals Society.
[2] Substitution per $O_{10}(OH)_2$ unit.
[3] Beidellite provided by G. Lagaly, Department of Inorganic Chemistry, University of Kiel, Kiel, Federal Republic of Germany.
[4] As cited in Tsipursky and Drits (1984).

failed to reexpand in either water or Mg + glycerol. Sample NG-1, however, reexpanded to 18 Å in glycerol. Further treatment of Li-saturated and heat-treated samples SWy-1 and SAz-1 in a saturating medium of distilled water or Mg + glycerol for 20 weeks caused no reexpansion beyond 9.7 Å.

Expansion of samples SWy-1, SAz-1, and B 18/4 in n-alkylammonium chloride solutions as a function of time is plotted in Figure 2. The illustration shows that sample SAz-1 did not expand (9.7 Å after 24 hr) or expanded only slightly (10.0 Å after 20 weeks) when incubated in hexylammonium chloride solution. Sample SWy-1 gradually expanded to 12.5 Å (Figure 2) with hexyl- and to 13.5 Å (monolayer, not shown in Figure 2) with octadecylammonium chloride in 20 weeks. Sample B 18/4 sorbed a monolayer (13.4 Å) of dodecylammonium ions in 3 weeks and maintained the same spacings for as long as 20 weeks. The spacings obtained for sample B 18/4 were 13.2 Å with heptyl-, 13.3 Å with octyl-, 13.5 Å with pentadecyl-, and 14.1 Å with hexadecylammonium ions after 20 weeks. The spacings for all the samples with hexyl-, dodecyl-, and octadecylammonium ions before Li-saturation and heat treatment are also listed in Table 2.

DISCUSSION

The inability of samples SWy-1, SAz-1, and B 18/4 to reexpand beyond 9.6 Å with glycerol after Li-saturation and heat treatment indicates that the predominant charge of the minerals is in the octahedral sheets and that the migrating Li^+ ions effectively neutralized this octahedral charge. Further, the inability of samples SWy-1 and SAz-1 aged in Mg + glycerol or distilled water for 20 weeks to reexpand beyond 9.7 Å indicated little back migration of Li^+ ions to interlayers or to the saturating medium. Greene-Kelly (1955), however, indicated that the reverse migration of Li^+ ions occurs at higher temperature due to greater stability of a hydrated Li^+ ion in interlayer positions than that of an unhydrated Li^+ ion in octahedral coordination. Sample NG-1, on the other hand, expanded to 18 Å with glycerol following Li-saturation and heat treatment, suggesting that the charge was predominantly in the tetrahedral sheet.

As seen from Figure 2, a gradual reexpansion of Li-saturated samples SWy-1 and B 18/4 to a monolayer (13.5 Å) and of sample SAz-1 to 10.0 Å after 20 weeks by n-alkylammonium ions indicates that these samples

Table 2. Layer charge and X-ray powder diffraction analyses of expansion properties of the samples.

Sample[1]	Layer charge/ $O_{10}(OH)_2$	MgG (Å)	K300G (Å)	Li300G (Å)	Li300 (H_2O) (Å)	nC6 (Å)	nC12 (Å)	nC18 (Å)
SWy-1	0.28	18.12	17.70	9.60	9.60	13.4	15.0	17.8
SAz-1	0.39	17.81	14.10	9.60	9.60	13.8	18.1	21.4
B 18/4	0.41	18.12	14.10	9.60	ND	13.8	17.8	21.3
NG-1	0.38 (0.36)[2]	18.05	14.05	18.16	ND	13.7	17.5	20.2

[1] See Table 1 for sources of samples.
[2] Value in parenthesis is after Li-saturation and heat treatment (tetrahedral charge).
G = glycerol; nC6 = hexylammonium ion; nC12 = dodecylammonium ion; nC18 = octadecylammonium ion; Mg + G = Mg-saturated and glycerol solvated; K300G = K-saturated, heated at 300°C, and glycerol solvated; Li300G = Li-saturated, heated at 300°C, and glycerol solvated; Li300 (H_2O) = Li-saturated, heated at 300°C, and incubated in distilled water for as long as 20 weeks; ND = Not determined.

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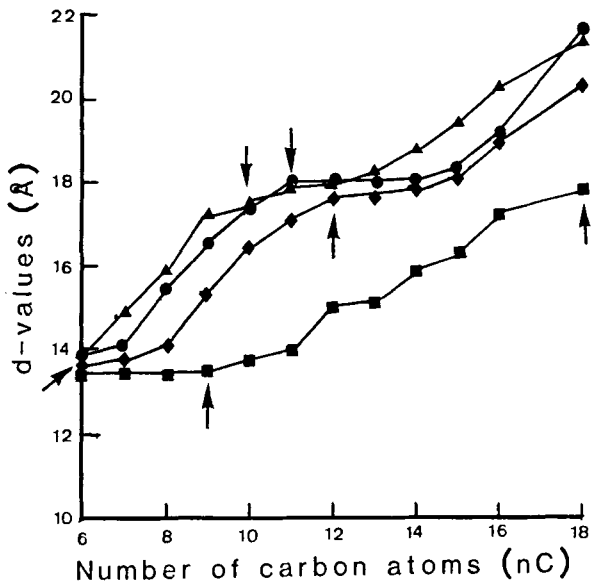


Figure 1. Variations in basal spacings of samples SWy-1 (■), SAz-1 (●), B 18/4 (▲), and NG-1 (◆) with chain length (nC) of alkylammonium ions. The monolayer to bilayer transitions are indicated by arrows and represent the extent of charge heterogeneity.

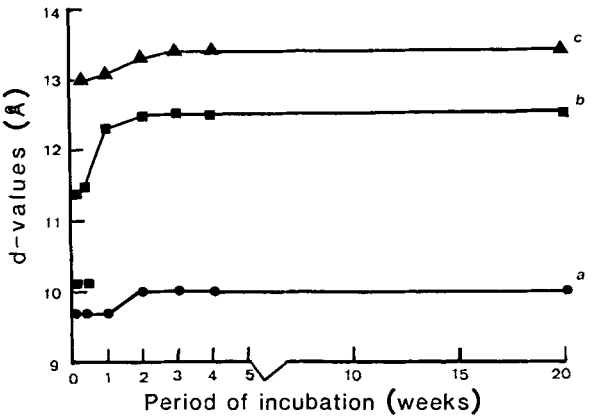


Figure 2. Reexpansion (Å) of n-alkylammonium ions exchanged samples following Li-saturation and heat treatment as a function of time: (a) sample SAz-1 (●) and (b) sample SWy-1 (■) exchanged with hexylammonium ions; (c) sample B 18/4 (▲) exchanged with dodecylammonium ions. Notice the two d(001) reflections (first four data points) observed for sample SWy-1 in 24 and 48 hr of incubation which indicate the different rates of exchange of the organic cations in the interlayers.

possess both collapsed and expanded interlayers. The expanded interlayers most likely resulted from layers having a population of tetrahedral charge, whereas the collapsed layers apparently had no tetrahedral charge. From the rate and the degree of expansion by n-alkylammonium ions, the following tetrahedral relationship among the three smectites exists: SAz-1 < SWy-1 < B 18/4, in accord with the values given in Table 1. Sample SAz-1 has little or no tetrahedral charge and no evidence of interlayer sorption, whereas sample B 18/4 has the largest tetrahedral charge and supported only a monolayer of dodecylammonium ions within 3 weeks. Clementz and Mortland (1974) also reported similar results for a reduced-charge Upton, Wyoming, montmorillonite that had been saturated with trimethyl- and tetra-n-propylammonium ions for 15 hr. They also indicated that the charge reduction proceeded in an inhomogeneous fashion. In fact, all of the minerals used in the present study have heterogeneous charge distribution, as indicated by the broad transition from monolayer to bilayer formation (Figure 1 of the present study; Stul and Mortier, 1974). The inability of samples to reexpand beyond 9.7 Å after Mg + glycerol or water treatment (Table 2, columns 5 and 6) could be due to the fact that the coulombic attractions of negative charge on the silicate layer were so small that they could not support or attract Mg^{2+}, glycerol, or water molecules in the interlayers. For Mg^{2+}, either the solvated cations could not penetrate the collapsed interlayers or they were exchanged but were unable to solvate; the latter possibility is less likely than the former. The expansion of these minerals by n-alkylammonium ions, however, demonstrates that these organic cations are more effective in penetrating the collapsed layers.

To estimate layer charge by alkylammonium ion-exchange requires a monolayer-to-bilayer transition; therefore, the formation of only a monolayer or less in samples SWy-1 and SAz-1 after treatment for as long as 20 weeks indicates no back migration of Li^+ ions under the conditions specified. Thus, a combination of the Greene-Kelly test and alkylammonium ion-exchange may be extended to estimate the tetrahedral and octahedral charge in 2:1 minerals containing considerable amounts of charge on both sheets.

Ross and Hendricks (1945) defined montmorillonite as a mineral whose negative charge was all on the octahedral sheet and beidellite as a mineral in which all the negative charge was on the tetrahedral sheet. Ideal montmorillonites or beidellites, however, are rare in nature (Schultz, 1969; Tsipursky and Drits, 1984); i.e., montmorillonites or beidellites seldom have only octahedral or tetrahedral charge. The Greene-Kelly test unambiguously differentiates ideal montmorillonites and beidellites; however, it must be reevaluated for nonideal phases. Greene-Kelly (1955) indicated that some expansion occurs with glycerol solvation if the sample contains >30% tetrahedral substitution or <70% Li^+ ions in the interlayer spaces. Therefore, for convenience, he suggested the terms beidellite for those minerals having >50% tetrahedral substitution and montmorillonite for minerals having >50% octahedral substitution. Calvet and Prost (1971) determined that

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a minimum of 20% of the CEC was needed to expand the Li-treated and heated montmorillonites for ethylene glycol, 30% for glycerol, and 50% for water. Schultz (1969), working with 83 clay samples, reported no appreciable shift in the 9.6-Å line for beidellites containing from 0 to 35% reexpandable layers. Surprisingly, none of these workers referred to the importance of the magnitude of the tetrahedral or octahedral charge.

From the present study, the magnitude of octahedral or tetrahedral substitutions appears to be as critical as their relative percentages in the identification of beidellites or montmorillonites by the Greene-Kelly test. The amount of substitution is especially important to clay minerals having low total or low tetrahedral charge. The Greene-Kelly test relies solely on the swelling of the mineral due to the remaining tetrahedral charge after octahedral charge has been neutralized by Li-saturation and heat treatment. Swelling is not possible if the magnitude of negative charge on the silicate layers does not exceed the value necessary to support cations or polar molecules in the interlayers.

Similarly, as described above, a quantitative estimate of layer charge by alkylammonium ion-exchange requires the formation of at least the monolayer (~13.5 Å) to bilayer (~17.7 Å) transition; this transition seems to be achieved only if the layer charge $>0.24/O_{10}(OH)_2$ unit (Maes *et al.*, 1979). Thus, regardless of the percentage of charge distribution in octahedral or tetrahedral sheets, a quantitative estimate of tetrahedral charge following the Greene-Kelly test may be possible if the remaining charge is ≥ 0.24/half unit cell (Table 1, Figure 1). The inability of low-charge minerals (<0.24) to form (at least) a bilayer with alkylammonium ions demonstrates the limitation of alkylammonium ion-exchange to estimate layer charge in minerals having charges <0.24. The ability of very low charge clay minerals (<0.24), however, to exchange some alkylammonium ions, but not glycerol or water molecules, differentially with time gives a qualitative estimate of layer charge.

As suggested by Greene-Kelly (1955), 50% octahedral or tetrahedral substitution may be a convenient criterion to distinguish montmorillonite from beidellite; this estimate, however, is rather difficult to make both by the Greene-Kelly test and by alkylammonium ion exchange. In a low-charge mineral, the Greene-Kelly test will always overestimate the montmorillonitic character, whereas alkylammonium ion exchange following the Greene-Kelly test will fail to give a quantitative estimate of charge. In using the Greene-Kelly test, sample variability and charge heterogeneity should be considered. Nadeau *et al.* (1985) found that the Unterrupsroth beidellite (B2) is composed of separable materials of varying montmorillonitic (particle size <1.4 μm) and beidellitic (particle size >3 μm) character. Sample B 18/4 used in the present study was obtained from the same general location as sample B2 of Nadeau *et al.* (1985), however, sample B 18/4 showed more montmorillonitic character (Table 2, Figure 2), and two separate phases were not detected. This sample, then, should be classified as montmorillonite rather than beidellite.

CONCLUSIONS

Lack of X-ray-detectable back migration of Li^+ ions from octahedral sites allows the study of the reduced-charged behavior of Li-saturated and heat-treated clays, even under conditions where the samples must remain in the saturating medium for a considerable period of time. This procedure may be extended to employ the Greene-Kelly test combined with alkylammonium ion exchange to estimate the layer charge located in either the octahedral or tetrahedral sheet of an expanding 2:1 clay mineral having considerable charge on both sheets. Low-charge minerals, however, having tetrahedral charge <0.24/half unit cell can not be completely characterized by alkylammonium ion exchange. The magnitude of tetrahedral or octahedral charge is more important than the relative proportions of octahedral or tetrahedral charge for the identification of montmorillonite and beidellite by the Greene-Kelly test. Considering the existing techniques for identification, a need still exists for the refinement of criteria or the development of a direct and sensitive technique for distinguishing montmorillonite from beidellite.

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