American Mineralogist, Volume 75, pages 970–982, 1990

Variations in interlayer cation sites of clay minerals as studied by ^{133}Cs MAS nuclear magnetic resonance spectroscopy

CHARLES ARTHUR WEISS, JR.,* R. JAMES KIRKPATRICK, STEPHEN P. ALTANER
Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green St., 245 Natural History Building, Urbana, Illinois 61801-2999, U.S.A.

ABSTRACT

This paper describes the results of a ^{133}Cs MAS NMR study of a number of Cs-exchanged clay minerals and the relationship of the ^{133}Cs chemical shift to chemical and structural parameters. In hectorite (Weiss et al., 1990), Cs occupies a number of different sites depending on the structure, composition, and hydration state of the clay. Increased rotational distortions of the basal O sheet, total layer charge, and tetrahedral Al^{3+} substitution for Si^{4+} correlate with increased deshielding of the ^{133}Cs chemical shifts for both hydrated slurry and dehydrated samples. Correlations for the slurries are poorer because of the distances between the tetrahedral sheets and the Cs in solution. Al^{3+} substitution for Si^{4+} has a greater effect on the ^{133}Cs chemical shift of Cs in a less- (possibly nine-) coordinated site of sample dried at 450 °C than that for the more highly (possibly 12-) coordinated site. Motional averaging between sites inferred to be the Stern and Gouy layers occurs for other smectite minerals. The signal for adsorbed Cs in a CsCl-kaolinite slurry at 0.01 M is probably at defect sites or on a small amount of a second phase (possibly smectite).

INTRODUCTION

With the advent of high-field superconducting magnets and pulse Fourier-transform spectrometers, high-resolution NMR spectroscopy has become an important method in the investigation of the static structure and dynamic behavior of cation adsorption on clay minerals (Bank et al., 1989; Weiss et al., 1990) and zeolites (Chu et al., 1987; Ahn and Iton, 1989; Tokuhiro et al., 1989). Before the availability of this method, cation sites, especially on clay minerals, were difficult to study because the small crystal size of clay minerals prevents use of single-crystal diffraction methods. For clay minerals, NMR methods can characterize structural sites occupied by adsorbed cations in dry samples and clay-water suspensions and can give information on the rates of cation exchange between those sites.

In this study high-resolution magic-angle-spinning (MAS) NMR spectroscopy has been used to examine the structural sites occupied by ^{133}Cs adsorbed on a variety of phyllosilicate minerals and to investigate the chemical and structural parameters that affect the ^{133}Cs chemical shift. Because it has a 100% natural abundance and a small electric quadrupolar moment ($Q = -3 \times 10^{-3} \cdot 10^{-28}$ m^2), which causes narrower NMR line widths relative to other quadrupolar nuclides (Weiss et al., 1990), ^{133}Cs was chosen for this study.

Cations are adsorbed onto clay minerals to balance negative charge on the 2:1 layer structure caused by substitution of lower charge cations for more highly charged cations in the tetrahedral or octahedral sheets (e.g., Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} or Li^+ for Mg^{2+} in the octahedral sheet). Broken bonds on the edges of crystallites may also cause development of a small charge.

Proposed sites of cation exchange on 2:1 clay minerals (e.g., illite, vermiculite, and smectite) include basal surface, edge-interlayer, and internal-interlayer sites (Bolt et al., 1963). Phyllosilicates with relatively large layer charges (e.g., vermiculite and the smectite group minerals: montmorillonite, hectorite, saponite, and beidellite) have relatively large exchange capacities that are dominated by sorption in the interlayer. Phyllosilicates that have very small layer charges (e.g., kaolinite, pyrophyllite, and talc) have small but finite exchange capacities apparently caused by sorption on basal surfaces and the edges of crystallites. Recent high-resolution TEM work reveals the presence of smectite layers on the surfaces of some kaolinite crystals, which may account for ion exchange (Egelton et al., 1989).

In montmorillonite and hectorite the layer charge is developed dominantly in the octahedral sheet, whereas in beidellite, saponite, and vermiculite, it is derived primarily from Al^{3+} substitution for Si^{4+} in the tetrahedral sheet.

In all smectite minerals under atmospheric conditions there is considerable interlayer H_2O, many interlayer cations are hydrated, and these interlayer cations do not come into direct contact with the basal O atoms of the tetrahedral layer (Eirish and Tret'yakova, 1970). Heating or exchange with large monovalent cations (which have

---

* Present address: U.S. Department of Agriculture, Eastern Regional Research Center, Philadelphia, Pennsylvania 19118, U.S.A.

0003–004X/90/0910–0970$02.00

TABLE 1. Localities and structural formulae for 2:1 phyllosilicates and the 1:1 phyllosilicate kaolinite examined in this study

Sample	Locality	Structural formula	Reference*
Dioctahedral			
1) Kaolinite	Washington County, Georgia, USA	$M^{+}_{0.01}\cdot[(Al_{3.90}Ti_{0.08}Fe^{3+}_{0.01}Mg_{0.01})(Si_{3.91}Al_{0.09})O_{10}(OH)_8]$	1
2) Pyrophyllite	Unknown	$Al_4Si_8O_{20}(OH)_4$	2
3) Montmorillonite	Crook County, Wyoming, USA	$M^{+}_{0.70}\cdot[(Al_{2.99}Mg_{0.52}Fe^{3+}_{0.42}Fe^{2+}_{0.01})(Si_{7.97}Al_{0.03})O_{20}(OH)_4]$	3
4) Montmorillonite	Gonzales County, Texas, USA	$Ca^{2+}_{0.31}Na^{+}_{0.11}K^{+}_{0.01}\cdot[(Al_{3.04}Mg_{0.84}Fe_{0.09}Ti_{0.04})Si_8O_{20}(OH)_4]$	4
5) Montmorillonite	Amargosa desert, California, USA	$M^{+}_{0.97}\cdot[(Al_{2.72}Mg_{1.01}Fe^{3+}_{0.29}Ti_{0.02})(Si_{7.90}Al_{0.10})O_{20}(OH)_4]$	5
6) Montmorillonite	Otay, California, USA	$M^{+}_{1.25}\cdot[(Al_{2.69}Mg_{1.20}Fe^{3+}_{0.11})(Si_{7.95}Al_{0.05})O_{20}(OH)_4]$	6
7) Beidellite	Black Jack Mine, Idaho, USA	$M^{+}_{1.10}\cdot[(Al_{3.91}Mg_{0.02}Fe_{0.06})(Si_{6.95}Al_{1.05})O_{20}(OH)_4]$	7
8) Illite/smectite	NA	NA	NA
9) Muscovite	Synthetic	$K^{+}_{2}\cdot[Al_4(Si_6Al_2)O_{20}(OH)_4]$	2
Trioctahedral			
10) Talc	NA	$Mg_6Si_8O_{20}(OH)_4$	2
11) Hectorite	Hector, California, USA	$Na^{+}_{0.38}Mg_{0.14}Sr^{2+}_{0.02}K^{+}_{0.02}\cdot[(Mg_{5.31}Li_{0.69})(Si_{7.98}Al_{0.02})O_{20}F_{2.2}OH_{1.8}]$	8
12) Saponite	Ballarat, California, USA	$M^{+}_{0.98}\cdot[(Mg_{5.79}Al_{0.12}Fe_{0.07})(Si_{6.85}Al_{1.15})O_{20}(OH)_4]$	7
13) Synthetic F-rich phlogopite	Synthetic	$K^{+}_{2}\cdot[Mg_6(Si_6Al_2)O_{20}(F,OH)_4]$	2
14) Magnesium-rich vermiculite	Llano County, Texas, USA	$Mg^{2+}_{0.80}Ca^{2+}_{0.10}Na^{+}_{0.04}K^{+}_{0.01}\cdot[(Mg_{5.59}Al_{0.33}Fe_{0.04}Ti_{0.04})(Si_{5.69}Al_{2.31})O_{20}(OH)_4]$	8

Note: NA = Not Available.

* Reference for chemical composition: (1) Jepson and Rowse (1975), (2) Assumed stoichiometric composition, (3) Stucki et al. (1984), (4) This study, (5) Foster (1953), (6) Schultz (1969), (7) Callaway and McAtee (1985), (8) Weiss et al. (1990).

a low surface charge density) causes dehydration of the interlayer, and the cations become directly coordinated by the basal O atoms (Eirish and Tret'yakova, 1970; Leonard and Weed, 1967). The results of this study show that Cs occupies different sites depending on the hydration state and mineral composition and that the ^{133}Cs NMR chemical shift and rate of exchange between sites are also sensitive to these factors.

EXPERIMENTAL METHODS

The ^{133}Cs NMR spectra were obtained using the methods described in Weiss et al. (1990) at a frequency of 47.2 or 65.6 MHz. The Fourier-transform NMR spectrometers used are based on 8.45 and 11.7 T solenoid magnets (Oxford Instruments) and automated with Nicolet 1280 data systems, 293B pulse programmers, and Diablo model 40 disc systems for data storage. At 8.45 T, the spectra were measured using a probe with a stator with an outside diameter of 7 mm at temperatures from 80 to −100 ± 3 °C (Doty Scientific Instruments). Sapphire rotors were used at room temperature (~22 °C) and typically spun at 5–6.4 kHz in dry N_2 or air. At 11.7 T, the spectra were measured using a probe with a stator with an outside diameter of 5 mm at temperatures from room temperature (~22 °C) (Doty Scientific Instruments). Only vermiculite and artificially weathered synthetic F-rich phlogopite were examined at this field. The variable-temperature spectra were acquired using Macor rotors sealed with O rings, which typically spun in the range 2.8–4.3 kHz in dry N_2. The spinning angle was set by maximizing the spinning sidebands of the ^{2}D spectrum of solid CD_3COOAg (D_3 silver acetate).

The ^{133}Cs chemical shifts are reported in parts per million (ppm) relative to 0.1 M CsCl solution at ambient temperature (~22 °C). The ^{133}Cs chemical shift for aqueous Cs^+ is concentration dependent, and for a 0.1 M CsCl solution there is an ~1.66 ppm shift to less shielded (higher frequency) values from that at infinite dilution (Halliday et al., 1969; Haase et al., 1977). Typical $\pi/2$ pulse lengths for the reference 0.1 M CsCl solution were 12 μs. Typical pulse lengths used for the measured spectra were 1–2 μs.

A nonlinear least-squares χ-square minimization Levenberg-Marquardt routine (Press et al., 1986) was used to fit all NMR spectra with Lorentzian-Gaussian functions.

SAMPLES

The samples chosen for this study are monomineralic Fe-poor 2:1 phyllosilicates and the 1:1 sheet silicate kaolinite. Table 1 lists representative chemical analyses, localities, and structural formulae for these samples. The hectorite from Hector, San Bernadino County, California (CMS-SHCa-1), the montmorillonite from Gonzales County, Texas (STx-1), the montmorillonite from Crook County, Wyoming (SWy-1), the montmorillonite from Otay, California (SCa-1), the saponite from Ballarat, California (SapCa-1), the vermiculite from Llano County, Texas (VTx-1), and the kaolinite from Washington County, Georgia (KGa-1) were obtained from the Clay Minerals Society. The beidellite sample from the Black Jack Mine, Carson district, Owyhee County, Idaho, was obtained from the Smithsonian Museum (24679). The talc, pyrophyllite, and Amargosa montmorillonite (Amargosa desert, California) samples are from the Grim collection at the University of Illinois at Urbana-Champaign. The synthetic F-rich phlogopite sample is from the mineral collection of the Department of Geology, at the University of Illinois at Urbana-Champaign (synthesis conditions and chemical analyses described in Kohn and Hatch, 1955). The synthetic muscovite and illite/smectite samples were obtained from S. Altaner at the University of Illinois at Urbana-Champaign.

The vermiculite crystals used were hand-picked from the polymineralic bulk material, treated with 0.1 M HCl to remove residual calcite, and comminuted in a mill (Bel-Art Products) to <95 μm. The other coarse-grained phyllosilicates, muscovite and synthetic F-rich phlogopite, were also reduced to <95 μm. The beidellite sample was not size-fractioned because of the small amount available (~1 g). For the other samples, a size fraction <1 μm was obtained from the original material by centrifuging the dispersed sample. X-ray diffraction analysis using a Siemens D-500 powder diffractometer with Cu*Kα* radiation led to the determination that all the samples used are monomineralic.

NMR spectra were obtained after Cs-exchange in various hydration states and for some of the minerals slurried in CsCl solution.

The slurry samples were prepared by reacting 0.5 g of clay minerals with 50 mL of a CsCl solution of 0.01 M or 0.1 M overnight in a sealed bottle in a rocking water bath maintained at 60 °C. For NMR analysis, the slurry samples were prepared by carefully removing a portion of the clay mineral from the bottle and placing it in a rotor after minimizing the amount of solution in the rotor.

During variable-temperature NMR data measurement, constant temperature was maintained with a temperature controller that regulated a heater in the probe. The control thermocouple was Copper-Constantan and was mounted in the air line between the heater and the housing. For experiments above room temperature, the heater regulated the drive gas (N_2) temperature. For experiments below room temperature, the N_2 drive gas was passed through liquid N_2 and then heated to the desired temperature.

Dry powder samples were examined at 100% relative humidity (RH), and room humidity (~25% RH) and after drying at 100 °C and 450 °C. These drying conditions were chosen because analysis of TGA data using the methods of Weiss et al. (1990) show that the interlayers of these clay minerals are partially dehydrated at 100 °C and fully dehydrated at 450 °C, but that decomposition of the T-O-T framework does not occur below 450 °C.

The samples examined as dry powders were prepared by exchanging 0.5 g of the size fraction <1 μm of the pyrophyllite, montmorillonite, talc, hectorite, and saponite samples; 0.5 g of the <95-μm size fraction of muscovite, synthetic F-rich phlogopite, and vermiculite samples; and 0.5 g of the unfractionated beidellite sample in 50 mL of a CsCl solution at 0.1 M, decanting the solution, washing the clay minerals in 150 mL of deionized H_2O, drying them at 60 °C for 1 h, and then allowing them to rehydrate overnight in ambient air (~25% RH) at room temperature. NMR spectra were obtained at this point. These samples were then allowed to rehydrate overnight in a 100% RH deionized H_2O atmosphere at 60 °C. These samples were visibly wet and were rapidly loaded into NMR rotors. They did not dry out during NMR analysis. Partially dehydrated samples were prepared from the rehydrated samples by drying them at 100 °C for 1 h in air. To prevent rehydration during data collection, these samples were loaded in and analyzed using dry N_2. Dehydrated samples were prepared by drying for 1 h at 450 °C in air the sample that had been dried at 100 °C. These samples were also loaded at room temperature in dry N_2 and analyzed under a dry N_2 atmosphere to prevent rehydration. The differences between the NMR spectra of the sample dried at 100 °C and the sample dried at 450 °C indicates that they did not rehydrate during analysis.

An artificially weathered Fe-free synthetic F-rich phlogopite was prepared in a manner similar to that proposed by Scott and Reed (1962a, 1962b) by placing 1 g of sample in 15 mL of a solution of 1 N NaCl and 0.067 N $NaBPh_4$ (with 1 meq of EDTA added to prolong the activity of the $NaBPh_4$) at 60 °C in a water bath for 7 d. The solution was changed every 2 d to remove liberated K. Both the weathered synthetic F-rich phlogopite and a vermiculite sample were exchanged with 0.5 M CsCl at 60 °C in a water bath overnight, drawn through a millipore filter, rinsed with 20 mL of 0.5 M CsCl solution, dried at 100 °C in an oven, and allowed to rehydrate in ambient air before NMR analysis (~25% RH).

Unexchanged and Cs-exchanged hectorite samples <1-μm and vermiculite samples <95 μm were chemically analyzed using X-ray fluorescence for most major and minor elements, with the exception of Li (atomic absorption), F (wet chemical), and Cs (neutron activation), by X-Ray Assay Laboratories, Don Mills, Ontario, Canada.

The hectorite sample exchanged in a 0.1 M CsCl solution and washed in deionized water contained 7.62 wt% Cs_2O, indicating that ~97% of the total interlayer cations were Cs. A similarly treated vermiculite sample contained wt% 18.67 Cs_2O, indicating that ~70% of the total interlayer cations were Cs. A similarly treated Texas montmorillonite sample contained 10.77 wt% Cs_2O, indicating that ~98% of the total interlayer cations were Cs.

RESULTS

NMR spectra of slurry samples

The ^{133}Cs MAS NMR spectra of the 7 smectite samples (hectorite, saponite, montmorillonite, and beidellite) in a 0.1 M CsCl slurry measured at 25 °C all show at least 2 peaks, a narrow peak at ~−1.5–1.5 ppm, which Weiss et al. (1990) assign to Cs^+ in the small amount of solution in the slurries, and a broader peak with a more variable chemical shift, which Weiss et al. (1990) assign to Cs adsorbed on the clay minerals (Fig. 1). For the hectorite the latter peak is at the most shielded chemical shift of −16.5 ppm, the peaks for montmorillonite samples are in the range −6.1 to −8.9 ppm, the peak for saponite is at −5.1 ppm, and the two peaks for beidellite are at the most deshielded chemical shifts of 4.7 and 13.4 ppm. Spectra of the Amargosa, Otay, and Wyoming montmorillonite samples are similar to those of the Texas montmorillonite and are not shown. The results for hectorite were previously described by Weiss et al. (1990).

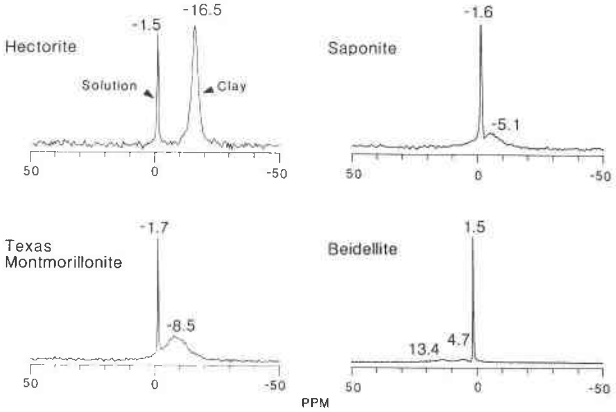

Fig. 1. The ^{133}Cs MAS NMR spectra of hectorite, montmorillonite, saponite, and beidellite in a 0.1 M CsCl slurry collected at 8.45 T and 25 °C.

The ^{133}Cs MAS NMR spectra of the unweathered synthetic F-rich phlogopite, kaolinite, vermiculite, and mixed-layer illite/smectite in CsCl slurries at 0.01 M measured at 25 °C also all have a solution peak at ~ −1.5 ppm and a peak for adsorbed Cs (Fig. 2). The synthetic F-rich phlogopite spectrum shows a very broad peak centered at ~10 ppm, the kaolinite spectrum shows a narrower peak at ~4 ppm, and the spectrum of the illite/smectite sample shows a very small peak at ~1.4 ppm. The vermiculite spectrum differs from the others in that it contains a broad peak centered at ~56 ppm and large spinning sidebands. Note that the scale for this spectrum is different from that for the others.

Spectra of talc, pyrophyllite, and a synthetic muscovite specimen in CsCl slurries at 0.1 M show only the peak for Cs in solution. These phases have little exchange capacity.

Variable-temperature MAS NMR spectra

Previously published work using ^{133}Cs variable-temperature (VT) MAS NMR methods in the temperature range of ~80 to −100 °C has provided useful information about the structural environments and exchange dynamics of large cations in zeolites (Ahn and Iton, 1989; Tokuhiro et al., 1989) and the clay mineral hectorite (Weiss et al., 1990). Spectra of hectorite in CsCl slurries at temperatures below ~ −60 °C indicate the presence of two Cs sites, which Weiss et al. (1990) interpret to be due to Cs in the Gouy (diffuse) and Stern (tightly bound) layers of the traditional model of cations adsorbed on clay minerals. Between −60 and −10 °C this hectorite yields three peaks, which Weiss et al. (1990) assign to those two sites plus a motionally averaged peak. Above ~ −10 °C only the motionally averaged peak (and the solution peak) is present. To extend and verify these results, we have obtained ^{133}Cs VT MAS NMR spectra of Cs-exchanged saponite and kaolinite.

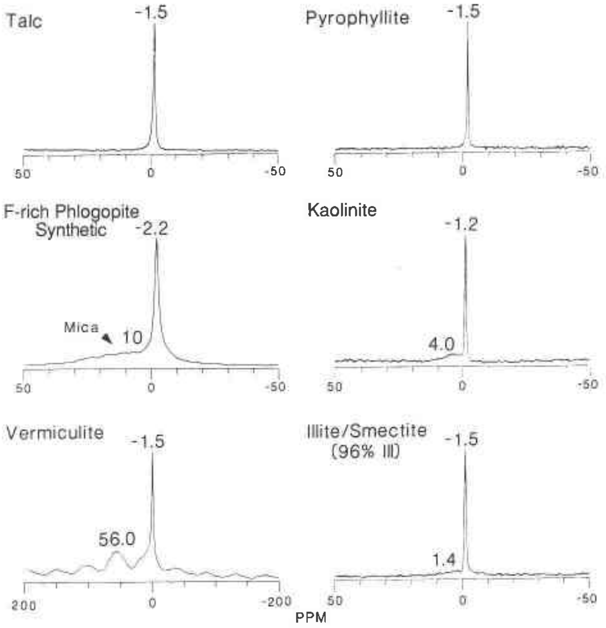

Fig. 2. The ^{133}Cs MAS NMR spectra of talc, pyrophyllite, synthetic F-rich phlogopite, kaolinite, vermiculite, and mixed-layered illite/smectite (with 96% illite layers) in a 0.1 M CsCl slurry collected at 8.45 T and 25 °C.

Saponite. The VT spectra of the saponite in a 0.1 M CsCl slurry obtained in the temperature range of 50–0 °C (Fig. 3) show two peaks: a broad one with a chemical shift that varies from −10 ppm at 50 °C to −6.8 ppm at 0 °C; and a narrower one that varies from −6.9 ppm at 50 °C to 0.1 ppm at 0 °C, which is readily attributable to Cs in the solution. At ~ −20 °C, there are three peaks: a broad peak at −6.0 ppm, a narrower peak at −30.4 ppm, and a narrow peak at 39.6 ppm. The 39.6 ppm peak is readily attributed to Cs in the residual solution (Weiss et

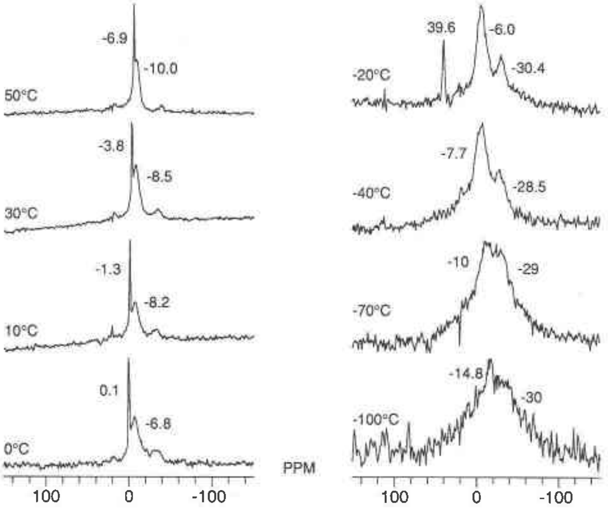

Fig. 3. The ^{133}Cs variable-temperature MAS NMR spectra of saponite in the temperature range of 50 to −100 °C.

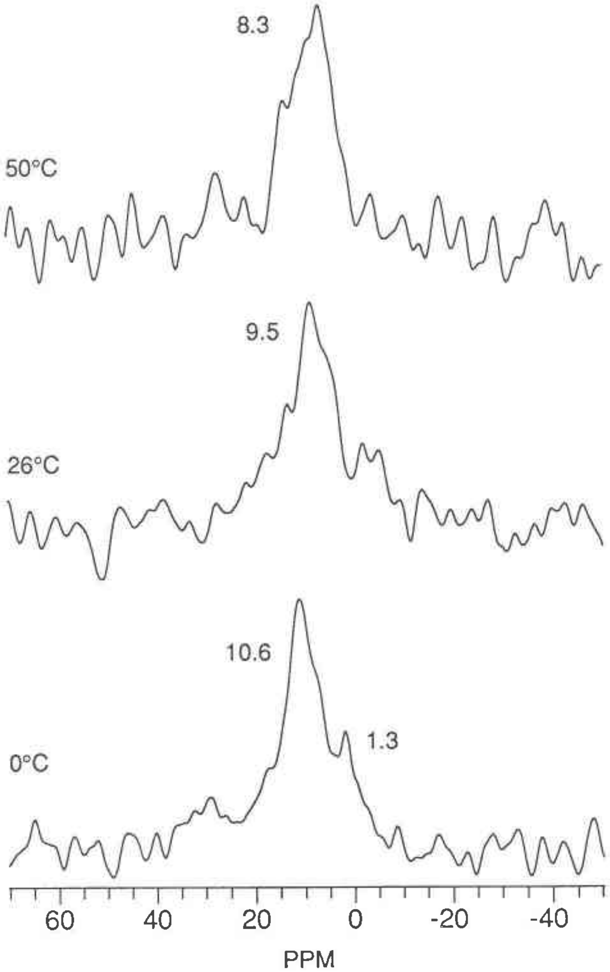

Fig. 4. The ^{133}Cs variable-temperature MAS NMR spectra of kaolinite in the temperature range of 50–0 °C.

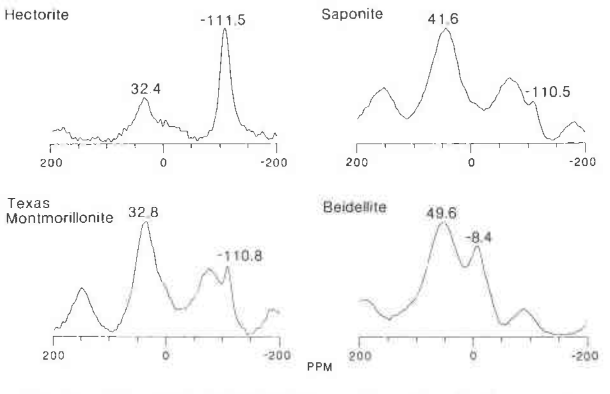

Fig. 5. The ^{133}Cs MAS NMR spectra of hectorite, montmorillonite, saponite, and beidellite measured at 8.45 T and 25 °C. The samples were prepared by exchange in a 0.1 M CsCl solution, washing in 150 ml of deionized H_2O, and drying at 450 °C.

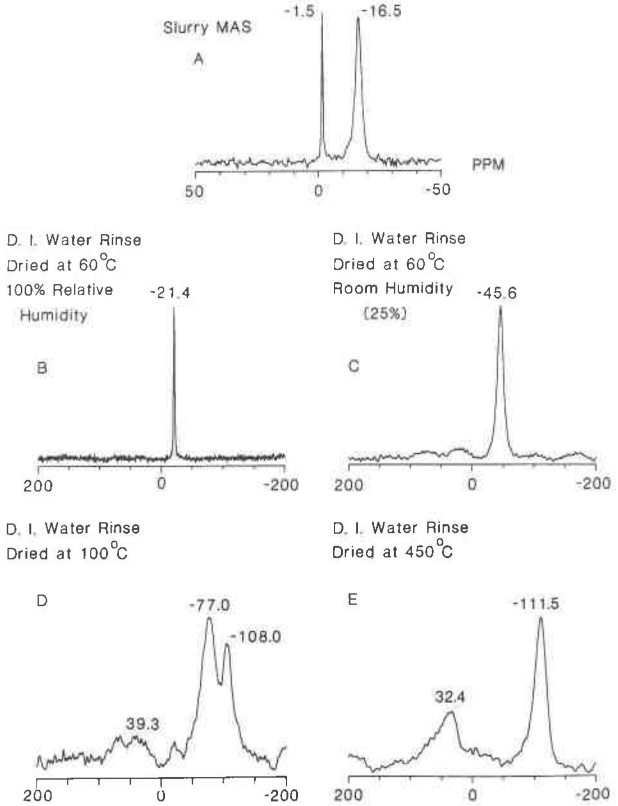

Fig. 6. The ^{133}Cs MAS NMR spectra of hectorite measured at 8.45 T and 25 °C as a function of hydration. The samples were prepared as indicated on each spectrum.

al., 1990). At temperatures below −40 °C, there is no solution peak, the peaks broaden, and the signal-to-noise ratio decreases. Nevertheless, it is clear that there are peak maxima in the vicinity of ∼−10 and −30 ppm. This behavior is very similar to that of the Cs-exchanged hectorite sample (Weiss et al., 1990), except that the resolution for the saponite sample is poorer.

Kaolinite. Variable-temperature ^{133}Cs MAS NMR spectra of kaolinite were obtained to understand the nature of adsorbed Cs on kaolinite in general, and to determine in particular if Cs in the Stern and Gouy layers is observable for minerals with lower layer charges, such as kaolinite. Furthermore, we felt this study might give useful information on the mechanism of the charge development for this mineral. Our ^{133}Cs variable-temperature MAS NMR spectra of kaolinite in a CsCl slurry at 0.01 M in the temperature range of 50–0 °C (Fig. 4) show two peaks: a broad one at 8–10 ppm and a narrow one at −1.5 ppm, attributed to Cs in the solution. At temperatures <∼−20 °C no signal was observed.

NMR spectra of samples dried at 450 °C

MAS NMR ^{133}Cs spectra of the 4 Cs-exchanged smectite minerals (hectorite, saponite, montmorillonite, and beidellite) dried at 450 °C, not rehydrated, and measured

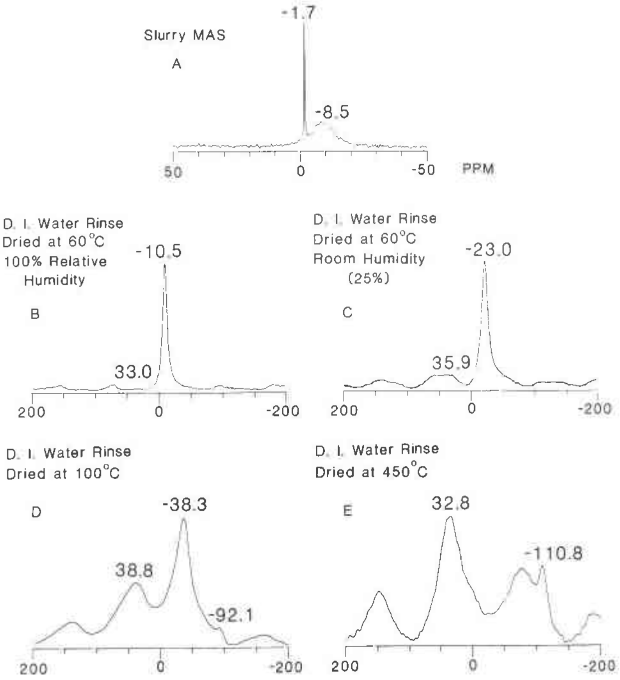

Fig. 7. The ^{133}Cs MAS NMR spectra of Texas montmorillonite measured at 8.45 T and 25 °C as a function of hydration. The samples were prepared as indicated on each spectrum.

at 25 °C (Fig. 5) all contain two true peaks and many spinning sidebands. One of these true peaks is broad, is in the chemical shift range ~30–50 ppm, and has associated spinning sidebands. The other peak is narrower and does not appear to have associated spinning sidebands. For the beidellite this narrower peak is at −8.4 ppm. For the hectorite, saponite, and montmorillonite specimens it is much more shielded, in the range −110.5 to −111.5 ppm.

EFFECT OF HYDRATION STATE ON STRUCTURAL ENVIRONMENT

To understand better the spectral differences between the slurry and the dehydrated samples dried at 450 °C, spectra of Cs-exchanged hectorite and Texas montmorillonite were obtained under various hydration states.

The hectorite sample in a CsCl solution at 0.01 M (Fig. 6A, also shown in Fig. 1) yields two peaks: a narrow one at ~−1.5 ppm due to Cs in the solution and a broader one at −16.5 ppm. The hectorite rehydrated at 100% RH yields a single narrow peak at −21.4 ppm (Fig. 6B). The hectorite at room humidity (~25% RH) yields two peaks: one at −45.6 ppm and a broader peak at 30 ppm that has associated sidebands (Fig. 6C). The hectorite dried at 100 °C yields three true peaks: one at 39.3 ppm, one at −77.0 ppm, and one at −108 ppm (Fig. 6D). The hectorite dried at 450 °C yields two peaks: one broader peak at ~32.4 ppm with associated spinning sidebands and a narrower one at −111.5 ppm (Fig. 6E).

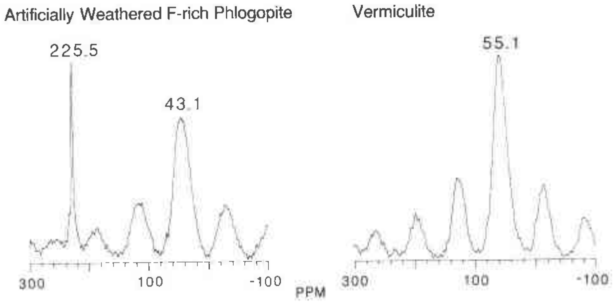

Fig. 8. The ^{133}Cs MAS NMR spectra of a weathered synthetic F-rich phlogopite and a Llano vermiculite measured at 11.7 T and 25 °C after the samples were exchanged in a 0.5 M CsCl solution and dried at 60 °C.

The spectra of the Cs-exchanged Texas montmorillonite vary in a generally similar way with changing hydration conditions (Fig. 7). This montmorillonite in a CsCl solution at 0.01 M yields two peaks: a narrow peak at −1.7 ppm due to Cs in solution and a broader peak at −8.5 ppm (Fig. 7A, also shown in Fig. 1). The sample rehydrated at 100% RH yields two peaks: one at −10.5 ppm with associated spinning sidebands and a very small broad peak at ~35 ppm (Fig. 7B). The room-humidity sample yields two peaks, both of which have sidebands; a relatively narrow one at −23.0 ppm and a broader one at 35.9 ppm (Fig. 7C). The sample dried at 100 °C yields three peaks: two broad ones at 38.8 and −38.3 ppm (with associated spinning sidebands) and one small narrow one at −92.1 ppm (Fig. 7D). The sample dried at 450 °C yields two true peaks: a broad one at 32.8 ppm with large sidebands and a narrower one at −110.8 ppm (Fig. 7E).

High-layer charge samples

MAS NMR ^{133}Cs spectra of vermiculite and an artificially weathered Fe-free synthetic F-rich phlogopite measured at room humidity, 25 °C, and 11.7 T (Fig. 8) were obtained to examine ^{133}Cs in interlayer sites in high layer-charge phases and to investigate the Cs-environment in weathered micas. These spectra are very similar to each other. The artificially weathered synthetic F-rich phlogopite yields one broad peak at 43.1 ppm with large sidebands and a very narrow peak at 225.5 ppm readily assigned to crystalline CsCl (Weiss et al., 1990); this sample was not dried after exchange. The vermiculite spectrum has one broad peak at 55.1 ppm, and similarly has large sidebands. As previously shown by Weiss et al. (1990), the ^{133}Cs MAS NMR spectra of this vermiculite do not change with varying hydration conditions from slurries that are totally hydrated to dehydration at 500 °C.

DISCUSSION

NMR spectra of slurry samples

Variable-temperature MAS NMR of saponite. The variable-temperature NMR data of the saponite slurries support the conclusions of Weiss et al. (1990) that the

TABLE 2. ^{133}Cs chemical shifts for phyllosilicates examined in this study

Name	^{133}Cs Chemical shift*				
	Slurry (ppm)	100% RH (ppm)	Room RH (ppm)	Dried at 100 °C (ppm)	Dried at 450 °C (ppm)
Dioctahedral					
1) Georgia kaolinite	4.0	0.70	11.0	−8.9/−20.7	NS
2) Pyrophyllite	NS	NS	NS	NS	NS
3) Wyoming montmorillonite	−8.9	−2.0	−21.5	NR	NR
4) Texas montmorillonite	−8.5	33.0/−10.5	35.9/−23.0	38.8/−38.3/−92.1	32.8/110.8
5) Amargosa montmorillonite	−6.7	−7.6	−21.6	42.1/−41.3/−99.4	42.6/−106.5
6) Otay montmorillonite	−6.1	−5.7	33.0/−18.2	26.2/−67.0/−96.8	33.0/−102.0
7) Black Jack beidellite	13.4/4.7	11.8/4.2	12.6/4.9	48.6/−13.4	49.6/−8.4
8) Illite/smectite (96% Ill)	1.4	0.8	−13.6/−39.4	−30.6/−75.6	BR
9) Synthetic muscovite	NS	NS	NS	NS	NS
Trioctahedral					
10) Talc	NS	NS	NS	NS	NS
11) Hectorite	−16.5	−21.4	30.0/−45.6	39.3/−77.0/−108.0	32.4/−111.5
12) Ballarat saponite	−5.1	−6.3	−24.2	34.1/−41.1/−94.2	41.6/−110.5
13) Synthetic F-rich phlogopite	10.0	25.2	5.9/−17.4	NS	NS
14) Llano vermiculite	56.0	57.2	56.6	55.0	56.6

Note: NS = No Signal; NR = Not Run; BR = Broad.
* Chemical shifts referenced from external 0.1 M CsCl solution.

^{133}Cs signal arises from Cs in the Stern and Gouy layers, and that this signal is motionally averaged at temperatures above ∼−20 °C. The narrow peak in the range −6.9–39.6 ppm in the saponite spectra is readily assigned to Cs in solution, because it has a similar behavior to other Cs solutions in this temperature range (Weiss et al., 1990).

The peak splitting and broadening for adsorbed Cs with decreasing temperature very closely parallels the behavior of the hectorite sample (Weiss et al., 1990). At temperatures above 10 °C the single clay mineral peak is due to motional averaging of Cs between the two sites. We note, however, the presence of spinning sidebands from the peak, which must reflect some unaveraged peak broadening, perhaps caused by second-order quadrupole or paramagnetic effects due to the presence of Fe in the sample. Such spinning sidebands do not occur for the hectorite. The peak splitting and broadening that begins at ∼0 °C and grows with decreasing temperature is due to a decrease in the rate of exchange of Cs between the sites represented by the two peaks near −30 and −10 ppm. The large breadth of these peaks is probably due to a combination of second-order quadrupole, inhomogeneous, and paramagnetic effects (see Weiss et al., 1990). These peaks are ∼10 ppm broader than those for hectorite discussed by Weiss et al. (1990), possibly reflecting paramagnetic broadening owing to the presence of ∼0.5 wt% Fe_2O_3 (Callaway and McAtee, 1985).

Weiss et al. (1990) provided detailed arguments for why the peak near −30 ppm is likely to arise from Cs in the Stern layer (tightly bound to the basal O atoms) and the less shielded peak is most likely due to Cs in the Gouy diffuse layer (not tightly bound to the basal O atoms). All these arguments are also appropriate for this sample, and we do not repeat them here. We do note, however, that the chemical shift of ∼−30 ppm for the peak assigned to Cs in the Stern layer of the saponite is essentially the same as for the hectorite. Because of the poorer resolution of the low-temperature spectra of the saponite, we have not simulated their behavior using NMR exchange theory (see Weiss et al., 1990, for a brief review).

As for the hectorite sample of Weiss et al. (1990), the presence of separate peaks for Cs in solution and Cs adsorbed on the clay mineral clearly indicates that Cs does not exchange between the solution and the sites represented by the other peak faster than ∼100 s^{-1}.

Room temperature NMR of slurry samples. The room temperature MAS NMR spectra of the montmorillonite and beidellite slurry samples are similar to those of the hectorite and saponite (Fig. 1; Table 2) in which motional averaging occurs at these temperatures. Although we do not have spectra at lower temperatures, the best interpretation of these spectra is that the narrow peak at ∼1.5 ppm is due to Cs in the solution and the broader peak or peaks to adsorbed Cs on the clay with the signal for Cs in the Stern and Gouy layers being motionally averaged. All of these samples are smectite and are expected to have their exchange sites in the interlayer with Stern and Gouy layers present if they are wet.

The two peaks for adsorbed Cs on the beidellite (Fig. 1) probably indicate that there is some heterogeneity in this sample that is on a physical scale large enough to eliminate exchange at rates >∼450 s^{-1} (as determined by the full width at half maximum (FWHM) of the narrower peak; see Harris, 1986 or Weiss et al., 1990). The ^{29}Si NMR data indicate that a similar beidellite from Unterrupsroth, West Germany, is heterogeneous and has components with different $^{[4]}$Al/($^{[4]}$Al + Si) ratios indicative of a montmorillonitic composition in the <1.4-μm size fraction [$^{[4]}$Al/($^{[4]}$Al + Si) = 0.084] and a beidellitic composition in the >3 μm fraction [$^{[4]}$Al/($^{[4]}$Al + Si) = 0.13, Nadeau et al., 1985]. Our results are consistent with this general idea. As for hectorite and saponite, the observation of separate peaks caused by Cs on the clay mineral and Cs in solution indicates that motional averaging of Cs between these two environments does not occur at a fast rate ($> \sim 60$ s^{-1}; see Weiss et al., 1990).

The spectrum of the illite/smectite sample (with 96% illite layers by XRD) in a slurry (Fig. 2) contains a large peak for Cs in solution but also a very small peak at ~1.4 ppm, which is probably due to adsorption of Cs in the interlayers of the smectite component. Again, this single peak is probably caused by motional averaging of Cs in the Stern and Gouy layers.

The vermiculite slurry sample is different from the others in that it contains a broad peak centered at ~56 ppm with associated large sidebands, in addition to the peak at -1.5 ppm owing to Cs in solution. Weiss et al. (1990) have interpreted the peak at 56 ppm to be due to dehydrated Cs in interlayer sites, probably with a coordination number of ~9. The Cs atoms in the vermiculite interlayer are expected to be dehydrated and tightly bound to the basal O atoms because of the large negative layer charge developed in the tetrahedral sheet (Walker and Cole, 1957). Note that this peak is unchanged for the slurry sample and the sample hydrated under ambient conditions (Figs. 2 and 8).

As expected, there is no observed Cs adsorption on talc and pyrophyllite (Fig. 2) or on synthetic muscovite (data not shown). The only signal in these spectra is the peak at -1.5 ppm owing to Cs in the solution. These samples are expected to have very small cation exchange capacities and no interlayer exchange sites.

In this context, the spectrum of the unweathered synthetic F-rich phlogopite slurry sample (Fig. 2) is unexpected, because although this mica should have no interlayer exchange sites, the spectrum contains a very broad peak centered at ~10 ppm in addition to the solution peak. For this sample the most likely site of exchange is at the edges of crystallites, where K could be removed and Cs adsorbed. Such sites could easily form on the frayed edges of the crystal fragments caused by comminution in the mill. From a structural (NMR) standpoint, this type of site would be less well defined than an interlayer site and thus yield a broader peak. Because this is an Fe-free synthetic sample the large peak breadth can not be due to heterogeneous broadening caused by Fe in the mica.

Kaolinite slurry samples. The spectra of the kaolinite slurry are interesting because they show evidence for Cs adsorption, but the VT behavior is substantially different from that of the smectite minerals hectorite and saponite. The kaolinite spectra contain only one peak, the signal disappears at low temperatures, and there is no observable peak splitting. The presence of the peak in the range between 10.6 and ~4 ppm (Figs. 2 and 4), however, clearly indicates some Cs adsorption.

The results of several previous studies bear on how these results should be interpreted. Experiments with Au sols indicate that at low pH the edges of the kaolinite crystallites have a positive charge and selectively adsorb negatively-charged Au particles (van Olphen, 1977). Therefore, cations should not be attracted to such sites. The basal surfaces of the kaolinite crystallites are often inferred to have a small negative layer charge because of a small amount of Al^{3+} substitution for Si^{4+} in the tetrahedral sheet (van Olphen, 1977; Everett, 1988). Unfortunately, ^{29}Si MAS NMR data for this sample does not provide evidence for any Al^{3+} substitution for Si^{4+} (Weiss, unpublished results; Everett, 1988).

There are three possible explanations for the observed Cs adsorption. There could be an aluminosilicate gel coating the kaolinite surface (Ferris and Jepson, 1975). The absence of a permanent exchange capacity for kaolinite at low pH, which Ferris and Jepson interpreted to indicate that there is no Al^{3+} substitution for Si^{4+} in the tetrahedral sheet of their particular kaolinite, supports this idea. There could also be single and double smectite layers on the {001} surfaces of some kaolinite crystallites. Such layers have been observed using high-resolution TEM for Georgia (U.S.A.) and St. Austell (Cornwall, UK) kaolinite (Eggelton et al., 1989). There could also be internal structural defects in the kaolinite crystallites that could have a local negative charge. These defects have also been observed in the Georgia and St. Austell kaolinite (Eggelton et al., 1989).

The VT behavior of the kaolinite slurry (Fig. 4) bears on this question. The spectra are substantially different from those of the hectorite and saponite slurries in that there is no peak splitting at low temperatures and the signal disappears below ~ −20 °C. Thus, there is not clear evidence of a signal from Cs in the Stern and Gouy layers. One possibility for these observations is that above ~0 °C, the peak is relatively narrow owing to motional averaging, but that at low temperatures any peak is so broad that no signal can be detected above the noise level. Such broadening could be due to unaveraged second-order quadrupole effects caused by very distorted sites, to heterogeneous broadening caused by a wide range of different adsorption sites, or to paramagnetic effects due to Fe impurities. These data seem to indicate that the adsorption sites are not in smectite layers on the surfaces of the kaolinite particles, because Cs in such sites should give lower temperature spectra similar to the smectite slurries. However, the signal-to-noise ratio is so low that broad peaks might not be detectible above the noise level. It is also possible that adsorption is occurring on a fine-grained aluminosilicate gel or on defect sites (Ferris and Jepson, 1975; van Olphen, 1977). For both of these cases, the exchange sites could be very asymmetrical (causing a large second-order quadrupole broadening) or have a wide range of local geometries (causing a large inhomogeneous broadening). Again, the peaks at lower temperatures could simply be too small and broad to be observed. Thus, present data are insufficient to distinguish among these possibilities. Variable-temperature experiments done with Cs-exchanged aluminosilicate gels or fine-grained aluminas (such as γ alumina) may help resolve these questions. It is clear, however, that NMR spectroscopy of exchanged cations has the potential to provide much useful information about cation exchange on low-charge materials.

NMR spectra of samples dried at 450 °C

The ^{133}Cs MAS NMR spectra of the smectite minerals (saponite, montmorillonite, and beidellite) dried at 450 °C are all similar to that of similarly treated hectorite described by Weiss et al. (1990). All contain two peaks, a broad one with a chemical shift in the range of ~30–50 ppm (with associated spinning sidebands) and a narrower one without major sidebands. The narrower peak for the montmorillonite samples, hectorite, and saponite is in the range from −110.5 to −111.5 ppm. For beidellite the narrower peak is at −8.4 ppm. For hectorite, Weiss et al. (1990) have argued that the narrow, shielded peak is due to Cs in high coordination (possibly 12-fold) with basal O atoms in the interlayer. Cs in such a site should be more shielded than that of the less coordinated (possibly ninefold) site inferred to yield the peak in the range of 30–50 ppm, because increasing coordination causes increased shielding for all cations so far studied (see Weiss et al., 1990, for references). Twelvefold and ninefold sites are readily formed between turbostratically stacked T-O-T clay mineral layers (Hecht and Geissler, 1970). The similarity of the spectra of the montmorillonite samples and the saponite to the hectorite spectra indicate a similar interpretation for them. The structures of these minerals are all very similar, and they have only slightly different chemical compositions (Table 1).

As for the spectra of the beidellite slurry, the results for the beidellite sample dried at 450 °C are difficult to interpret because of the possibility of a locally heterogeneous composition. The sample yields no peak at ~−110 ppm but instead a peak at −8.4 ppm, intermediate between the ranges for the broad deshielded peaks (30–60 ppm) and the narrow shielded peaks (−120 to −100 ppm). One possibility is that the two peaks are due to Cs in low-coordinated sites in two environments differing in the ratio $^{[4]}$Al/($^{[4]}$Al + Si) and that there are no highly coordinated 12-fold sites because of the large amount of structural distortion, as indicated by the large α value for beidellite ($\alpha = 14.5°$). Another possible interpretation is that the ^{133}Cs chemical shift is different from the others because this sample is still partially hydrated, although we consider this unlikely because TGA measurements for this beidellite indicate that the interlayer is fully dehydrated by 300 °C (Weir and Greene-Kelly, 1962; Schultz, 1969).

Effect of hydration state on structural environment

The great differences between the spectra of the slurry and samples dried at 450 °C (apparently fully dehydrated) clearly indicate large effects of clay hydration on the local Cs environments. Spectra of the Cs-exchanged hectorite and Texas montmorillonite were collected at 100% RH, ambient atmosphere (~25% RH), and dried at 100 °C to further investigate how these changes take place. The results (Figs. 6 and 7) are fully consistent with loss of hydration H_2O from the Cs and bonding of the Cs directly to the basal O atoms with decreasing hydration of the clay minerals. There is also clear evidence for some motional averaging in all samples that contain some interlayer H_2O.

At 100% RH, there appears to be sufficient H_2O in the interlayer to hydrate most of the Cs atoms, and the major peaks at −21.4 ppm for hectorite and −10.5 ppm for the montmorillonite appear to be motionally averaged, as illustrated by the spectrum of hectorite at 100% RH. For this sample, Weiss et al. (1990) have used VT ^{133}Cs MAS NMR methods to demonstrate that the narrow peak present at room temperature separates into two peaks at lower temperatures in a manner similar to the slurry spectra. The samples at 100% RH were visibly wet when measurements were made, and apparently there is sufficient H_2O present for the development of Gouy and Stern layers.

The narrower peaks in the room temperature spectra of the slurry, samples at 100% RH and samples at room humidity, thus reflect motional averaging of Cs between these two layers. The major peak in the spectrum of the montmorillonite sample at 100% RH is very similar to that of the hectorite but is broader and shows some sideband development, possibly due to some unaveraged second-order quadrupole broadening. That would indicate that the motion of the Cs is not totally symmetrical. However, it is more likely that it is caused by unaveraged paramagnetic broadening due to Fe. This sample contains 0.73 wt% Fe_2O_3.

The spectra of both samples at 100% RH also contain very small peaks near 30 ppm, indicating that under these conditions some of the interlayer Cs is dehydrated and in the less coordinated sites. At room humidity (~25% RH), more of the Cs atoms are not hydrated, as indicated by the increase in relative intensity of the peak at ~30–40 ppm for both the montmorillonite and hectorite. The appearance of this peak before the narrow peak at −110 ppm indicates that Cs preferentially enters these environments upon dehydration.

The narrow, shielded peak caused by more highly coordinated Cs first appears for the samples dried at 100 °C. Furthermore, as expected, the narrow, motionally averaged peaks for both the montmorillonite and hectorite spectra move to the right. Weiss et al. (1990) have used ^{133}Cs VT MAS NMR to show that this peak is due to motional averaging of Cs between the more and less highly coordinated sites, because with decreasing temperatures the intensities of the peaks for these sites increase and the motional averaging peak disappears. The shift of the position of the motional averaging peak to more shielded values occurs because its position is the average of the positions of the components weighted by the fraction of time that the average atom spends in each position (see Weiss et al., 1990). Because more of the Cs in the less coordinated sites stops participating in motional averaging at intermediate hydration states, the average Cs that does exchange spends more time in the more highly coordinated site, and the chemical shift of the motionally averaged peak becomes more shielded.

Along with the increased shielding and decreased intensity of the motionally averaged peak, the samples dried at 100 °C show a concomitant increase in the intensity of the components, the broad peak in the range of 30–40 ppm and the narrower peak in the range of −90 to −112 ppm. With further desiccation to 450 °C, motional averaging ceases, and only the narrow shielded and broad deshielded peaks with accompanying sidebands are observed. These sidebands are much larger for the Texas montmorillonite sample, which has a higher Fe content, indicating that they are probably due to paramagnetic broadening, which supports the idea that the sidebands in the slurry samples are also due to the effects of paramagnetic Fe.

A major contribution to the peak widths may be variations in site environments. The ^{133}Cs chemical shift is very sensitive to small changes in local environment compared to lower atomic number nuclei such as ^{23}Na, because Cs has many more electrons at greater distances that are sensitive to small environmental differences (Woessner, personal communication). Nutation experiments on hectorite (Weiss et al., 1990) show that the peaks for adsorbed Cs in the slurry, the sample at 100% RH, and the sample dried at 100 °C all have $\pi/2$ pulse widths of ~11 μs, similar to the value of 13 μs for the 0.1 M CsCl solution. This result indicates that most of the signal from all seven of the transitions is observed for those peaks. The quadrupole coupling constant (QCC) for these sites must be small, and therefore, the sites more symmetrical (Fukushima and Roeder, 1981). Similar experiments at 80 °C for the hectorite dried at 500 °C show that the $\pi/2$ pulse width for the peak at 30 ppm is only 5 μs, similar to the value of 3.25 μs expected if the signal from only the central transition is observed. Thus, this site has a larger QCC and must be less symmetrical.

High layer charge samples

The ^{133}Cs MAS NMR spectra of the vermiculite and artificially weathered Fe-free synthetic F-rich phlogopite measured at ambient conditions (Fig. 8) were obtained to examine ^{133}Cs in interlayer sites in high layer charge phases. These spectra are very similar, with one broad peak due to adsorbed Cs at 43.1 or 55.1 ppm with large associated sidebands. The spectrum of the weathered synthetic F-rich phlogopite also has a very narrow peak at 225.5 ppm due to crystalline CsCl (Weiss et al., 1990). The net layer charge of artificially weathered synthetic F-rich phlogopite should be ~−2 equiv/Si_8O_{20} and that of the vermiculite ~−1.85 equiv/Si_8O_{20}. In both cases the layer charge development is due primarily to tetrahedral Al^{3+} substitution for Si^{4+}. For the vermiculite, we have previously argued that there is only one Cs site (probably ninefold) because 12-fold sites cannot form (Weiss et al., 1990). These sites cannot form because the large amount of Al^{3+} substitution for Si^{4+} causes marked distortion as indicated by the large tetrahedron rotation angles (Table 3; see Weiss et al., 1987), which cause a decrease in size of the interlayer hexagonal void. Large cations such as Cs^+ (r = 1.96 Å in 12-fold coordination; Shannon and Prewitt, 1969), cannot fit into the relatively small cavity formed by two opposite hexagonal rings of O atoms in vermiculite (Barshad, 1948). Thus, it seems that such 12-fold, highly coordinated sites do not exist for Cs in vermiculite and other weathered micas. However, ninefold sites can form, because the Cs ion would have to fit into only one hexagonal ring of O atoms with only three O nearest neighbors from the other side of the interlayer. For vermiculite, the large peak width could be caused by heterogeneous line broadening due to a range of sites with different isotropic chemical shifts or quadrupole coupling constants or caused by paramagnetic effects due to the ~1710 ppm of Fe in the sample. However, the synthetic F-rich phlogopite sample is an Fe-free synthetic sample, and its peak broadening cannot be due to paramagnetic Fe. Most likely the relatively broad peaks for these samples are due to Cs in a range of slightly different environments, possibly caused by differing numbers of tetrahedral Al next-nearest neighbors.

^{133}Cs chemical shift correlations

It is well known that the ^{29}Si and ^{27}Al NMR chemical shifts of phyllosilicates are correlated to a number of compositional and structural parameters, including dioctahedral or trioctahedral substitutions, the ratio $^{[4]}$Al/($^{[4]}$Al + Si), total layer charge, and distortions of the hexagonal rings of basal O as measured by the tetrahedral rotation angle, α (Weiss et al., 1987; Woessner et al., 1989). Although the number of Cs-containing samples we have examined is limited because of the scarcity of low-Fe clay minerals and the lack of Cs-bearing micas, there appear to be similar correlations for the ^{133}Cs chemical shifts.

For the slurry samples that undergo motional averaging the best correlation of the ^{133}Cs chemical shift appears to be with the ratio $^{[4]}$Al/($^{[4]}$Al + Si), with the ^{133}Cs chemical shift becoming less shielded with an increasing ratio of $^{[4]}$Al to ($^{[4]}$Al + Si) (Fig. 9). This trend parallels the ^{27}Al and ^{29}Si trends. There appear to be separate trends for dioctahedral and trioctahedral phases. Hectorite has the most shielded chemical shift of −16 ppm and also has the smallest $^{[4]}$Al/($^{[4]}$Al + Si) ratio, ~0. Beidellite has the least shielded chemical shifts and a large $^{[4]}$Al/($^{[4]}$Al + Si) ratio, ~0.131. The beidellite sample has two peaks and is probably heterogeneous. If this is true, and the two peaks represent two different $^{[4]}$Al/($^{[4]}$Al + Si) ratios, the $^{[4]}$Al/($^{[4]}$Al + Si) ratios associated with each peak are greater and less than the bulk composition. In this case, the more shielded ^{133}Cs peak is associated with the lower $^{[4]}$Al/($^{[4]}$Al + Si) ratio and the less shielded ^{133}Cs peak with the higher $^{[4]}$Al/($^{[4]}$Al + Si) ratio.

We would expect a correlation of the ^{133}Cs chemical shift with $^{[4]}$Al/($^{[4]}$Al + Si), even though motional averaging occurs in the slurry samples, because the position of these peaks is the weighted average of the positions of

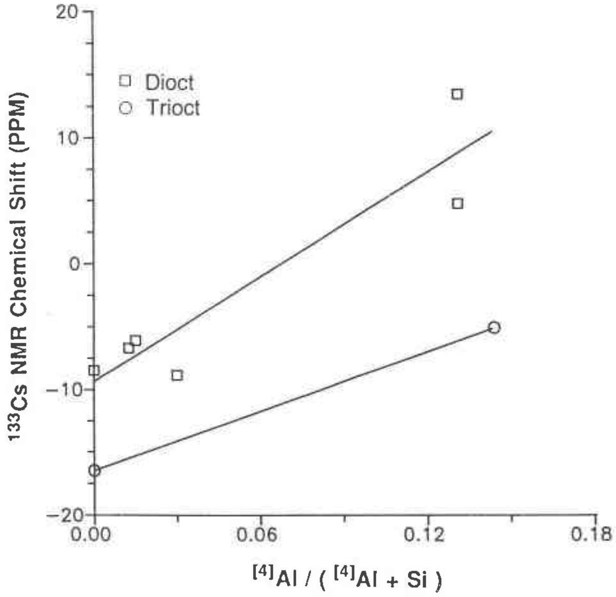

Fig. 9. Plot of ^{133}Cs MAS NMR chemical shifts vs. amount of $^{[4]}$Al substitution for phyllosilicates in 0.1 M CsCl slurries. The squares (□) represent dioctahedral phases and the circles (○) trioctahedral phases. The NMR spectra were measured at 8.45 T and at room temperature.

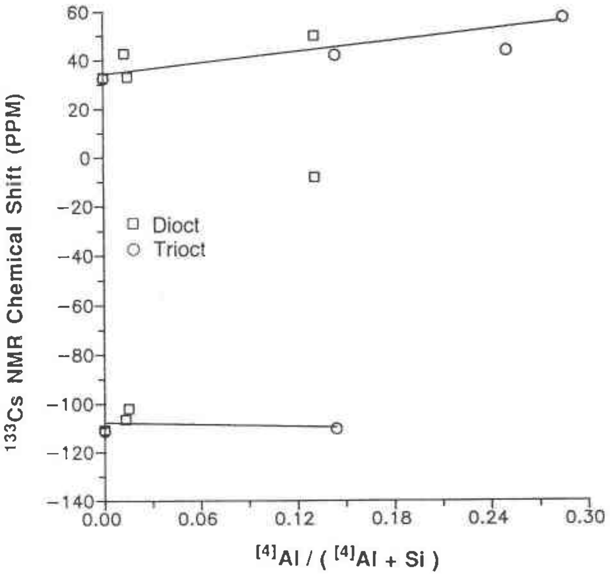

Fig. 10. Plot of ^{133}Cs MAS NMR chemical shifts vs. amount of $^{[4]}$Al substitution for phyllosilicates after exchange in 0.1 M CsCl, washed in deionized H_2O, and dried at 450 °C. The squares (□) represent dioctahedral phases and the circles (○) trioctahedral phases. The NMR spectra were measured at 8.45 T and at room temperature.

the peaks from the Stern and Gouy layers, and the number of Cs in each of these environments and their chemical shifts are likely to be related to the composition and structure of the samples.

The ^{133}Cs chemical shifts of the slurry samples also show general trends of decreased shielding with increasing tetrahedral distortion, as measured by the tetrahedral rotation angle, α, and with greater total layer charge, but the correlations are very poor (Tables 2 and 3). It is not clear if there are separate trends for the dioctahedral and trioctahedral minerals. The correlation with total layer charge is particularly poor. Samples with similar amounts of tetrahedral Al^{3+} but different total layer charge caused by substitutions of octahedral Mg^{2+} for Al^{3+} or Li^{+} for Mg^{2+} have chemical shifts similar to samples with no octahedral substitutions. For instance, the montmorillonite samples have very different total layer charges but very similar ^{133}Cs chemical shifts. Furthermore, the hec-

Table 3. Fraction of $^{[4]}$Al substitution, total layer charge, and calculated tetrahedral rotation angles (α) for phyllosilicates examined in this study

Sample	$\frac{^{[4]}\text{Al}}{^{[4]}\text{Al} + \text{Si}}$	Total layer charge	α_{calc} (°)	Reference*
Dioctahedral				
1) Georgia kaolinite	0.02	0.02	NA	1
2) Pyrophyllite	0.00	0.00	11.9	2
3) Wyoming montmorillonite	0.03	0.70	11.0	3
4) Texas montmorillonite	0.00	0.74	10.6	4
5) Amargosa montmorillonite	0.01	0.97	NA	5
6) Otay montmorillonite	0.01	1.25	10.6	6
7) Black Jack beidellite	0.13	1.10	14.5	7
8) Illite/smectite (96% Ill)	NA	NA	NA	NA
9) Synthetic muscovite	0.25	2	15.5	2
Trioctahedral				
10) Talc	0	0	0.0	2
11) Hectorite	0.00	0.72	6.1	8
12) Ballarat saponite	0.14	0.98	6.6	7
13) Synthetic F-rich phlogopite	0.25	2	9.7	2
14) Llano vermiculite	0.28	1.97	9.9	8

Note: NA = Not Available.

* Reference for chemical data: (1) Jepson and Rowse (1975), (2) Assumed stoichiometric composition, (3) Stucki et al. (1984), (4) This study, (5) Foster (1953), (6) Schultz (1969), (7) Callaway and McAtee (1985), (8) Weiss et al. (1990).

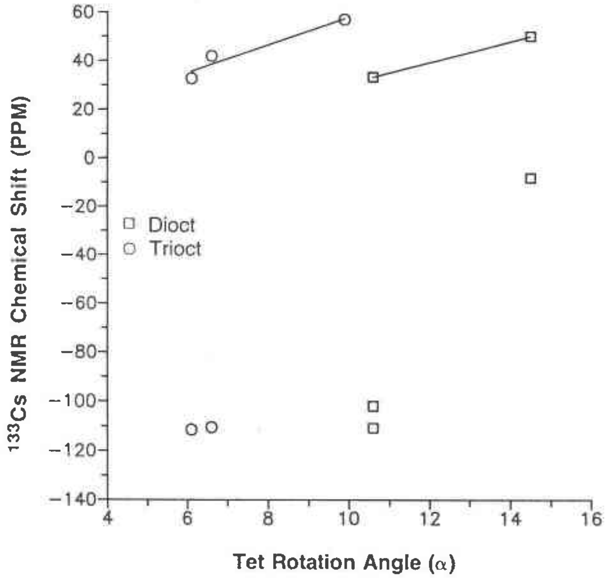

Fig. 11. Plot of ^{133}Cs MAS NMR chemical shifts vs. tetrahedral rotation angle (α) for phyllosilicates after exchange in 0.1 M CsCl, washed in deionized H_2O, and dried at 450 °C. The squares (□) represent dioctahedral phases and the circles (○) trioctahedral phases. The NMR spectra were collected at 8.45 T and at room temperature.

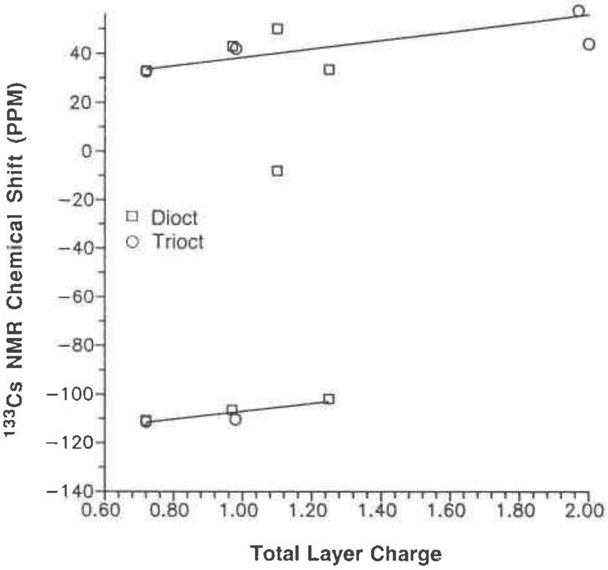

Fig. 12. Plot of ^{133}Cs MAS NMR chemical shifts vs. total layer charge for one unit cell for phyllosilicates after exchange in 0.1 M CsCl, washing in deionized H_2O, and drying at 450 °C. The squares (□) represent dioctahedral phases and the circles (○) trioctahedral phases. The NMR spectra were measured at 8.45 T and at room temperature.

torite and Wyoming and Texas montmorillonite have similar total layer charges, but hectorite has a chemical shift more shielded by ~10 ppm. This lack of correlation is not totally unexpected, because the parameters that should have the greatest effect on the ^{133}Cs chemical shift are those associated with the tetrahedral sheet, i.e., those that are closest to the Cs. In the fully hydrated samples, the Cs is presumably even further from the T-O-T layers because of the presence of the H_2O molecules.

For the samples dried at 450 °C there appear to be correlations of decreased ^{133}Cs shielding of the less coordinated site with an increasing ratio of $^{[4]}$Al/($^{[4]}$Al + Si) (Fig. 10), an increasing tetrahedral rotation angle, α (Fig. 11), and an increasing total layer charge (Fig. 12). As for the slurry samples, the best correlation is with $^{[4]}$Al/($^{[4]}$Al + Si), but there do not appear to be different trends for dioctahedral and trioctahedral phases. There may be separate trends for dioctahedral and trioctahedral phases with α values, but there are not enough data to verify this conclusion.

There does not seem to be a correlation of the ^{133}Cs chemical shift of the most shielded (most highly coordinated) site with any of the structural parameters except perhaps for the total layer charge. The chemical shifts of this site in the dioctahedral and trioctahedral phases are not separated. Because of the uncertainties with the beidellite sample, the ^{133}Cs chemical shifts of beidellite were not included in the correlations with $^{[4]}$Al/($^{[4]}$Al + Si) and total layer charge.

Changes in the Cs environment more profoundly affect the less coordinated (deshielded) site, as indicated by the greater slopes of the trends for the peaks in the range 30–60 ppm, compared to those in the range of −100 to −120 ppm. This is as expected, because the Cs-O bonds are shorter for the less coordinated site, and small changes in environment should have a greater effect on the electron distribution of this site.

CONCLUSIONS

Motional averaging of Cs on clay minerals as described for the mineral hectorite (Weiss et al., 1990) is confirmed for other smectites such as saponite and montmorillonite. At temperatures below −20 °C, two distinct peaks ascribed to Cs in Stern and Gouy layers are observed for saponite. The ^{133}Cs MAS NMR spectra of montmorillonite and hectorite as a function of hydration indicate that motional averaging of Cs between the Stern and Gouy layers occurs in samples at 100% RH, but that at room relative humidity (~25%) and after drying at 100 °C, some motional averaging occurs between Cs in sites coordinated by the basal O atoms of the adjacent T-O-T layers. These sites must have different coordinations, probably nine and 12. After complete dehydration at 450 °C there is no motional averaging, and there are only two peaks that are ascribed to Cs in sites with large coordination numbers (probably 12-fold) and sites with smaller coordination numbers (probably ninefold).

For the slurry samples, there are general trends of deshielding at Cs with increased Al^{3+} substitution for Si^{4+}, total layer charge, and tetrahedral rotation that parallel similar trends observed for ^{29}Si (Weiss et al., 1987) and ^{27}Al (Woessner, 1989). These ^{133}Cs correlations are much more scattered than those for ^{29}Si and ^{27}Al.

For the samples dried at 450 °C there appear to be correlations of decreasing ^{133}Cs shielding for the broad deshielded peak with an increasing ratio of $^{[4]}$Al/($^{[4]}$Al + Si), an increasing tetrahedral rotation angle, α, and an increasing total layer charge, with the correlation with the ratio of $^{[4]}$Al/($^{[4]}$Al + Si) being the best. This substitution should have the greatest effect on the ^{133}Cs chemical shift, because of the proximity of the tetrahedral sheet to the interlayer. The chemical shifts of the narrow, shielded peak do not change with any of these parameters, except perhaps for total layer charge.

Variable-temperature MAS NMR reveals the presence of adsorbed Cs on kaolinite at temperatures ≥ 0 °C for the clay in a 0.01 M CsCl slurry, but this adsorption is probably at defect sites or on a small amount of a second phase.

ACKNOWLEDGMENTS

This work was supported by a grant from NSF EAR 87-06929. Computing facilities were provided by the University of Illinois Laboratory for Supercomputing in Hydrogeology. We thank B. Phillips for use of the computer program NMRFIT to fit NMR spectra, D. Woessner and B. Reynolds for their helpful reviews, and J. Daly for help in revising the manuscript. The beidellite sample from the Black Jack Mine, Carson District, Owyhee County, Idaho, no. 24679, was kindly provided by the Smithsonian Institution.

REFERENCES CITED

Ahn, M.-K., and Iton, L.E. (1989) Cesium-133 NMR studies of cation siting and site exchange dynamics in hydrated CsNa-A zeolite. Journal of Physical Chemistry, 93, 4924–4927.

Bank, S., Bank, J.F., and Ellis, P.D. (1989) Solid-state ^{113}Cd nuclear magnetic resonance study of exchanged montmorillonites. Journal of Physical Chemistry, 93, 4847–4855.

Barshad, I. (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves, and water content. American Mineralogist, 33, 655–678.

Bolt, G.E., Sumner, M.E., and Kamphorst, A. (1963) A study of the equilibria between three categories of potassium in an illitic soil. Soil Science Society of America Proceedings, 27, 294–299.

Callaway, W.S., III, and McAtee, J.L., Jr. (1985) Magnetic susceptibilities of representative smectites. American Mineralogist, 70, 996–1003.

Chu, P-J., Gerstein, B.C., Nunan, J., and Klier, K. (1987) A study by solid-state NMR of ^{133}Cs and ^{1}H of a hydrated and dehydrated cesium mordenite. Journal of Physical Chemistry, 91, 3588–3592.

Eggelton, R.A., Taylor, G., and Walker, P.H. (1989) The cation exchange capacity of kaolinite. International Clay Conference, Strasbourg, 127.

Eirish, M.V., and Tret'yakova, L.I. (1970) The role of sorptive layers in the formation and change of the crystal structure of montmorillonite. Clay Minerals, 8, 255–266.

Everett, D.H. (1988) Basic principles of colloid science, 243 p. The Royal Society of Chemistry, London.

Ferris, A.P., and Jepson, W.B. (1975) The exchange capacities of kaolinite and the preparation of homoionic clays. Journal of Colloid and Interface Science, 51, 245–259.

Foster, M.D. (1953) Geochemical studies of clay minerals: II. Relation between ionic substitution and swelling in montmorillonite. American Mineralogist, 38, 994–1006.

Fukushima, E., and Roeder S.B.W. (1981) Experimental pulse NMR: A nuts and bolts approach, 539 p. Addison-Wesley Publishing Co., Reading, Massachusetts.

Haase, A.R., Kerber, M.A., Kessler, D., Kronenbitter, J., Krüger, H., Lutz, O., Müller, M., and Nolle, A. (1977) Nuclear Magnetic Shielding and quadrupole coupling of ^{133}Cs in cesium salt powders. Zeitschrift für Naturforschungen, 32a, 952–956.

Halliday, J.D., Richards, R.E., and Sharp, R.R. (1969) Chemical shifts in nuclear resonances of caesium ions in solution. Proceedings of the Royal Society of London, A 313, 45–69.

Harris, R.K. (1986) Nuclear magnetic resonance spectroscopy, 260 p. Longman, Essex, England.

Hecht, A.-M., and Geissler, E. (1970) Nuclear magnetic resonance and relaxation of adsorbed water in synthetic fluor montmorillonite. Journal of Colloid and Interface Science, 34, 32–35.

Jepson, W.B., and Rowse, J.B. (1975) The composition of kaolinite—An electron microscope microprobe study. Clays and Clay Minerals, 23, 310–317.

Kohn, J.A., and Hatch, R.A. (1955) Synthetic mica investigations, VI: X-ray and optical data on synthetic fluor-phlogopite. American Mineralogist, 40, 10–21.

Leonard, R.A., and Weed, S.B. (1967) Influence of exchange ions on the b-dimension of dioctahedral vermiculite. Clays and Clay Minerals, 15, 149–161.

Nadeau, P.H., Farmer, V.C., McHardy, W.J., and Bain, D.C. (1985) Compositional variations in beidellite. American Mineralogist, 70, 1004–1010.

Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T. (1986) Numerical recipes: The art of scientific computing, 818 p. Cambridge University Press, Cambridge, Massachusetts.

Schultz, L.G. (1969) Lithium and potassium absorption: Dehydroxylation and structural water content of aluminous smectites. Clays and Clay Minerals, 17, 115–149.

Scott, A.D., and Reed, M.G. (1962a) Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron: II. Biotite. Soil Science Society of America Proceedings, 26, 41–45.

——— (1962b) Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron: III. Illite. Soil Science Society of America Proceedings, 26, 45–48.

Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B25, 925–946.

Stucki, J.W., Golden, D.C., and Roth, C.B. (1984) Effects of reduction and reoxidation of structural iron on the surface charge dissolution of dioctahedral smectites. Clays and Clay Minerals, 32, 350–356.

Tokuhiro, T., Mattingly, M., Iton, L.E., and Ahn, M.-K. (1989) Variable-temperature magic-angle-spinning technique for studies of mobile species in solid state NMR. Journal of Physical Chemistry, 93, 5584–5587.

van Olphen, H. (1977) An introduction to clay colloid chemistry (2nd edition), 318 p. Wiley-Interscience, New York.

Walker, G.F., and Cole, W.F. (1957) Vermiculite minerals. In R.C. Mackenzie, Ed., The differential thermal investigation of clays, p. 191–206. Mineralogical Society, London.

Weir, A.H., and Greene-Kelly, R. (1962) Beidellite. American Mineralogist, 47, 137–146.

Weiss, C.A., Jr., Altaner, S.P., and Kirkpatrick, R.J. (1987) High resolution ^{29}Si NMR spectroscopy of 2:1 layer silicates: Correlations among chemical shift, structural distortions, and chemical variations. American Mineralogist, 72, 935–942.

Weiss, C.A., Jr., Kirkpatrick, R.J., and Altaner, S.P. (1990) The structural environments of cations adsorbed on clays: ^{133}Cs variable-temperature MAS NMR spectroscopic study of hectorite. Geochimica et Cosmochimica Acta, 54, 1655–1669.

Woessner, D.E. (1989) Characterization of clay minerals by ^{27}Al nuclear magnetic resonance spectroscopy. American Mineralogist, 74, 203–215.

MANUSCRIPT RECEIVED NOVEMBER 27, 1989
MANUSCRIPT ACCEPTED JULY 12, 1990