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^{133}Cs NMR and XPS investigation of cesium adsorbed on clay minerals and related phases

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Abstract— ^{133}Cs MAS NMR and Cs XPS were used to study the adsorption of Cs on kaolinite, montmorillonite, corundum, and gibbsite from 0.1 N and 0.01 N CsCl solutions. XPS spectra for all samples except gibbsite contain strong signals associated with Cs $3d_{3/2}$ and $3d_{5/2}$ photopeaks. This result indicates that minerals without exchangeable cation sites have a tendency to sorb Cs on surfaces and along grain boundaries, although less than 1 mol% Cs is observed on these surfaces. Multiple surface or interlayer sites for Cs cannot be resolved from the individual Cs XPS peaks. The ^{133}Cs NMR data, combined with TEM/XRD data for kaolinite show the following: (1) For montmorillonite, most of the Cs is adsorbed in the interlayers and at room humidity is motionally averaged among two or more sites at room temperature. (2) The spectra for kaolinite are similar to those of montmorillonite, and the tightly bonded Cs in our sample appears to be in expandable interlayers which exist as mixed layers with kaolinite and not as discrete smectite. (3) The Cs environments in both montmorillonite and kaolinite are sensitive to humidity. (4) For kaolinite the ^{133}Cs chemical shift changes at low temperature and 100% humidity, indicating that the interlayer charge of its expandable layers is very small. (5) No ^{133}Cs NMR signal could be detected for gibbsite or corundum. ^{133}Cs NMR may be a useful probe of the presence and characteristics of expandable layers in kaolinite.

1. INTRODUCTION

Clay minerals are abundant in many near-surface geological environments and are highly sorptive due to their small particle sizes, large surface areas, and many chemically active surface defect sites. Recognition of the significance of these minerals has recently increased because of the need for environmental remediation. For instance, the reaction of metal cations with mineral surfaces in and near hazardous chemical and radioactive waste sites often controls the fates of these species. ^{137}Cs is an important component of nuclear waste and its storage and migration in natural environments have been studied by many investigators (Alberts and Wahlgren, 1981; Chittenden, 1983; Beasley and Jennings, 1984; Maiti et al., 1989; Santschi et al., 1990). In this respect, the reaction of Cs with clay minerals is very important (Tamura and Jacobs, 1960).

Clay particles can carry a net negative charge compensated by the positive charge of adsorbed cations. The origin of this charge on the clay particles can be isomorphic substitution, lattice imperfections, broken bonds at the edges of the particles, and exposed structural hydroxyls (Swartzen-Allen and Matijević, 1974). The principal source of the permanent negative charge on 2:1 clay particles is isomorphic substitution (van Olphen, 1977). For example, montmorillonite has a net negative charge due to the substitution of Mg^{+2} for Al^{+3} in the Al octahedral sheet. For 1:1 clay minerals such as kaolinite, broken bonds at crystallite edges are thought to be the largest sources. The surface charge due to crystallite edges is controlled by protonation and deprotonation of surface hydroxyl groups and, therefore, depends on the solution pH. The basal surfaces of some kaolinites may carry a constant charge due to isomorphic Al^{+3} for Si^{+4} substitution (Swartzen-Allen and Matijević, 1974). There has been a great deal of research on the origin of the permanent negative charge of kaolinite (Ferris and Jepson, 1975; Bolland et al., 1976; van Olphen, 1977; Herrington et al., 1992; Zhou and Gunter, 1992), but the conclusions remain controversial.

Recent studies have attempted to examine the kinetics of the sorption behavior of Cs on illite (e.g., Comans et al., 1991; Comans and Hockley, 1992). These studies provide a detailed evaluation of the kinetic process of Cs adsorption by clay minerals from solution; they lack an atomic foundation for testing the sorption mechanisms occurring at mineral surfaces. An atomistic and fundamental understanding of the critical sorption mechanisms can be obtained by the use of surface-sensitive spectroscopic techniques, which provide direct information about the possible cation adsorption sites. ESR (electron spin resonance) spectroscopy (Monsef-Mirzai and McWhinnie, 1982), XAS (X-ray absorption spectroscopy) (O'Day et al., 1994), XPS (X-ray photoelectron spectroscopy) (Koppelman and Dillard, 1977; Koppelman et al., 1980; Dillard et al., 1983), and NMR (nuclear magnetic resonance) (Bank et al., 1989; Luca et al., 1989; Laperche et al., 1990; Weiss et al., 1990a,b; Tinet et al., 1991; Kloprogge et al., 1992; Lambert et al., 1992) have been used for the study of adsorption of cations on kaolinite and other clay minerals.

Surface analysis by XPS, formerly known as electron spectroscopy for chemical analysis (ESCA), is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy spectrum of the electrons emitted. The usefulness of the technique for the present study is its ability to provide compositional data for the volumes of the sample within approximately 30–90 Å of the surface based on the

attenuation length of electrons in the materials (Seah and Dench, 1979; Hochella, 1988). Details of the technique and the general application of XPS to geological materials are reviewed by Hochella (1988). There have been no previous studies of Cs sorption onto minerals using this analytical technique, however, Wagner et al. (1986) provide a summary of the XPS binding energy shifts for a variety of Cs inorganic compounds.

With the advent of high-field solenoid magnets, solid state NMR has become a useful tool to investigate cations in clays and zeolites. ^{1}H and ^{2}D NMR have been used to investigate clay-water systems and the structure of water in clay interlayers (Woessner and Snowden, 1969; Hecht and Geissler, 1970, 1973; Hougardy et al., 1976; Woessner, 1977, 1980; Kadi-Hanifi, 1980; Sposito and Prost, 1982; Fripiat and Letellier, 1984; Grandjean and Laszlo, 1989a,b; Delville et al., 1991).

^{133}Cs (I = 7/2) has also proven useful in characterizing the structural sites occupied by Cs adsorbed on clay minerals (Weiss et al., 1990a,b). It has 100% natural abundance, a large NMR chemical shift dispersion, and a small electric quadrupole moment. Thus ^{133}Cs NMR spectra have narrower lines for solids than those of other alkali elements. Cesium-exchanged hectorite and other clay minerals in slurries yield two peaks, one a motionally averaged peak due to adsorbed Cs and the other one due to Cs in solution. At low temperatures the motionally averaged peak for adsorbed Cs separates into two peaks representing two different Cs environments in the clay interlayers. Weiss et al. (1990a) assigned one of the peaks to Cs relatively tightly bonded to the basal oxygens and the other to Cs less tightly bonded to the basal oxygens.

^{7}Li, ^{23}Na, ^{39}K, ^{111}Cd, and ^{113}Cd have also been used to study the cation behavior in clay interlayers (Bank et al., 1989; Luca et al., 1989; Laperche et al., 1990; Tinet et al., 1991; Kloprogge et al., 1992; Lambert et al., 1992). The chemical shifts and other characteristics of their NMR spectra are affected by hydration state, pH, temperature, and reacted materials. Lambert et al. (1992) could discriminate between mobile and fixed forms of K^+ in a series of montmorillonites submitted to increasing numbers of wetting and drying cycles.

^{133}Cs NMR has also proven useful for probing cation sites in zeolites and can provide information about the cation exchange rates among different sites (Chu et al., 1987; Ahn and Iton, 1989, 1991; Tokuhiro et al., 1989). Like smectite, mordenite, and zeolite A yield one motionally averaged ^{133}Cs peak at room temperature and two or three peaks in the dehydrated state or at low temperatures.

There has been no comprehensive NMR study of cations adsorbed on kaolinite. Weiss et al. (1990b) showed a few spectra, but the resolution was poor and they could not assign the peaks. In this paper we present ^{133}Cs MAS NMR and XPS data for Cs adsorbed on kaolinite, montmorillonite, corundum, and gibbsite and discuss the results and implications.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

The materials for this study were chosen to provide a series of mineral structures with increasing complexity: corundum (Al octahedra), gibbsite (layer structure of hydrated Al octahedra), kaolinite (hydrated layer structure of alternating Al octahedra and Si tetrahedra), and montmorillonite (2:1 layer clay composed of an Al-deficient octahedral sheet between two Si tetrahedral sheets with an interlayer that contains cations and water molecules). The corundum sample is synthetic and was obtained from Fisher Scientific. The gibbsite is from Ouro Preto, Brazil. The kaolinite is from Washington County, Georgia. The montmorillonite is from Apache County, Arizona (Cheto variety). The latter two samples (KGa-1 and SAz-1) are from the standard collection of The Clay Minerals Society.

All minerals were processed by ultrasonically washing the material in distilled water, followed by a methanol wash, and a distilled water wash. The corundum and gibbsite were hand ground with an agate mortar and pestle and then sieved. The 325–400 sieve size fraction was used. The clay minerals were not subjected to any grinding.

Cesium-adsorption experiments were performed by placing approximately 1.0 g of the mineral samples in polyethylene reaction vessels with 100 ml 0.1 N or 0.01 N CsCl solution for 5 days. Experiments were done at 25°C and 50°C for both concentrations. The high concentrations were used to ensure a significant amount of Cs adsorption. No additional background electrolyte or pH buffer was used. The reaction vessels were agitated using a shaking tray in a constant temperature water bath throughout the duration of the experiment to maintain a significant portion of the mineral powder in suspension. Temperatures were controlled to ±0.1°C. The pH remained at approximately 6 throughout the experiments.

Additional adsorption experiments were required for the kaolinite samples due to the inability of these fine powders to remain in the sample holder during the XPS analysis under high vacuum. Monomineralic slabs of the same kaolinite (KGa-1) were obtained from The Clay Minerals Society. Four samples were cut into approximately 5 mm × 5 mm × 10 mm parallelepipeds and Cs-exchanged under identical experimental conditions as the powders.

Treated samples were isolated from the CsCl solutions by first decanting the solution and then pouring the remaining solution onto a flat filter paper positioned on a Buchner funnel with an attached vacuum pump. Approximately 2–3 ml of the appropriate stock solution were used to suspend any remaining powder from the reaction vessel and then poured onto the filter paper. The filter papers and powders were allowed to air dry. Equal splits of each sample were selected for XPS and NMR analyses. The kaolinite slabs were simply removed from the reaction vessel using tweezers and allowed to air dry. These slabs were examined by only XPS.

2.2. XPS

The XPS analyses were performed using a Perkin Elmer PHI 5400 instrument using Mg K_α X-rays and a take-off angle of 45°. Sample powders were pressed into an indium holder and placed in the sample chamber at a vacuum of approximately 2×10^{-9} torr. Due to the previously noted problem with the kaolinite powder samples, the kaolinite slabs were used and were simply positioned in a sample holder with set screws. XPS spectra were obtained by multiple scans at 1 eV per step for the survey scans and 0.1 eV per step for the detailed scans; 20 msec/step count time was used for obtaining appropriate photoelectron counts in both cases. Adventitious carbon (C 1s) provides an internal standard for monitoring and correcting the energy shifts associated with sample charging, a significant problem associated with analysis of insulators such as these mineral phases (Wagner et al., 1986). Before each spectral scan an argon ion beam was used to sputter sample material from the surface and provide a fresh surface for analysis. Carbon and other surface contaminants can be removed in this fashion, while still monitoring the distribution of Cs in and on the mineral.

2.3. NMR Spectroscopy

The ^{133}Cs NMR spectra were obtained at 65.5 MHz using a home-built spectrometer that consists of an 11.7-T superconducting magnet (Oxford Instruments) and a Nicolet model 1280 computer and pulse programmer. At room temperature, the samples were spun at 8–9 kHz in a silicon nitride rotor using a 5 mm probe manufactured by

Doty Scientific (Columbia, South Carolina). Spectra were collected at room humidity for all the samples. Spectra were also collected at 100% R. H. for montmorillonite exchanged at 0.1 N, 50°C and for the kaolinite exchanged at 0.1 N, 25°C. A 1 μs sampling pulse was used for the room temperature data. The $\pi/2$ values of the solid samples are essentially identical to those of 0.1 N CsCl solution (11–13 μs) as was previously reported by Weiss et al. (1990a) for their Cs-exchanged hectorite. This result indicates that the effective ^{133}Cs quadrupole coupling constant is very small (Samoson and Lippmaa, 1983). The kaolinite samples required up to 20,000 scans because of their small Cs content, but for montmorillonite samples several hundred scans were enough for a good signal to noise ratio. The ^{133}Cs chemical shift are reported in parts per million (ppm) relative to an external 0.1 M CsCl solution at room temperature.

For the low temperature experiments, the same spectrometer was used, but the sample was spun in sapphire rotors at 4–5 kHz in dry N_2 with a different 5 mm Doty Scientific MAS probe. The montmorillonite sample reacted at 0.1 N, 50°C and the kaolinite sample reacted at 0.1 N, 25°C were chosen for the low temperature experiments at room humidity, and the same samples that were examined at room temperature and 100% R. H. were used for the low temperature analysis at 100% R. H. Temperatures as low as −100°C were maintained by cooling the spinning gas (Weiss et al., 1990a,b). Four μs pulses were used for the kaolinite samples at low temperature in order to obtain a satisfactory signal-to-noise ratio in a limited time. There is no noticeable difference in peak shape in spectra collected at room temperature with 4 μs and 1 μs pulses.

Two kaolinite samples (0.1 N, 25°C and 0.01 M, 50°C) were heated at 450°C for an hour in air and NMR spectra were collected immediately to avoid rehydration. The kaolinite structure is not stable above 500°C (Brown and Brindley, 1980).

2.4. Other Analysis Methods

Atomic absorption analysis (Perkin Elmer PC5100) was used to determine the bulk Cs content of the kaolinite samples. The samples were initially dissolved in 1.0 M HF solutions, and subsequently a matrix blank, two calibrated standards, and dilution with a 0.5 M Na solution (to enhance the Cs signal) were used for analysis. The atomic absorption instrument was calibrated using a linear Cs concentration vs. current curve with the origin through zero. The samples were first analyzed and concentrations were determined using the original calibration curve, and the instrument was then completely recalibrated and the samples reanalyzed using a new calibration curve. Results for the duplicate analyses were similar.

A detailed transmission electron microscope (TEM, Philips CM30 operating at 300 kV) examination of the standard kaolinite and one sample of the reacted kaolinite (0.1 N, 50°C) was undertaken to determine the microstructural characteristics of the mineral before and after treatment with the CsCl solution. Both samples were dispersed dry on TEM support grids for this examination.

XRD (X-ray diffraction) was used to check for any new phases or alteration of the kaolinite samples due to Cs exchange. The X-ray diffractometer has a Dapple Systems goniometer and computer system; the X-ray generator is a Philips XRG 3100 system.

Due to the significant results encountered in our XPS and NMR analysis of the kaolinite materials (see below) we chose to limit the XRD and TEM analysis part of this study to kaolinite.

3. RESULTS

3.1. XRD and TEM

XRD analysis of the kaolinite samples can detect only kaolinite, and can determine no change after the Cs exchange experiments. However, TEM analysis of the untreated kaolinite indicates that it includes approximately 1–2 volume percent titanium oxide particles 50–60 nm in diameter (Fig. 1). No other phases were observed based on energy dispersive spectrometer (EDS) analysis and the absence of extra reflections in electron diffraction patterns. Our kaolinite (KGa-1) has been reported to be pure without any other clays (Pruett and Webb, 1993; Pruett, 1995). The EDS spectra from the reacted kaolinite are similar to those of the unreacted particles except for a very small Cs L_α peak, suggesting only a limited amount of Cs on or in the kaolinite. The largest d-spacing observed from the electron diffraction patterns of the aggregates of randomly oriented particles is 7.2 Å, corresponding to the layer spacing of kaolinite. This result supports the absence of any other phases, in particular Cs halides and hydroxides, as indicated by the X-ray diffraction results. The average kaolinite grain size is approximately 0.3 μm.

3.2. XPS

The Cs atoms, occurring as surface species or in interlayers, can be identified by the dominant Cs $3d_{3/2}$ and Cs $3d_{5/2}$ XPS lines near 730 and 740 eV (Figs. 2–6). C KLL and Cs MNN Auger lines also occur and are related to photoelectron transitions. For instance, Fig. 5 clearly shows the changes in the XPS spectra due to the exchange of Cs^+ for Ca^{+2} in the interlayer of montmorillonite. Adventitious hydrocarbon (C 1s) is observed on the surfaces of all samples prior to argon sputtering.

The spectra presented in Figs. 2–6 demonstrate the sensitivity of XPS for identifying elements associated with surface components, including small traces of contaminants. Besides exhibiting the adventitious carbon peaks, Fig. 2 also has significant XPS intensity associated with Na and F. These contaminants are related to the original production of the synthetic corundum powder and the use of flux compounds. The contaminants were readily removed by exposure of the sample to the CsCl solution, and is demonstrated in Fig. 2 where the Cs XPS peaks are observed for the treated sample. A comparison of the XPS spectra for the original gibbsite and treated gibbsite samples suggests no exchange of Cs (Fig. 3). The kaolinite slab samples, in contrast, show a significant increase in the Cs XPS peaks after sample treatment (Fig. 4). The XPS spectrum for the untreated kaolinite sample exhibits signals from Zn that are probably associated with contamination derived from the sawing of the sample slab. The XPS spectra for the montmorillonite sample exhibit the most significant amount of Cs sorbed onto any of the treated minerals (Fig. 5). The Cs XPS signals retain significant intensity after Ar sputtering of the treated kaolinite and montmorillonite samples (Figs. 4, 5); the Ar $2p_{1/2}$ photoelectron signal from the implanted Ar is observed.

There are no definitive changes in the positions of the Cs-peaks or the appearance of additional peaks that would suggest multiple Cs surface and/or interlayer sites. Even at high resolution in the binding energy range of 724–749 eV, there are no differences in the energies of the Cs $3d_{3/2}$ and Cs $3d_{5/2}$ peaks in the spectra of the kaolinite and montmorillonite that can be related to different sorption or exchange sites (Fig. 6).

Semiquantitative Cs analyses for the samples treated with 0.1 N CsCl at 50°C were obtained based on the area under

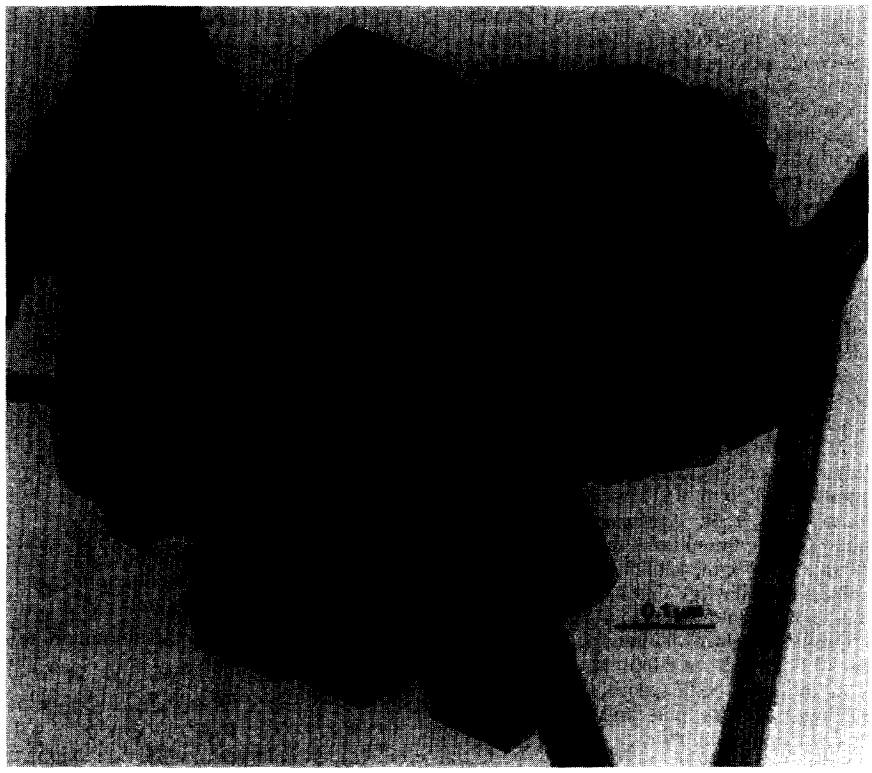

FIG. 1. TEM photograph of Georgia kaolinite (KGa-1) used in our experiments.

the appropriate XPS peaks (for example, Cs $3d_{5/2}$) and instrument-based sensitivity factors (Kibel, 1992). Although far from being truly quantitative (Hochella, 1988), these analyses provide a relative basis of comparison of Cs bound at the mineral surface. The values determined are mol% Cs for the volume of sample within 30–60 Å of the surface. No Cs XPS signal was observed for any of the starting mineral samples. The corundum sample sorbed 0.2 mol% Cs whereas the gibbsite powder failed to exhibit any measurable Cs (Figs. 2, 3). The kaolinite slab sample exhibited 1 mol% Cs that was reduced to 0.3 mol% Cs after sputtering (Fig. 4). The montmorillonite powder sorbed 2 mol% Cs that was reduced to 0.5 mol% Cs after sputtering (Fig. 5). The sputtering process removes surface Cs that is associated with the Cs compounds that form as a result of the air drying of the samples immediately after the exchange experiments. These results suggest the sorption capacity for these minerals to be montmorillonite > kaolinite > corundum > gibbsite. The greater Cs sorption capacity of montmorillonite is expected due to its interlayer exchange sites. It is difficult, however, to reconcile the lack of measurable Cs for the gibbsite sample relative to the slight sorption capacity observed for corundum.

The bulk Cs concentrations for the kaolinite sample obtained by atomic absorption analyses (Table 1) indicate that no Cs was present for the untreated kaolinite, and that a significantly greater amount of Cs is sorbed at 0.1 N CsCl than at 0.01 N. The observed concentrations are 0.87 mol% for 0.1 N and 0.56 mol% for 0.01 N and are consistent with the XPS analyses. Note that these values are expected to run a bit high relative to the XPS results due to the contribution of any surface compound that precipitates during drying. The 0.1 N value is in good agreement with the unsputtered XPS result.

3.3. NMR

At room temperature and room humidity the ^{133}Cs NMR spectra of the Cheto montmorillonite peak are in the range −18 to −12 ppm (Fig. 7). Those of the kaolinite samples contain a large, relatively narrow peak at more shielded (more negative) chemical shifts in the range −40 to −25 ppm along with other small peaks or shoulders at less shielded chemical shifts (Fig. 8). We observe no ^{133}Cs NMR signal from the corundum and gibbsite samples. For both montmorillonite and kaolinite, the chemical shifts of the samples reacted in 0.1 N CsCl solution are less shielded (less negative) than those reacted in 0.01 N CsCl solution at the same temperature. The difference is greater for kaolinite (4 and 14 ppm) than for montmorillonite (1 and 4 ppm). The chemical shifts of the samples reacted at 25°C are also less shielded than those reacted at 50°C, except for the montmorillonite in 0.01 N CsCl solution. The intensities of the side bands in the spectra for the montmorillonite samples reacted in 0.1 N CsCl solution are larger than for those reacted in 0.01 N CsCl solution, possibly indicating that there are some differences in the dynamics of Cs in those samples. This is not the case for the kaolinite samples.

At 100% R. H. and room temperature the chemical shifts of both montmorillonite and kaolinite are less shielded (−5

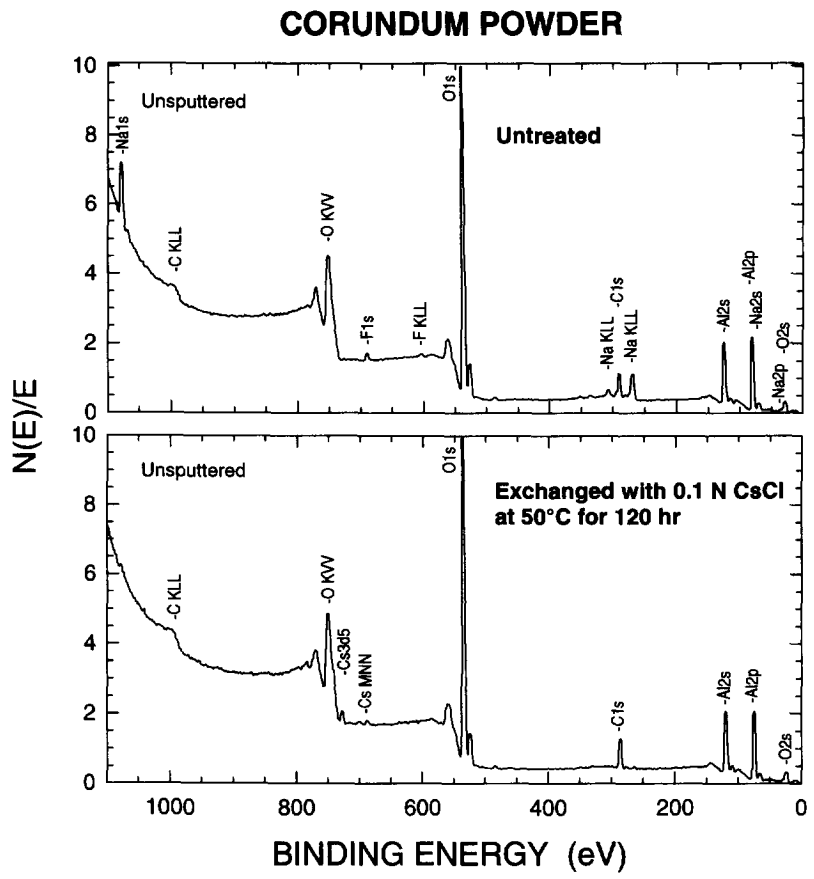

FIG. 2. XPS spectra for the corundums untreated (top) and treated with 0.1 N CsCl at 50°C for 120 h. (bottom).

ppm and 2 ppm, respectively; Figs. 9, 10) than at room humidity (−16 ppm and −25.8 ppm, respectively; Figs. 7 and 8). The chemical shifts for kaolinite are more sensitive to humidity than those of montmorillonite. Kaolinite (0.1 N, 25°C) at a reduced humidity dried in a desiccator over solid $CaSO_4$ for one day has a chemical shift of −93 ppm (Fig. 11). Only the spectrum of the kaolinite sample at 100% humidity lacks spinning sidebands.

The low temperature NMR spectra of the montmorillonite samples at both room humidity and 100% R. H. (Figs. 9, 12) show increased peak broadening with decreasing temperature, but no significant change in peak maximum. Separate peaks indicative of different, well-defined structural environments such as those observed for Cs in hectorite (Weiss et al., 1990a) are not observed.

The low temperature NMR spectra of the kaolinite show increasing peak widths with decreasing temperature (Figs. 10, 13). The chemical shift (peak maximum) of the room humidity sample does not change greatly, but that of the 100% R. H. sample becomes much less shielded (2 ppm at room temperature, 32 ppm at −80°C). For the 100% R. H. sample, spinning side bands appear at −20°C and become larger with decreasing temperature.

The NMR spectra of the kaolinite samples change significantly after heating at 450°C (Fig. 14). For both samples (0.1 N, 25°C and at 0.01 N, 50°C) there are now two peaks, a broad one near −15 ppm and a narrow one near −70 ppm.

4. DISCUSSION

The combined XPS, NMR, and other data including chemical analyses presented here provide a more complete picture of the structure and dynamical behavior of adsorbed Cs than previously possible, especially for kaolinite.

4.1. XRD and TEM

The XRD and TEM data are consistent with the hypothesis that most of the Cs occurs as adsorbed species on surfaces or in interlayer sites and that the amount of precipitated CsCl is negligible. The lack of a ^{133}Cs NMR peak near 228 ppm supports this conclusion (Weiss et al., 1990a). Therefore, our results represent the behavior of Cs on the mineral surfaces or in the interlayers. The small amount of TiO_2 in the kaolinite has no detectable effect on the data.

4.2. XPS

XPS is a sensitive and useful analytical tool for the identification of Cs on the surface or in interlayer sites. These Cs atoms can be readily identified by the Cs $3d_{3/2}$ and Cs $3d_{5/2}$ XPS lines (Figs. 2–6). The presence of the XPS lines for all our samples except gibbsite shows that Cs is present on the surfaces of the minerals or in interlayers, but our data show no peak shifts which could indicate the existence of multiple Cs sites. Photoelectron energies are sensitive to the local bonding environments and

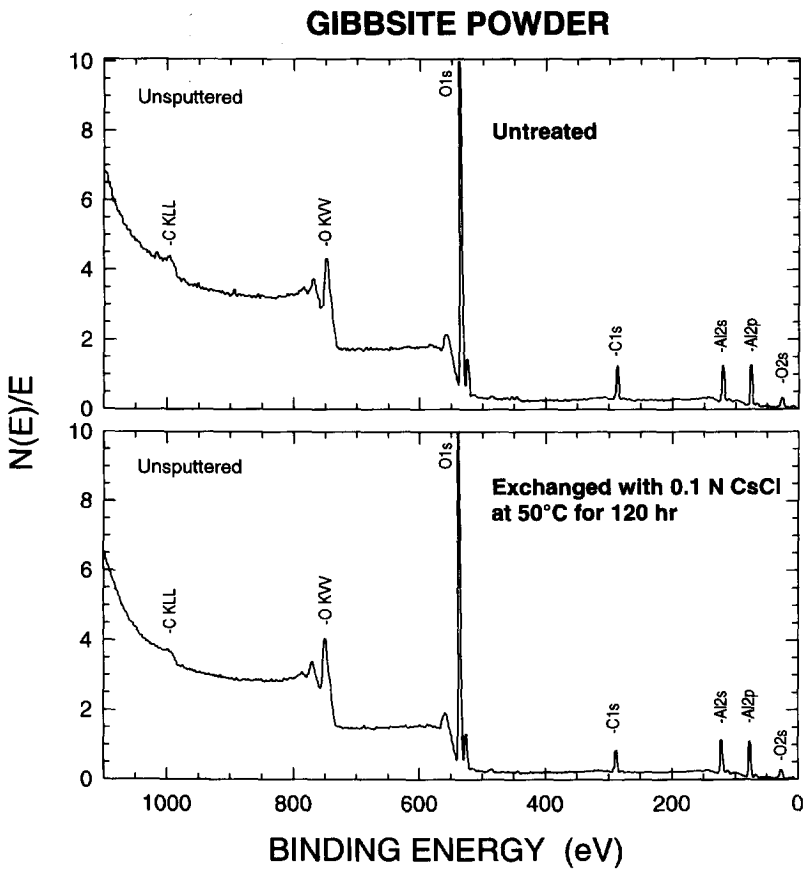

FIG. 3. XPS spectra for the gibbsites untreated (top) and treated with 0.1 N CsCl at 50°C for 120 h. (bottom).

different bonding environments could cause such peak shifts. Our results are consistent with the idea that Cs forms outer-sphere complexes with similar nearest-neighbor coordinations on surfaces and in interlayers. Thus, the ability of XPS to resolve different Cs sites appears to be limited. The lack of a Ca signal for montmorillonite after Cs-exchange is evidence for essentially complete replacement of interlayer Ca by Cs.

The XPS data for the sputtered kaolinite and montmorillonite samples provides additional information about these Cs environments (Figs. 4 and 5). After sputtering, the intensities of the Cs $3d_{3/2}$ and Cs $3d_{5/2}$ XPS lines are reduced due to the removal of any surface precipitates of Cs and sorbed Cs complexes. The intensity after sputtering arises from Cs in interlayers (for the case of montmorillonite) and/or Cs adsorbed on grain boundaries or internal surfaces. The kaolinite sample also includes a component that we interpret as arising from a smectite-like interlayer Cs that contributes to the net XPS signal (see discussion below).

The XPS signal from the corundum sample is probably due to Cs adsorbed at the negatively charged and hydrated Al sites on the surface similar to the broken bonds on clay mineral edges. Gibbsite probably has similar adsorption sites, but the Cs content is too small to be detected by XPS.

4.3. NMR

4.3.1. Montmorillonite

The NMR results for the Cheto montmorillonite samples show that the Cs is in interlayer sites and that its structural environments and dynamical behavior are similar to those of other smectites. Although we did not thoroughly investigate the possible impurities in this sample we are sure that most of the NMR signal is from interlayer sites due to the large exchange capacity of montmorillonite interlayers compared to other possible surface sites. The ^{133}Cs NMR chemical shifts at room temperature reported here are within the range of ^{133}Cs chemical shifts for smectite (Fig. 7, Weiss et al., 1990a,b). The values for Cheto montmorillonite (−16 ppm at room humidity and −5 ppm at 100% R. H.) are only slightly different from those of Texas montmorillonite (−23 ppm at room humidity and −10.5 ppm at 100% R. H.) and other montmorillonites. For smectite, the ^{133}Cs chemical shift at a given relative humidity becomes less shielded (more positive) with increasing $^{IV}Al/(^{IV}Al + Si)$ ratio, but the relationships for dioctahedral and trioctahedral phases are different (Weiss et al., 1990a,b). The small chemical shift difference between our montmorillonite and previously studied montmorillonites is probably due to a difference in the composition of the octahedral sheet rather than tetrahedral sheet. The montmorillonite interlayer charge comes from substitution in the octahedral sheet and Cheto sample has a larger amount of MgO (6.46 wt%) and Fe_2O_3 (1.42 wt%) than many other montmorillonites (van Olphen and Fripiat, 1979).

The chemical shift differences among the Cheto montmorillonite samples exchanged at different solution concentrations (less shielded peaks at lower solution concentrations)

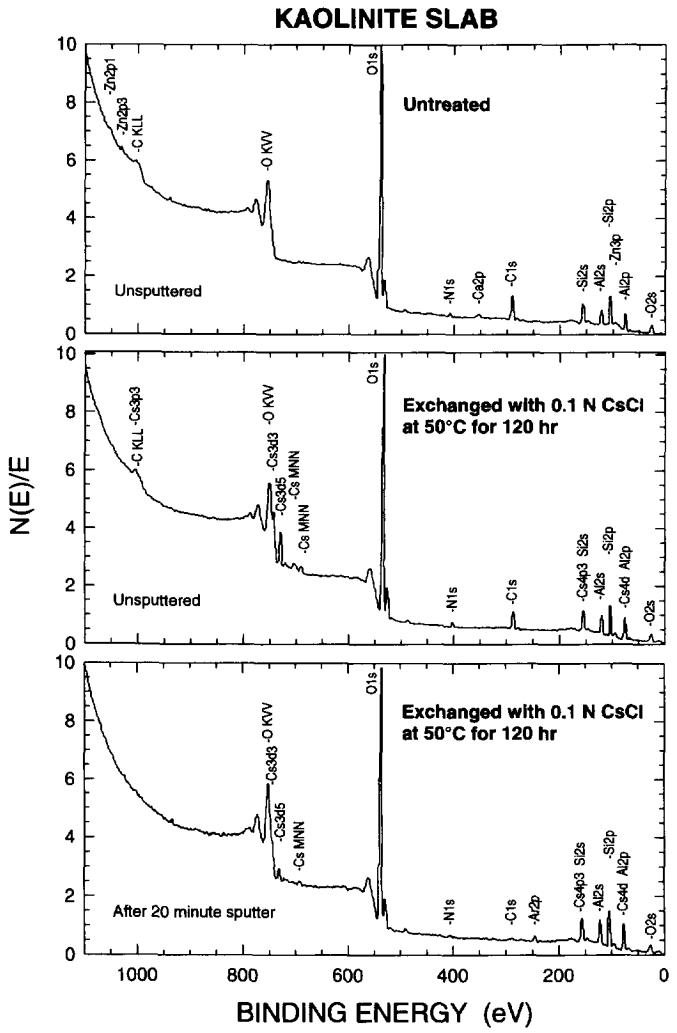

FIG. 4. XPS spectra for the kaolinite slabs untreated (top) and treated with 0.1 N CsCl at 50°C for 120 h. (middle), and after argon sputtering for 20 min for the treated sample (bottom).

are probably due to the effects of varying Cs interlayer concentration. The chemical shift of ^{133}Cs in solution becomes less shielded with increasing CsCl concentration due to short range ion-solvent and ion-ion interactions (Halliday et al., 1969; Haase et al., 1977). The Cs concentration (Cs/H_2O ratio) in the montmorillonite interlayers is larger at greater solution concentration, and thus the Cs chemical shifts become less shielded with increasing solution concentration. The greater intensities of the spinning side bands in the samples exchanged at greater solution concentration may indicate that the frequency of motion of Cs decreases with increasing Cs-concentration resulting in decreased averaging of chemical shift anisotropy and quadrupolar broadening.

The chemical shift change with humidity (less shielded chemical shifts at higher humidities) for montmorillonite is related to changes of the hydration state of Cs in the interlayer (Figs. 9, 12). Based on IR data, Sposito and Prost (1982) suggest that the first stage of water adsorption by smectites with monovalent cations in the interlayers is the solvation of the exchangeable cations by three water molecules per cation, and that the second stage is the formation of an octahedral solvation complex. Since the state of hydration depends only on the ability of the exchangeable cation to be solvated themselves, it is not necessarily accompanied by the formation of complete monolayers of water molecules in the interlamellar space. Cesium has a very low hydration energy, causing Cs-exchanged montmorillonites to have only one water layer even at high relative humidity (MacEwan and Wilson, 1980). The completion of this water layer probably depends on humidity. With increasing humidity the Cs environment in the interlayer becomes more similar to that of Cs in water (δ_i near 0 ppm), although the chemical shift for our montmorillonite remains negative.

Increase of the Cs peak widths with decreasing temperature indicates that at room temperature Cs in the interlayer is in motion at frequencies of at least 10^4 Hz, and that at lower temperatures the frequency of this motion decreases (Figs. 9, 12). We do not observe the peak splitting caused by the decreased rate of motion at low temperatures previously observed by Weiss et al. (1990a,b) for hectorite and other

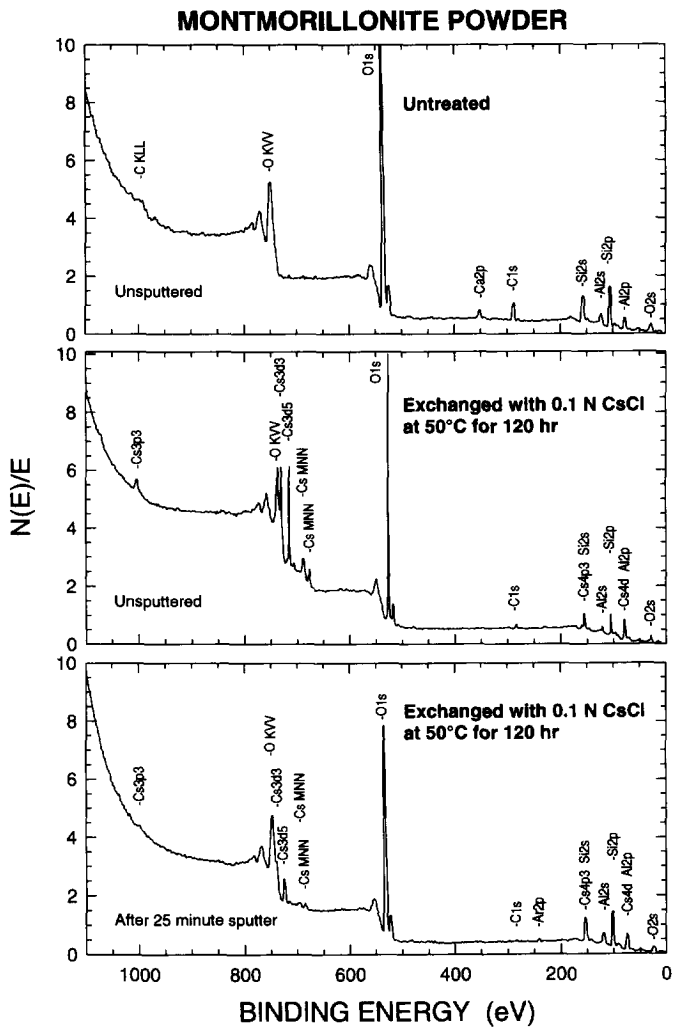

FIG. 5. XPS spectra for the montmorillonites untreated (top) and treated with 0.1 N CsCl at 50°C for 120 h. (middle), and after argon sputtering for 20 min for the treated sample (bottom).

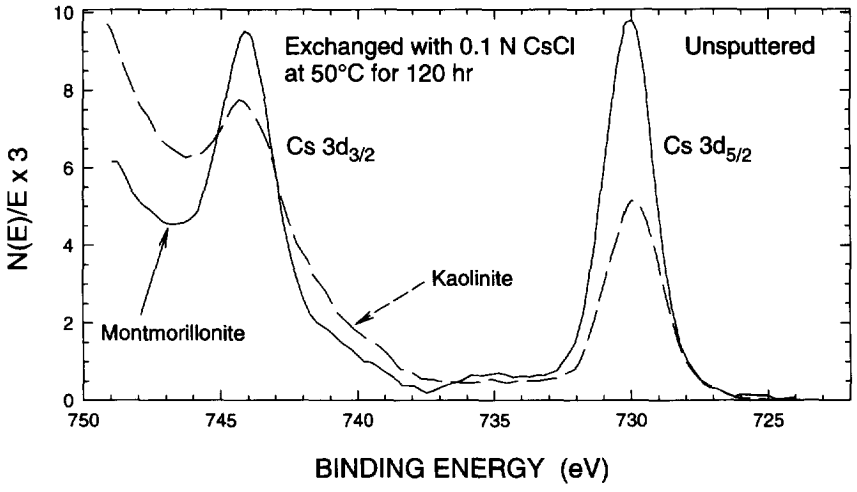

FIG. 6. Comparison of the Cs XPS peaks for the kaolinite slab and montmorillonite in the binding energy range of 724 to 749 eV.

Table 1. Mole % Cs on kaolinite exchanged at different CsCl concentrations and temperatures as determined by AA analysis of dissolved samples.

Concentration	0.01 N	0.01 N	0.1 N	0.1 N
Temperature	25°C	50°C	25°C	50°C
Mole %	0.62	0.56	1.24	0.87

smectites probably due to the larger paramagnetic broadening observed for our sample. Weiss et al. (1990a,b) examined an iron-poor hectorite and the spectra of their sample show well-resolved peaks at low temperature. Their saponite also shows resolved peaks, but the resolution is not as good as for hectorite, probably also due to paramagnetic peak broadening. Our montmorillonite contains 0.14 Fe atoms/unit cell whereas their saponite has 0.07.

4.3.2. *Kaolinite*

The NMR results for our kaolinite samples suggest that most of the tightly adsorbed Cs is present in a very small amount of smectite-like interlayers interstratified in kaolinite. The ^{133}Cs chemical shifts of the main peaks for the reacted kaolinite samples occur over a slightly larger range (−40 to −25 ppm) than those of the montmorillonite samples but are generally in the range of those for Cs-exchanged smectites (−45 to 5 ppm; Weiss et al., 1990a,b). The ^{133}Cs chemical shifts become less shielded with increasing solution concentration, paralleling the behavior of montmorillonite (Fig. 8). The Cs contents of the kaolinite samples increase with increasing solution concentration and decreasing reaction temperature (Table 1). Thus kaolinites with greater Cs concentrations yield less shielded peaks, the same trend as for our montmorillonite samples.

The range of chemical shifts for the main peaks at room temperature (Fig. 8) are not due to different humidities, because these spectra were all collected at the same room humidity, but the effect of relative humidity on the chemical shifts of the kaolinite is the same as for montmorillonite:

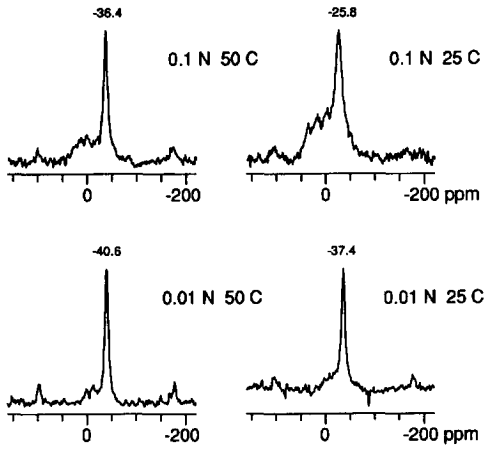

FIG. 8. ^{133}Cs MAS NMR spectra of Georgia kaolinite reacted with 0.1 and 0.01 N CsCl solutions at 25 and 50°C.

less shielded chemical shifts at higher humidity (Figs. 8, 10). The R. H. dependence of the kaolinite, however, is greater than for the montmorillonite, consistent with a low layer charge. At room R. H. the chemical shifts for kaolinite are −40 to −25 ppm, and at 100% R. H. it is 2 ppm, close to the solution CsCl chemical shift. For montmorillonite they are −12 to −18 ppm at room humidity and −5 ppm at 100% humidity. For the kaolinite, the chemical shift near 0 ppm, lack of spinning sidebands, and narrower peak width at 100% R. H. than at room R. H. indicate that at 100% R. H. the Cs in it behaves as if it were in aqueous solution. We would expect Cs to behave like a cation in solution at small interlayer charges because it interacts less strongly with the clay, and is more easily hydrated. Ordinary smectites with large layer charges do not show these spectral features. In the limit of high layer charge, Weiss et al. (1990a) show that ^{133}Cs chemical shifts of the high layer charge clay mineral vermiculite do not change with varying hydration conditions from slurries (fully hydrated), to dehydration at 500°C.

Because we find no discrete smectite in the kaolinite observable with TEM, the expandable layers may occur as

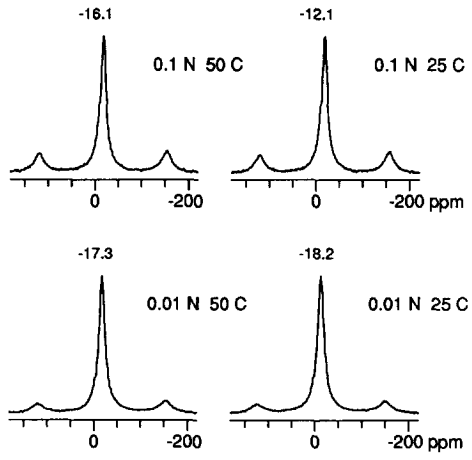

FIG. 7. ^{133}Cs MAS NMR spectra of Cheto montmorillonite reacted with 0.1 and 0.01N CsCl solutions at 25 and 50°C.

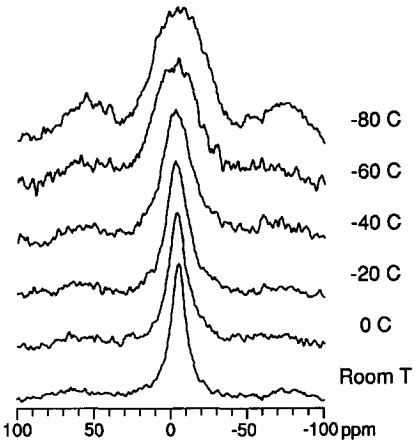

FIG. 9. ^{133}Cs MAS NMR spectra of Cheto montmorillonite (0.1 N, 50°C) collected at 100% humidity with decreasing temperature.

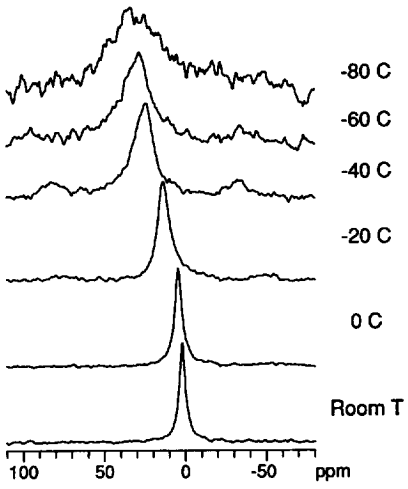

FIG. 10. ^{133}Cs MAS NMR spectra of Georgia kaolinite (0.1 N, 25°C) collected at 100% humidity with decreasing temperature.

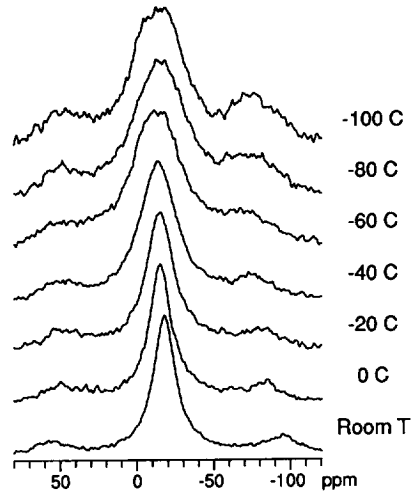

FIG. 12. ^{133}Cs MAS NMR spectra of Cheto montmorillonite (0.1 N, 50°C) collected at room humidity with decreasing temperature.

smectite-like interlayers interstratified in the kaolinite. Mixed layer kaolinite/smectite is a common mineral formed during the weathering of smectite to kaolinite, and is abundant in soils. There have been several studies of its origin, structure, and composition (see review by Hughes et al., 1993). Expandable layers in kaolinite have also been observed by HRTEM (Lee et al., 1975; Eggleton et al., 1989). The layer charge of these expandable layers varies from 0 to that of illite (Jaynes et al., 1989; Hughes et al., 1993), and it is, therefore, not surprising that our kaolinite has smectite-like interlayers with a low layer charge. XRD data and previous reports (Pruett and Webb, 1993; Pruett, 1995) suggest that these smectite-like interlayers are hard to detect due to their small concentration, but that they are important in cation adsorption. The results shown here also support the conclusion that these layers exist as mixed layers in kaolinite, because the spectral characteristics of discrete smectite are quite different at low temperature and at 100% R. H. (Weiss et al., 1990a,b).

With decreasing temperature, the NMR spectra of our kaolinite samples show increasing peak width, as for the montmorillonite (Figs. 9, 10, 12, 13). This result indicates that at room temperature the Cs in the kaolinite is undergoing motional averaging at frequencies $> 10^4$ Hz. An important characteristic of the kaolinite data is that the ^{133}Cs chemical shift at 100% R. H. becomes significantly less shielded with decreasing temperature. This change is consistent with the idea that at low temperatures some of the interlayer water behaves as if it is frozen and thus the Cs concentration in the remaining, effectively mobile water increases. ^{133}Cs chemical shifts become less shielded (more positive) with increasing solution concentration (Halliday et al., 1969; Haase et al., 1977). Due to the surface force field, a fraction of the water in the clay-water system and other porous materials remains unfrozen even at low temperature (Anderson and Tice, 1971; Homshaw, 1981; Fripiat and Letellier, 1984). For the kaolinite, the relatively large change of chemical shift between 0°C and −40°C suggests that there is a significant change in the fraction of frozen water in the interlayer of our kaolinite between those temperatures.

The NMR spectra of the kaolinite samples heated at 450°C for 1 hour also support the idea that most of its Cs is in interlayer sites (Fig. 14). Weiss et al. (1990a,b) report that similarly heated hectorite and other smectites yield two slightly broadened peaks near 0 and −100 ppm, similar to our spectra. They interpreted this observation to indicate that

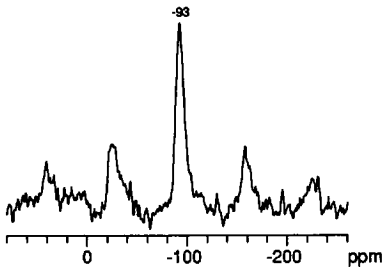

FIG. 11. ^{133}Cs MAS NMR spectrum of Georgia kaolinite (0.1 N, 25°C) dried in a desiccator over solid $CsSO_4$ for one day.

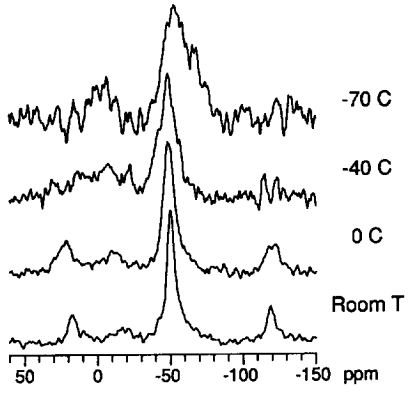

FIG. 13. ^{133}Cs MAS NMR spectra of Georgia kaolinite (0.01 N, 50°C) collected at room humidity with decreasing temperature.

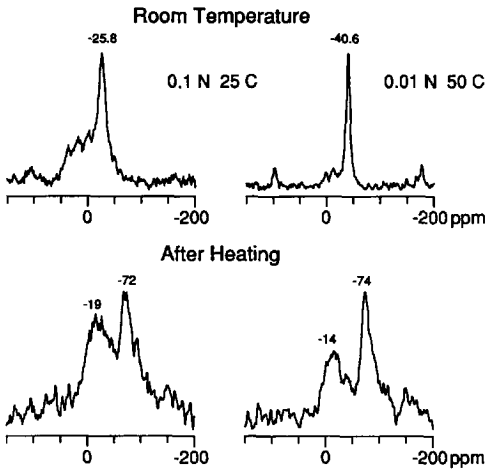

FIG. 14. ^{133}Cs MAS NMR spectra of Georgia kaolinite after heating at 450°C for 1 hour. Dehydration eliminates motional averaging and causes formation of two different sites represented by the peaks near −73 and −16 ppm.

Cs in interlayers collapsed by heating occurs in two different sites, possibly with ninefold and twelvefold coordination. Cesium in other environments such as on exposed basal surfaces or edge sites is not expected to behave this way. Therefore, although the main source of permanent (pH independent) negative charge on kaolinite has been controversial, it appears that for our sample it is associated with expandable layers.

The other small peaks that are less shielded than the main peaks are probably due to Cs on the broken edges of kaolinite. Much of the Cs originally on these sites has probably been lost due to washing during sample preparation. Cesium is loosely bonded to these sites compared to the other Cs in the interlayer.

We failed to observe NMR signal for the corundum and gibbsite because of the low Cs concentrations. Although NMR is very sensitive to the local environments of cations it requires a large enough population for signal detection.

5. CONCLUSIONS

XPS provides a convenient analytical tool for examining the surface Cs composition of exchanged and sorbed minerals. Sorbed Cs is observed for the reacted montmorillonite, kaolinite, and corundum, but not for the gibbsite. XPS analyses performed after sputtering of the surfaces suggests that a significant amount of the Cs is bound in the interlayer sites of the montmorillonite. They are also consistent with Cs occurring in expandable sites in the kaolinite. The XPS peaks provide no evidence for multiple surface or interlayer sites for Cs in any of the samples.

^{133}Cs MAS NMR provides important structural and dynamic information about the Cs adsorbed onto montmorillonite and kaolinite. In montmorillonite, all detectable Cs is adsorbed in the interlayer and is undergoing motional averaging at room temperature. For kaolinite, the results show that much of the adsorbed Cs is in a very small amount of smectite-like interlayers. These layers probably occur as mixed layers in the kaolinite. For kaolinite the ^{133}Cs chemical shift range, peak broadening at low temperatures, and peak separation after heating are similar to montmorillonite. However, the greater sensitivity to humidity and decreased shielding at 100% R. H. and at low temperature are consistent with the idea that the layer charge of the expandable layers in our kaolinite is small. ^{133}Cs MAS NMR is likely to be a useful probe of the presence and smaller charge of expandable layers in kaolinite.

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