



PII S0016-7037(96)00257-8

^{133}Cs NMR study of cesium on the surfaces of kaolinite and illite

YEONGKYOO KIM,¹ R. JAMES KIRKPATRICK,¹ and RANDALL T. CYGAN²¹Department of Geology, University of Illinois, Urbana, IL 61801, USA²Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185, USA

Abstract— ^{133}Cs MAS NMR of Cs-exchanged illite, kaolinite, boehmite, and silica gel is shown to be a powerful tool to investigate the adsorption sites and atomic dynamics of Cs on mineral surfaces. Cesium is adsorbed on these mineral surfaces in primarily two ways: at sites relatively tightly bonded to the surface (Stern layer, Cs1) and at more loosely bonded sites in the diffuse (Gouy) layer (Cs2). For illite, both edge sites and crystallite basal surfaces are important adsorption sites. For kaolinite, edge sites, expandable layers, and probably crystallite basal surfaces are important. The ^{133}Cs NMR chemical shifts for the Cs1 site become more shielded (more negative) as the Si/Al ratio of the substrate phase increases, paralleling the chemical shift variations of other cations and consistent with this site being relatively tightly bonded to the surface. The ^{133}Cs NMR chemical shifts of Cs2 do not vary systematically with solid composition due to the larger distance of these sites from the surface and weaker electrostatic attraction to the surface compared to Cs1. Rather, the Cs2 chemical shifts are significantly influenced by relative humidity (R. H.) and Cs population (Cs/H₂O ratio) on the surface. The Cs1 chemical shifts vary less with these parameters. Cs2 is removed by washing with 1–5 mL of deionized water due to its weak attraction to the surface. The Cs1 chemical shifts become less shielded after washing and with decreasing solution concentration due to a decrease in the Cs surface density. At 100% R. H., Cs in the two sites undergoes motional averaging at frequencies > 100 kHz. With decreasing R. H., peaks for Cs on the two sites are resolved due to decreasing exchange frequencies related to a decreasing number of adsorbed water layers. Motional averaging at 100% R. H. is verified by low temperature experiments with illite.

1. INTRODUCTION

Metals are introduced into aqueous geochemical systems by many kinds of geological and human activity and can interact strongly with mineral surfaces. Understanding the mechanisms of adsorption of metals on minerals is important, because it can significantly influence their transport and redistribution. Adsorption on and exchange into clay minerals is often especially important, because of their large surface areas. ^{137}Cs is an important component of nuclear waste, is very soluble, and migrates easily in natural environments (Alberts and Wahlgren, 1981; Chittenden, 1983; Beasley and Jennings, 1984; Maiti et al., 1989; Santschi et al., 1990). Fundamental understanding of the interaction of Cs with clay minerals is necessary for proper evaluation of waste disposal and remediation, because sorption of Cs on clay minerals can determine its mobility (Tamura and Jacobs, 1960; Comans et al., 1991; Comans and Hockley, 1992).

This paper presents a ^{133}Cs nuclear magnetic resonance (NMR) study of Cs adsorbed on illite, kaolinite, boehmite, and silica gel which considerably expands on our understanding of how Cs (and by inference other alkali cations) interacts with clays (Weiss et al., 1990a,b; Kim et al., 1996). Kaolinite is very common and occurs as a weathering product, in hydrothermally altered rocks, and in sedimentary rocks (Murray, 1988). Illite is also very common, occurring in clastic sedimentary rocks, weathering environments, sedimentary and low-grade metamorphic rocks, and hydrothermal systems (Środoń and Eberl, 1984).

Cations adsorb on clay minerals because of their negative charge. Much of this charge develops due to isomorphic substitution in the octahedral and tetrahedral layers (e.g., Güven, 1988). Some occurs at broken crystallite edges,

which can have positive or negative charge due to protonation or deprotonation. Characterizing surface charge is complex due to the charge from defects, and in some cases its origin remains controversial.

For kaolinite, most of the surface charge comes from broken bonds at crystallite edges, but the basal surface may carry a permanent charge due to the Al⁺³ for Si⁺⁴ isomorphic substitution (Swartzen-Allen and Matijević, 1974; Ferris and Jepson, 1975; Bolland et al., 1976; van Olphen, 1977; Zhou and Gunter, 1992). The origin of permanent charge on kaolinite and even its existence, however, are still being debated (Bolland et al., 1976; Herrington et al., 1992; Kim et al., 1996). Most of the discrepancies in the literature data concerning the surface charge of kaolinite are probably due to differences in the purity of the samples used in different studies (Herrington et al., 1992). Kim et al. (1996) have shown that part of the Cs exchange capacity of at least our kaolinite (KGa-1) is probably from smectite-like interlayers mixed with kaolinite.

The cation exchange capacity (CEC) of illite is often due to expandable layers (Środoń and Eberl, 1984) and broken crystallite edges, but other possible adsorption sites include frayed edges, crystallite tops and bottoms, and illite interlayer sites. Sawhney (1970, 1972) found that illite adsorbs more Cs than vermiculite from dilute solutions (10⁻⁵ M Cs), but that the opposite is true in more concentrated solutions. Illite typically has a small CEC, whereas vermiculite has a large CEC. These results can be explained by the existence of a small number of frayed edge sites on illite which are highly selective for Cs adsorption. In contrast, vermiculite has a larger number of interlayer sites which are less selective for Cs. At low solution concentrations, the contribution of the highly selective sites dominates the

reaction. Frayed edge sites, however, have not been observed directly. Comans et al. (1991) and Comans and Hockley (1992) have proposed a model with two different mechanisms of Cs sorption onto illite. One of these mechanisms is instantaneous and reversible on a timescale of a few days and less. The other is irreversible, occurs at longer times, and is caused by Cs migration into the illitic interlayers. Slow Cs migration into interlayers was also proposed by Evans et al. (1983). In general, a multisite model is needed to explain the equilibrium experimental data (Bolt et al., 1963; Brouwer et al., 1983; Evans et al., 1983). These sites are commonly called planar or surface sites and frayed edge (wedge) sites, but such sites have not been directly verified and are not defined structurally.

Spectroscopic methods can provide direct information about the cation adsorption sites. For clay minerals XPS (X-ray photoelectron spectroscopy; Koppelman and Dillard, 1977; Koppelman et al., 1980; Kim et al., 1996), ESR (electron spin resonance spectroscopy; Monsef-Mirzai and McWhinnie, 1982), and XAS (X-ray absorption spectroscopy; O'Day et al., 1994) have proven to be useful. Solid state NMR has also become a useful tool, probing both cation adsorption sites and atomic scale dynamics (Bank et al., 1989; Luca et al., 1989; Laperche et al., 1990; Weiss et al., 1990a,b; Tinet et al., 1991; Klopogge et al., 1992; Lambert et al., 1992; Kim et al., 1996). Many cations including ^7Li , ^{23}Na , ^{39}K , ^{111}Cd , ^{113}Cd , and ^{133}Cs can be effectively studied by NMR. ^1H and ^2D NMR have also been used successfully 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; Fripiat and Letellier, 1984; Grandjean and Laszlo, 1989a,b; Delville et al., 1991).

^{133}Cs is a good candidate for NMR study because it has 100% natural abundance and a small electric quadrupole moment, and because its chemical shift is very sensitive to local structural environment. ^{133}Cs NMR has been used to probe cation sites and dynamics in zeolites and clays (see Kim et al. (1996) for a review).

There has been little NMR study of cations adsorbed on clay minerals without expandable layers, although Weiss et al. (1990b) show some data for kaolinite and Kim et al. (1996) show that some of the tightly bonded Cs on kaolinite is probably in expandable layers mixed with kaolinite. In this paper we present ^{133}Cs MAS NMR data for Cs-exchanged kaolinite (KGa-1) and a hydrothermal illite with almost no expandable layers. The results provide a more comprehensive picture of Cs adsorption on external mineral surfaces, including the effects of composition, structure, solution concentration, and relative humidity.

2. EXPERIMENTAL

2.1. Samples and Sample Preparation

To investigate the effects of surface composition, illite, kaolinite, boehmite, and a high-surface-area silica gel were used. The illite is from the Yangsan area, Korea, and was formed by hydrothermal alteration of rhyolite (Kim et al., 1990). It is white and contains a very small amount of Fe and almost no expandable layers (Intensity Ratio: $\text{Ir} = 1.03$, Šrodoň and Eberl, 1984). Its structural formula is $(\text{K}_{0.82}\text{Na}_{0.04}\text{Ca}_{0.01})(\text{Si}_{3.12}\text{Al}_{0.88})(\text{Al}_{1.98}\text{Mg}_{0.02})\text{O}_{10}(\text{OH})_2$. It contains a

small amount of anatase which was removed by gravity settling. The kaolinite is from Washington County, Georgia and was obtained from the Source Clay Repository of The Clay Minerals Society (KGa-1). No surface treatment was done for the kaolinite samples. The boehmite was obtained from Alpha Products and the silica gel from Brinkmann. Surface areas measured using nitrogen adsorption with an ASAP 2400, Micrometrics instrument are $7.8 \text{ m}^2/\text{g}$ for the illite and kaolinite, $159 \text{ m}^2/\text{g}$ for the boehmite, and $390 \text{ m}^2/\text{g}$ for the silica gel.

In the Cs exchange experiments, 0.5 g of each sample was mixed with 50 mL of CsCl solution for 5 days at 25°C in Teflon bottles in a water bath. No additional background electrolyte or pH buffer was used. The initial pH was about 6.2 and the final pH values were 5.61, 4.60, 7.77, and 5.74 for silica gel, illite, kaolinite, and boehmite, respectively. Most of the experiments were done at a solution concentration of 0.1 M CsCl. For kaolinite and illite, 10^{-2} , 10^{-3} , and 10^{-4} M CsCl solutions were also used for similar experiments. Illite was also reacted for 54 days and 58 days in 10^{-1} M and 10^{-2} M CsCl solutions to investigate the effects of longer reaction time.

After the reaction, all samples were vacuum filtered using a Millipore filter system and air-dried. The samples were stored in relative humidities of $\approx 0\%$, 30%, 70%, 90%, and 100% in plastic containers for at least 5 days before the NMR spectra were collected. $\approx 0\%$ humidity was obtained using solid P_2O_5 , and 30%, 70%, and 90% humidities were obtained with saturated solutions of CaCl, KI, and KNO_3 , respectively, at room temperature. 100% humidity was obtained over deionized water. Some of the samples were washed during vacuum filtering with 1 mL, 2 mL, or 5 mL of deionized water. One of the illite samples at 0.1 M CsCl was kept at 100% R. H. after washing with 2 mL deionized water. An illite sample washed with 2 mL of deionized water was heated in air at 500°C for an hour before the NMR spectra were collected. Cesium contents of some of the samples after vacuum filtering were determined by atomic absorption analysis (Thermo Jarrel Ash, Video 12E) at the microanalysis laboratory of the School of Chemical Science, University of Illinois at Urbana-Champaign.

2.2. NMR Spectroscopy

The ^{133}Cs NMR spectra were collected 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. The samples were spun at 5–9 kHz depending on the chemical shifts of the peaks and side bands in silicon nitride and alumina rotors using two different 5 mm probes manufactured by Doty Scientific (Columbia, South Carolina, USA). The samples equilibrated at controlled R. H. values were quickly loaded into the MAS NMR rotors in air. Spectra were also collected for all the samples at room humidity. A $4 \mu\text{s}$ pulse was used to obtain a satisfactory signal-to-noise ratio. The $\pi/2$ value for 0.1 M CsCl solution is 11–13 μs , close to that of Cs on our samples. There is no noticeable difference in peak shape in spectra collected with 4 μs and with shorter pulses.

Low temperature spectra for illite reacted at 0.1 M CsCl solution were collected using the same spectrometer. The sample was spun at the magic angle in a ceramic rotor at 4–5 kHz in dry N_2 with a 5 mm probe. Temperatures from room temperature to -60°C were maintained by cooling the spinning gas using liquid nitrogen. Illite was chosen for the low temperature experiments because of its large Cs content and relatively large peak splitting at room humidity.

The ^{133}Cs chemical shifts are reported in parts per million (ppm) relative to external 0.1 M CsCl solution at room temperature.

3. RESULTS

3.1. NMR Results

The ^{133}Cs NMR spectra for all phases investigated are sensitive to humidity, solution concentration, and sample washing. Bulk mineral composition has a significant effect on the chemical shift, and humidity and temperature affect the chemical shift and dynamical behavior.

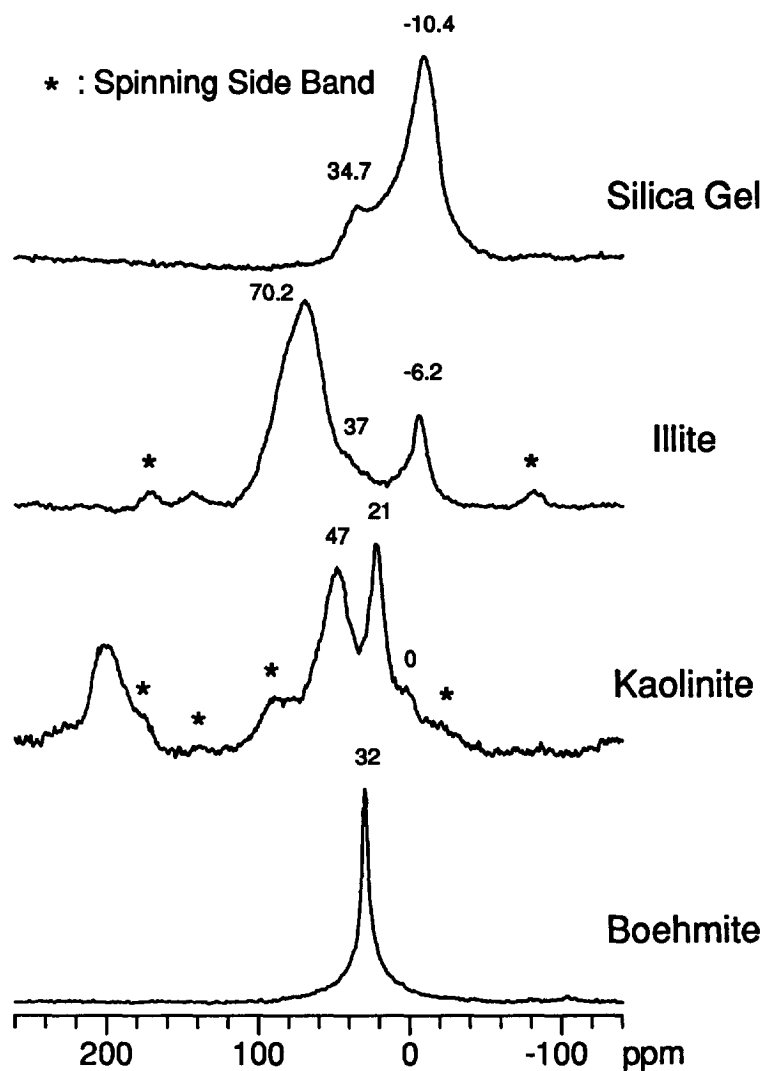


FIG. 1. ^{133}Cs MAS NMR spectra of the indicated phases reacted with 0.1 M CsCl solution at 25°C for 5 days. Spectra were collected at room humidity (ca 35%).

The room temperature (R. T.) and room humidity ($\approx 35\%$) spectra of kaolinite, illite, and silica gel contain two or more central peaks, but that of boehmite only one (Fig. 1). The peak maxima of adsorbed Cs are in the range from -10 ppm to 70 ppm, well within the expected range (Weiss, 1990a,b). Kaolinite also yields a peak at 205 ppm due to CsCl precipitate from residual solution. The spectrum of silica gel contains a large peak at -10.4 ppm and a smaller shoulder at 34.7 ppm. That of illite contains a broad, large peak with a maximum at 70.2 ppm, a small peak at -6.2 ppm, and a shoulder near 37 ppm. Kaolinite yields two peaks with similar relative intensities at 21 ppm and 47 ppm, a small peak near 0 ppm, and the peak for CsCl precipitate at 205 ppm. The single peak for boehmite is at 32 ppm.

Varying R. H., which affects the amount of surface-adsorbed water, has broadly similar effects on the spectra of all the phases (Fig. 2). At $\approx 0\%$ R. H. the peak widths are quite broad, except for the -44.4 ppm peak for illite. The chemical shifts of peaks that are negative at room humidity

are more negative at 0% R. H. and those with positive values at room humidity are more positive. All peaks become narrower with increasing R. H., and at least at 100% R. H. all the samples yield only one relatively narrow peak without spinning side bands.

For silica gel, the peak with the negative chemical shift at room humidity is broader at $\approx 0\%$ R. H., and is more shielded (more negative) with a peak maximum of -32 ppm (Fig. 2A). There is also unresolved intensity at positive chemical shifts, consistent with a broadening of the peak near 50 ppm. At 30% R. H., the spectrum is generally similar to that at room humidity, with a large peak at -15.8 ppm and a small peak at 49.3 ppm. At 70% R. H., however, there is only one peak at -3.5 ppm. This peak becomes narrower at 90% and 100% R. H., but the chemical shift does not change significantly.

Changing R. H. has a similar effect on the spectra of illite (Fig. 2B). At $\approx 0\%$ R. H. there is a narrow peak at -44.4 ppm and a broad band of very low intensity from 0 – 200

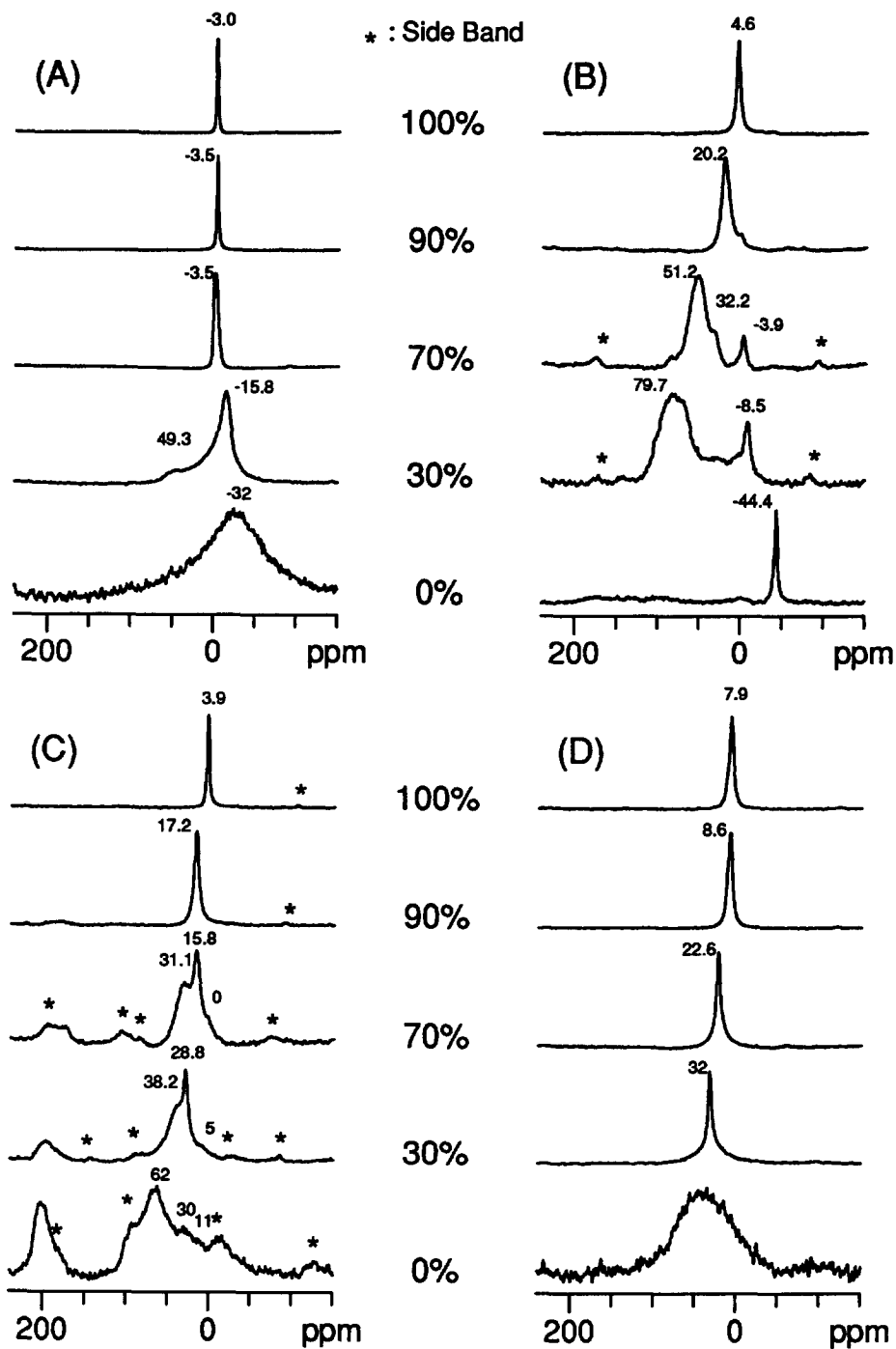


FIG. 2. ^{133}Cs MAS NMR spectra of silica gel (A), illite (B), kaolinite (C), and boehmite (D) collected at the indicated relative humidities after reaction with 0.1 M CsCl solution for 5 days.

ppm. At 30% R. H. there is a large, broad peak at 79.7 ppm, as at room humidity, and the more negative peak is less shielded at -8.5 ppm. There is also significant intensity between these peaks, with a broad maximum near 30 ppm and perhaps a maximum near 0 ppm. At 70% R. H. peak separation is smaller, and there are two peaks at 51.2 and -3.9 ppm and a shoulder at 32.2 ppm. At 90% R. H. there are two peaks, a large one at 20.2 ppm and a small one near 0 ppm. At 100% R. H. there is a single peak at 4.6 ppm.

The effect of varying R. H. on the spectra of kaolinite is more complex (Fig. 2C). At $\approx 0\%$ R. H. there are two broad peaks at about 30 and 62 ppm, perhaps a peak near 11 ppm, and a large broad peak at 205 ppm. The peak at 30 ppm corresponds to the 21 ppm peak at room humidity and the peak at 62 ppm to the 47 ppm peak at room humidity. At 30% R. H., there is a narrow peak at 28.8 ppm, a broader shoulder at 38.2 ppm, a low, poorly resolved peak near 5 ppm, and the peak near 200 ppm. At 70% R. H. there is a

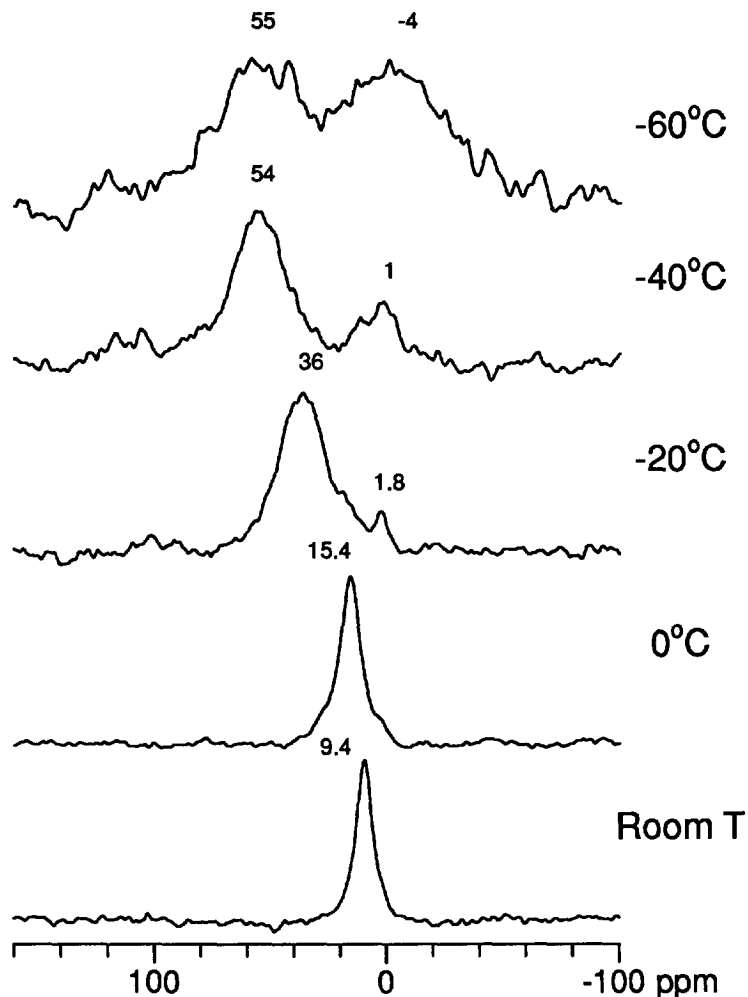


FIG. 3. ^{133}Cs MAS NMR spectra of illite collected at 100% R. H. and temperatures from room temperature to -60°C after reaction with 0.1 M CsCl for 5 days.

narrow peak at 15.8 ppm, a broad one at 31.1 ppm, a shoulder at 0 ppm, and intensity near 200 ppm. At 90% R. H., there is one peak at 17.2 ppm and some intensity near 200 ppm for crystalline CsCl. At 100% R. H., there is a single, narrow peak at 3.9 ppm. Overall, the chemical shifts become more shielded (less positive) with increasing R. H.

Boehmite yields only one peak at all R. H.'s. (Fig. 2D). At $\approx 0\%$ R. H. the peak is broad with a maximum at 40 ppm and a tail to less positive values. With increasing R. H. from 30% to 100%, the chemical shift changes from 32 ppm to 7.9 ppm, but the peak is narrow at all R. H. values $\geq 30\%$.

^{133}Cs spectra for illite at 100% R. H. collected with decreasing temperature show a trend similar to that at room temperature with decreasing R. H. (Fig. 3). Below 0°C there are multiple peaks, which become broader and more separated with decreasing temperature. The spectrum at -20°C is remarkably similar to that at R. T. and 70% R. H., although the chemical shifts are slightly different. The chemical shift change is greatest for the less shielded (more positive) peak. The relative intensity of the more shielded (more negative) peak increases with decreasing temperature.

Sample washing also has a large effect on the room R. H. spectra of all the phases examined (Fig. 4). The spectra of silica gel washed with 1 and 5 mL of water contain only one broad peak near -33 ppm with a decreased signal-to-noise ratio relative to the unwashed sample (Fig. 4A). The spectra of illite washed with 1, 2, and 5 mL of water all contain one narrow peak near -8 ppm and a broader peak centered near 35 ppm (Fig. 4B). There is no significant change in peak shape and chemical shift with varying amounts of wash water. At 100% R. H. the washed illite samples yield one narrow peak at 4.8 ppm, consistent with dynamical averaging (data not shown). The spectra for kaolinite show the largest effect of washing (Fig. 4C). After washing with 1, 2, and 5 mL of deionized water, there is a sharp peak at -24.5 ppm and a broader one at -7.2 ppm. The amount of wash water has no effect. All the CsCl precipitate is removed. For boehmite the only effects of washing are a decreased signal-to-noise (S/N) ratio and a slightly more shielded peak maximum (3 ppm, Fig. 4D). The decrease in S/N ratio is greater than for the other phases. The spectrum for boehmite washed with 5 mL of water shows

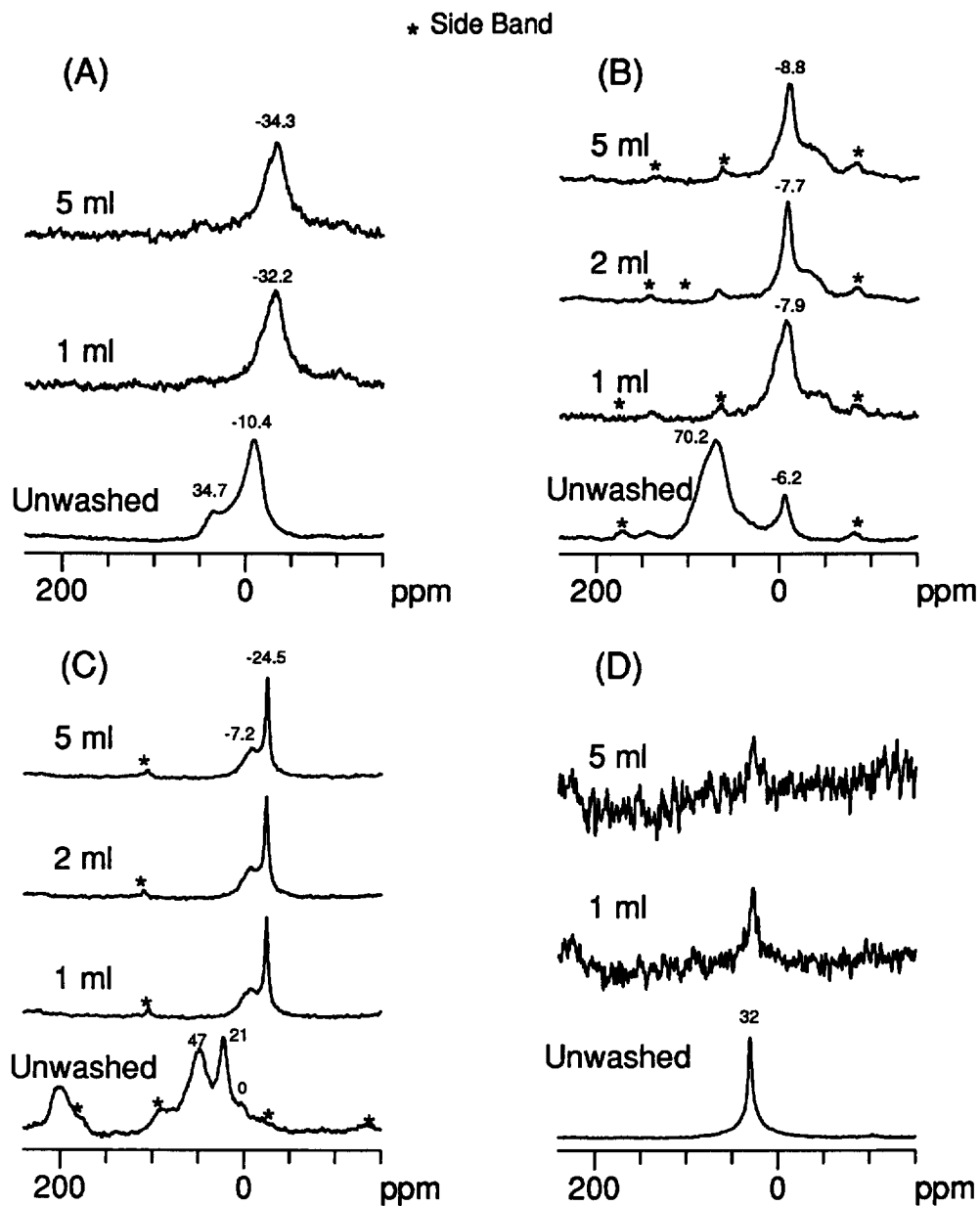


FIG. 4. ^{133}Cs MAS NMR spectra of silica gel (A), illite (B), kaolinite (C), and boehmite (D) collected at room humidity after washing with the indicated amounts of deionized water.

weaker signal relative to that of the sample washed with 1 mL.

For illite and kaolinite, the effects of reaction at decreasing CsCl solution concentration are broadly similar to those of washing (Fig. 5). At 10^{-2} M illite yields a peak at -8.2 ppm and a broader underlying component at about the same chemical shift. The chemical shift of the narrow peak becomes more shielded with decreasing concentration, and the signal-to-noise ratio decreases, consistent with the observed decrease in the amount of adsorbed Cs at lower CsCl concentrations (Fig. 5A). The broad underlying component may also be present at lower concentrations. For kaolinite at 10^{-2} M, there are two peaks, a sharp one at -23.6 ppm and a

broader one at 7.2 ppm, similar to those collected after washing (Fig. 5B). At 10^{-3} M there are also two peaks, but the peak maximum of the broad peak is at -9.4 ppm, its relative intensity is less, and the sharp peak is at -25.6 ppm. At 10^{-4} M, there are a sharp peak at -39 ppm and a shoulder at more negative chemical shifts. The S/N ratio decreases with decreasing solution concentration.

Heating of the illite sample washed with 2 mL of deionized water also causes spectral changes (Fig. 6). After heating there are two peaks at -61.6 ppm and -13.5 ppm. The separation of the peaks is much less than was found for smectites and expandable layers in kaolinite (Weiss et al., 1990a,b; Kim et al., 1996).

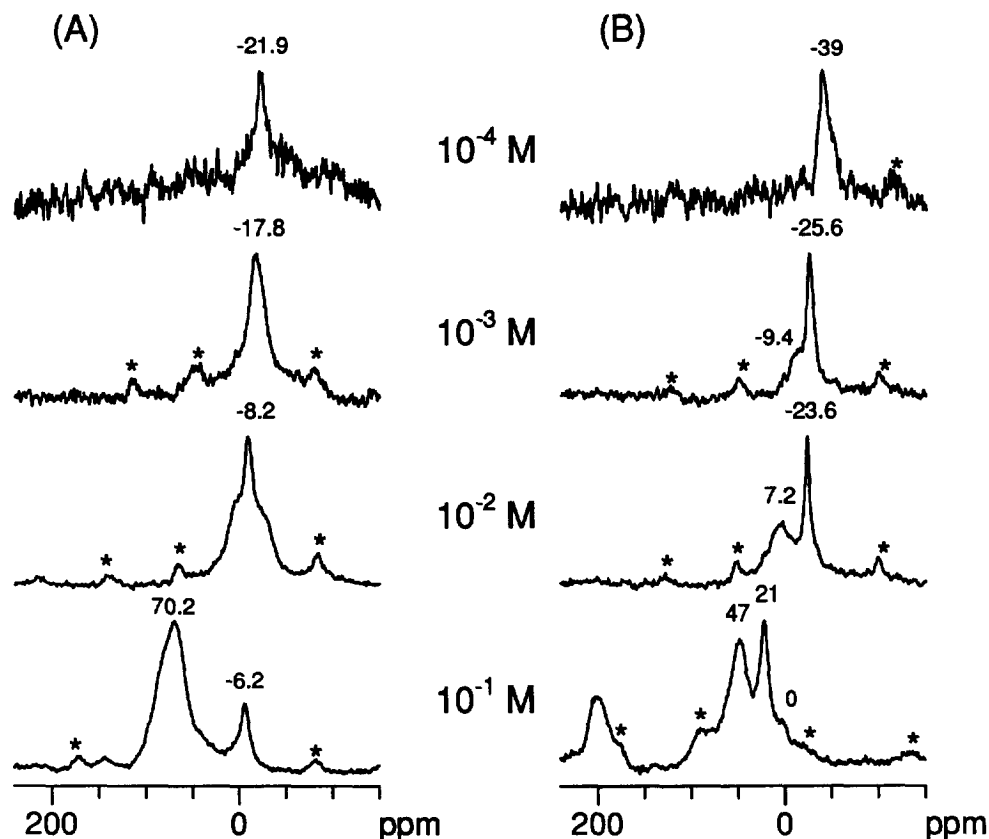


Fig. 5. ^{133}Cs MAS NMR spectra of illite (A) and kaolinite (B) reacted at the indicated CsCl solution concentrations for 5 days. Spectra were collected at room humidity.

Time of reaction also affects the illite spectra (Fig. 7). At 10^{-1} M CsCl, the only major effect of increased reaction time is to move the broader peak from near 70.2 ppm to near 48.1 ppm. Because the position of this broad peak is very sensitive to R. H., this difference may be due to varying room R. H. At 10^{-2} M CsCl, however, after 54 days the broad peak overlapping the main peak decreases or disappears, and there is another small peak at -46.4 ppm.

3.2. Chemical Analysis

Chemical analysis of our samples shows that at 10^{-1} M CsCl the illite contains the largest amount of Cs, and boehmite and kaolinite the least (Table 1). At solution concentration of 10^{-2} M and less and after washing, only illite contains Cs above the detection limit of 0.4 wt%. For illite, the amount of Cs decreases with decreasing solution concentration, but washing removes only about $\frac{1}{3}$ of it at 10^{-1} M. Illite has the largest amount of Cs per unit surface area and kaolinite has the next largest (Table 2). Silica gel and boehmite both have relatively low values.

4. DISCUSSION

4.1. Peak Assignments and Structural Environments

Our ^{133}Cs NMR data show that R. H., solid composition and structure, solution concentration, washing, reaction time,

and heating all affect the behavior of Cs on oxide surfaces. Understanding the effects of these parameters is essential to peak assignment and interpretation of the spectra.

The effects of R. H. on the Cs behavior are related to the number of surface adsorbed water molecules. The general behavior of the R. H. dependence of the extent of water adsorption for minerals is reasonably well known (Miyata, 1968; McCafferty and Zettlemyer, 1971; Klier et al., 1973; Pashley and Kitchener, 1979; Newmann, 1987; Parks, 1990). For kaolinite and mica, at $\approx 0\%$ R. H. there is either no water or a few adsorbed molecules, and the content of adsorbed water increases with increasing R. H. At typical room humidities (30–70%), there are 1–3 water layers (about 1.5 layers at our 35% R. H.), and at 100% R. H. there is a thick water film. Thus, the spectral behavior of surface Cs reflects changes in the Cs environments as the thickness of the water film changes.

The spectra for all the samples except boehmite contain two or more ^{133}Cs peaks, indicating that solid composition and structure are also important factors. All the peaks except for the CsCl precipitates in the kaolinite samples can be assigned to surface species in a way analogous to the ^{133}Cs peaks for Cs in smectite interlayers (Weiss et al., 1990a,b; Kim et al., 1996). Peaks that are more shielded (more negative), narrower, vary less with sample condition, vary more with sample composition, and have larger sidebands are due to Cs on sites that more tightly bonded to the surface. Peaks

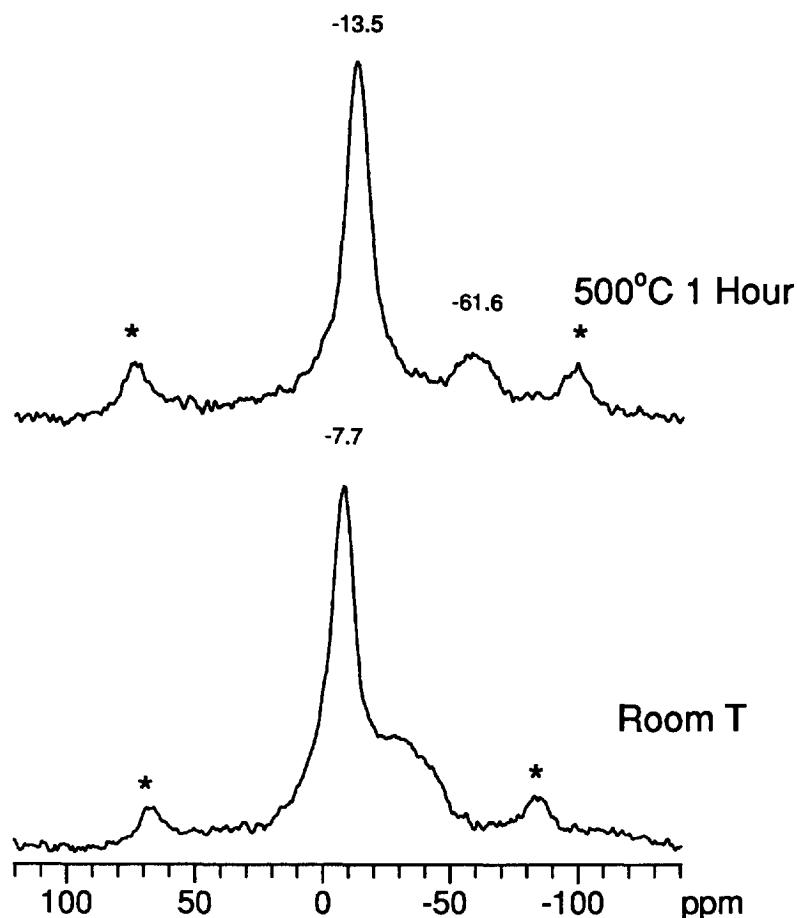


FIG. 6. ^{133}Cs MAS NMR spectra of illite collected after washing with 2 ml of deionized water and the same sample heated for 1 hour at 500°C .

that are less shielded, broader, vary significantly with sample condition, vary little with solid composition, and have fewer or no spinning sidebands are due to Cs less tightly bonded to the surface. Unlike strongly hydrated cations such as Li^+ , Ca^{2+} , and Mg^{2+} , weakly hydrated cations such as K^+ and Cs^+ are expected to come into direct contact with the surface, pushing aside the water molecules separating the cation from the surface (McBride, 1994). This direct contact with the oxygens of the surface causes the nearest and next nearest neighbor environments, and thus the chemical shifts, to be different from those of loosely bonded Cs, resulting at least two peaks.

Because the samples were exchanged in an aqueous solution and most of them had some water molecules adsorbed on their surfaces during analysis, an electrical double layer (EDL) model provides useful insight into the surface adsorption (see e.g., Parks, 1975, and Davis and Kent, 1990, for more detailed discussion). In EDL theory the charge on the solid is, for the most part, assumed to be limited to the surface (surface charge) and there is a layer of counter ions in contact with the surface (the Stern layer) and a layer of ions in the aqueous phase near the surface (the Gouy or diffuse layer). For a negatively charged surface, the Gouy layer contains an excess of cations and a deficiency of anions

(Fig. 8). An increase in cation concentration in the bulk solution causes a compression of the diffuse layer and a relative shift of counter-ions from the diffuse layer to the Stern layer. However, the total excess of cations and the deficiency of anions are the same at both solution concentrations (the area abc for (A) and $a'b'c'$ for (B), top of Fig. 8). The excesses and deficiencies vary with surface charge (the area abc for (A) and $a'b'c'$ for (B), bottom of Fig. 8), with a larger surface charge causing a larger total excess and deficiency of cations and anions.

For the reasons described above, we assign the more shielded peaks at -10.4 ppm for silica gel, -6.2 ppm for illite, and 21 ppm for kaolinite, and the single peak at 32 ppm for boehmite at room humidity to Cs relatively tightly bonded to deprotonated surface oxygens (which we will call Cs1). We assign the less shielded peaks at 34.7 ppm for silica gel, 70.2 ppm for illite, and 47 ppm for kaolinite to Cs loosely bonded in the diffuse layer in the surface water film (Cs2). Assignment of the minor peaks is discussed more extensively below.

The occurrence of the peak for Cs2 appears to be the result of variably complete filtering of water from the sample and thus variable contents of Cs on the sample surface during NMR analysis. The illite and kaolinite samples were wet

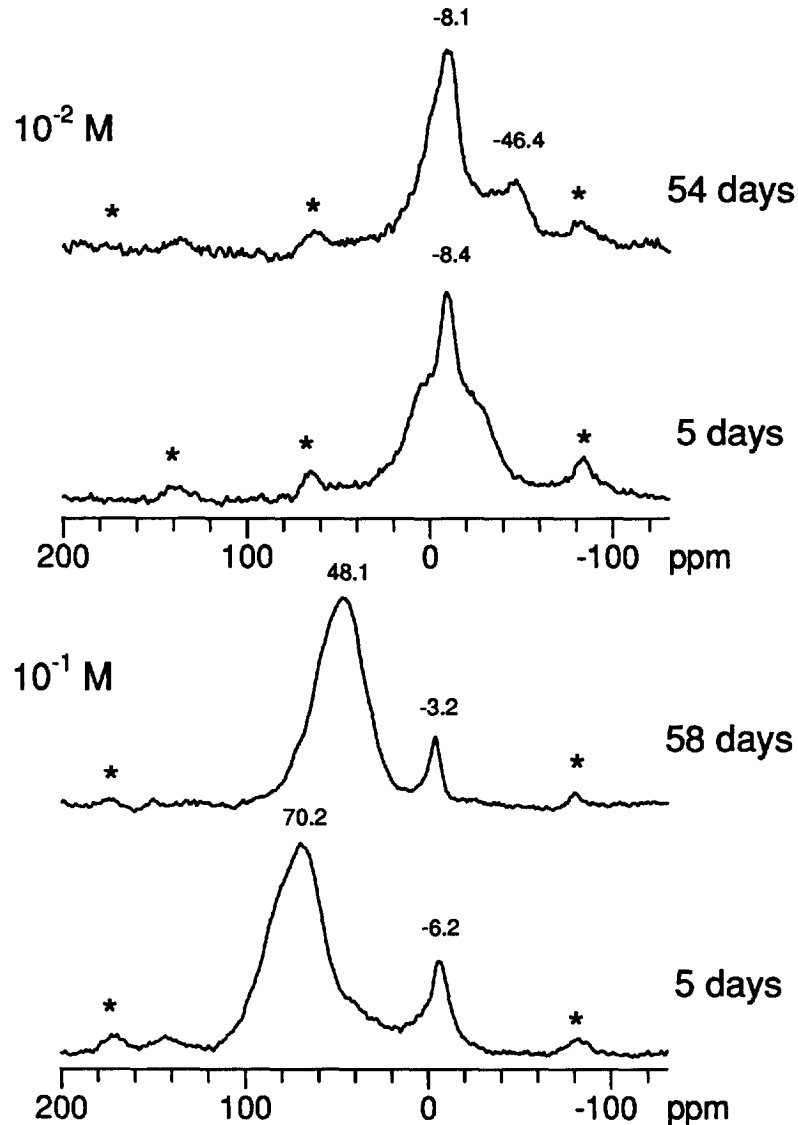
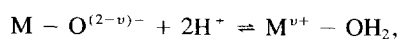


FIG. 7. ^{133}Cs MAS NMR spectra of illite reacted with the indicated CsCl solution concentrations for 5 days and for 54 or 58 days.

after filtering due to their low permeability, whereas the silica gel and boehmite were drier. Complete filtering would leave only Cs1 on the surface, whereas less complete filtering would leave both Cs1 and Cs2. A EDL model (bottom of Fig. 8) shows that less complete filtering [(2) in (A)], leaves more Cs2 and CsCl in solution than more complete filtering [(1) in A] on the surface. As a result, boehmite has a single peak for Cs1, and silica gel has a relatively large peak for Cs1 and only a small peak for Cs2. Illite and kaolinite, however, have relatively larger peaks for Cs2, and kaolinite even has CsCl precipitate from residual CsCl solution. The difference in the amount of Cs retained by illite and kaolinite may be due to their compositions, PZC's (points of zero charge), and permanent charge. The PZC is controlled by the surface reaction



where M is a metal ion on the surface, such as Al and Si, and ν is its bond valence (Yoon et al., 1979). This equation represents equilibrium at or near the PZC. The equilibrium constant for the reaction and thus the PZC is controlled by the composition. For SiO_2 the PZC is near pH 2, and for boehmite it is near pH 8 (Parks, 1965). The PZC for kaolinite is near pH 5, and that for illite should be lower due to its larger Si/Al ratio and probably also to the permanent charge on the tops and bottoms of its crystallites caused by Al substitution for Si (Parks, 1967). Therefore, at a given pH, illite has more negative surface charge than kaolinite and should attract more Cs^+ . In an EDL model, the total cation excess and anion deficiency at the same concentration is represented by (A) for illite and (B) for kaolinite in the lower figure of Fig. 8. If the thickness of the water film after filtering is the same for both (say plane 1 in Fig. 8), then kaolinite will have more CsCl in the remaining water than illite.

TABLE 1. Wt% Cs in Cs exchanged samples at different CsCl concentrations and in samples washed with different amounts of deionized water (DL = below detection limit).

Sample	10 ⁻¹ M	10 ⁻² M	10 ⁻³ M	10 ⁻⁴ M	1 ml Wash	5 ml Wash
Kaolinite	0.78	DL	DL	DL	DL	DL
Illite	4.43	2.3	1.58	0.57	2.92	2.76
Boehmite	0.56	-	-	-	DL	DL
Silica Gel	1.56	-	-	-	DL	DL

The chemical analyses suggest additional differences in the adsorption mechanisms on the different phases (Tables 1 and 2), with the amount of Cs per unit surface area much greater for illite and kaolinite than for silica gel and boehmite (Table 1). The presence of Cs2 on illite and kaolinite and CsCl precipitate on kaolinite are important factors, but if these were the only causes of the different Cs concentrations the amount of Cs1 per unit surface should be similar for all samples. This is not the case. Curve fits for the illite sample at room humidity show that Cs2 composes about 87% of the total surface Cs. This value assumes that all peaks contain the same amount of intensity from the non- ($1/2$, $-1/2$) nuclear transitions. Nutation experiments show no significant changes in the spectra at different pulse lengths, supporting this assumption. 13% of the total Cs on the illite corresponds to $740 \mu\text{gm}^{-2}$ ($0.033 N/\text{\AA}^{-2}$, N = number of Cs atoms) of Cs1 tightly bonded to the illite surface. This amount is about an order of magnitude greater than the Cs1 concentration of $43 \mu\text{gm}^{-2}$ ($0.0020 N/\text{\AA}^{-2}$) for silica gel and $35 \mu\text{gm}^{-2}$ ($0.0016 N/\text{\AA}^{-2}$) for boehmite, both of which develop surface charges only by deprotonation. Therefore, there must be an additional source of surface charge that attracts Cs more effectively to illite. Kaolinite appears to behave like illite in this regard, but its peaks overlap too much for good spectral simulation.

For illite, adsorption on the tops and bottoms of crystallites is the most likely origin of this increased Cs concentration. In our illite there is 0.88 Al/4 (Si + Al) substitution in the tetrahedral sheets, and this additional permanent negative layer charge probably contributes significantly to the Cs adsorption. Kaolinite may also have a small amount of Al substitution in the tetrahedral sheet (Pruett and Schroeder, 1995), and this permanent charge on the tops and bottoms of kaolinite crystallites may contribute to the relatively large amount of Cs on the kaolinite compared to silica gel and boehmite. Newmann et al. (1994) reported that the amount of Al in tetrahedral sheet is 0.4% in our kaolinite (KGa-1) based on ²⁷Al NMR spectroscopy.

A simple geometric calculation indicates that the illite surfaces are quite tightly packed with Cs. If Cs is unhydrated, it has an atomic radius of 1.67 Å and there can be a maximum 0.090 Cs atoms per Å². The hydrated radius of Cs, however, is 3.29 Å, and in this case the maximum number of Cs 0.023/Å. We observe 0.033 Cs1 per Å², close to the expected value.

Our peak assignments are similar to those of Weiss et al.

(1990a,b) for the ¹³³Cs NMR spectra of interlayer Cs in hectorite and other smectites. Although their conclusions are for Cs in smectite interlayers, the nearest and next-nearest atomic neighbor environments of Cs should be generally similar to those near surfaces and the spectral behavior should thus be similar. For smectites, low temperature NMR experiments show that the single R. T. peaks for interlayer Cs are due to motional averaging of Cs atoms between two sites represented by the two observed peaks at low temperature. One of these peaks is due to Cs relatively tightly bonded to the basal oxygens (Cs1-type) and the other to Cs less tightly bonded to the basal oxygens (Cs2-type). For our samples the Cs1 peaks are narrower than the less shielded ones for Cs2, as for smectites. The peaks for Cs1 are also less sensitive to R. H. changes (Fig. 2). The larger intensities of the spinning side bands from the peaks for Cs1 indicate that the motion of Cs1 is more restricted than that of Cs2, consistent with it being in direct contact with the surface.

4.2. Controls of Chemical Shifts

The chemical shifts of the peaks for Cs1 and Cs2 are controlled by many factors, and the observed relationships provide additional supporting evidence for our peak assignments. Most importantly, the chemical shifts for Cs1 vary systematically with solid composition, whereas those for Cs2 do not. The chemical shifts for alkali cations become more shielded as the number of the nearest neighbor anions (oxygen here) increases and also as the electronegativity of the next nearest neighbor (NNN) cations increases (Phillips et al., 1988; Xue and Stebbins, 1993). The same is true for small cations such as Si, P, and Al (Turner et al., 1986; Engelhardt and Michel, 1987; Kirkpatrick, 1988). Thus, because ¹³³Cs chemical shifts are very sensitive to local structure and composition, we expect the chemical shifts of Cs1 to be sensitive to variations of the electronegativities of the cations near the surfaces. Because the charges of the near-surface anions are not fully balanced by cations in the crystal, they contribute to the surface charge of the solid suspended in an aqueous medium. Cesium can be adsorbed onto deprotonated surface oxygens by electrostatic attraction ($M - O^{(2-v)} - Cs^+$), and the bond valence (v) of the NNN cation to the Cs should significantly affect the ¹³³Cs chemical shift. For Al in boehmite v is +0.5, and for Si in silica gel it is +1. The ¹³³Cs chemical shift for Cs1 for silica gel at

TABLE 2. Wt% Cs, surface area, and Cs amounts per unit area for the samples reacted in 10⁻¹ M CsCl solution.

Sample	Wt%	Surface Area m ² g ⁻¹	μgm^{-2}	Number of Cs Atoms per Å ²
Kaolinite	0.78	7.8	1000	0.045
Illite	4.43	7.8	5700	0.26
Silica Gel	1.70	390	44	0.0020
Boehmite	0.56	159	35	0.0016

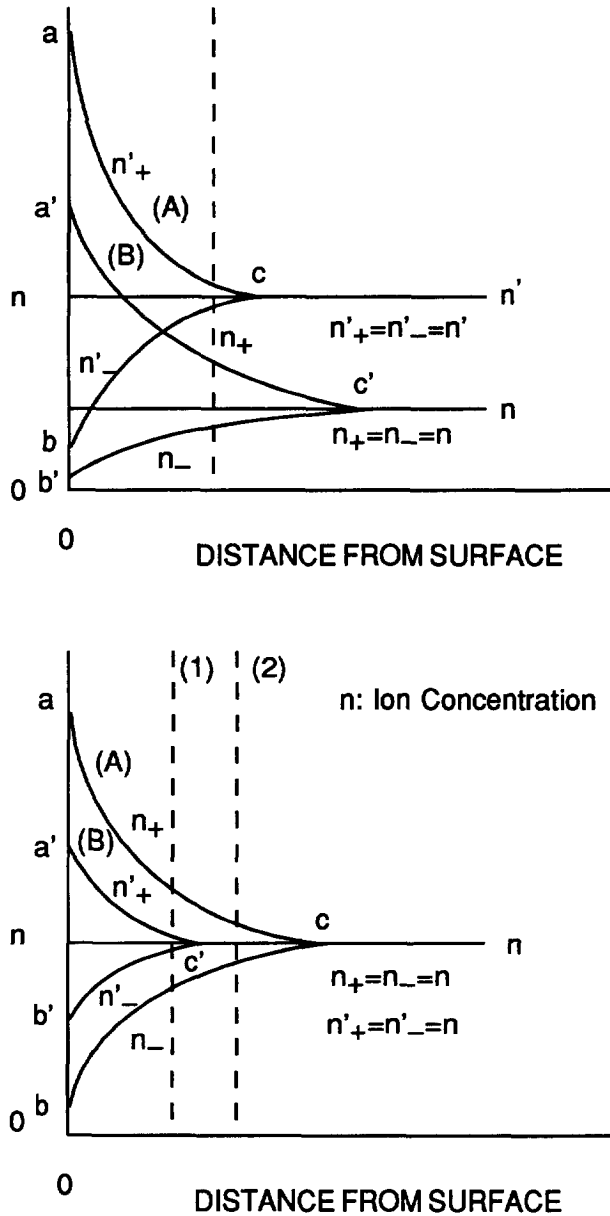


FIG. 8. Charge distribution in the diffuse (Gouy) layer over a mineral surface, at two electrolyte concentrations (n and n') for a clay with constant surface charge (top), and for different surface charge at the same electrolyte concentration (bottom).

room humidity is -10.4 ppm, and that of boehmite is 32 ppm in agreement with the expected trend. The effect of surface composition is relatively large, about 40 ppm for our samples, compared to the 600 ppm range of known ^{133}Cs chemical shifts (Power et al., 1994). Kaolinite layers are composed of paired Al octahedral sheets and Si tetrahedral sheets, and the average ν of an edge site for it is 0.75 . Illite layers are composed of two Si, Al tetrahedral sheets and an Al octahedral sheet between them, and for a 0.88 Al/4 (Si + Al) tetrahedral substitution, the average ν of an illite edge is 0.80 . These two average ν values are between those for boehmite and silica gel, and thus the average ^{133}Cs

chemical shifts for their Cs1 sites should be between those of boehmite and silica gel, with the more shielded shift for illite. The observed trend is as expected (Fig. 9), but the relationship is not linear. We interpret this nonlinear relationship to indicate that the adsorption sites are not purely on the edges sites of illite and kaolinite. Adsorption of Cs on the tops and bottoms of illite crystallites and possibly kaolinite basal surfaces appears important. The sources of surface and the structures of adsorption sites on the basal surfaces are different from those on the deprotonated crystallite edges, and these differences should effect the chemical shifts.

For illite, the less shielded intensity at 0 – 4 ppm at room humidity and 30% R. H. may be the Cs1 peak for the edge sites, and the sharp peak at -6.2 and -8.5 ppm at room humidity and 30% R. H. may be the Cs1 peak for the crystallite tops and bottoms (Figs. 1 and 2). This interpretation is consistent with the large fraction of Cs in Cs1 sites on crystallite tops and bottoms relative to Cs1 sites on edge sites as discussed above. SEM images of this illite also indicate that most of the surface area for this sample comes from tops and bottoms of crystallites (Kim et al., 1990). At $\approx 0\%$ R. H., the small broad peak near 0 ppm can be assigned to Cs1 on broken edges, because the Cs1 peaks for the other samples are also broad at $\approx 0\%$ R. H. The large peak for Cs1 on crystallite tops and bottoms is at -44.4 ppm, however, is quite narrow indicating that this environment is better defined than those of the other samples, even in the absence of coordinating water molecules. Most likely this narrow peak is due to Cs on illite crystallite tops and bottoms fitting into the ditrigonal holes of the tetrahedral sheet without coordinating water molecules. If we assume that all the ditrigonal holes of the illite crystallite tops and bottoms are filled with Cs, geometric calculation shows that there are 0.021 Cs per \AA^2 , assuming that all surface area is on crystallite tops and bottoms. This value is slightly less than the observed value of 0.033 Cs/ \AA^2 for the tightly bonded Cs. Thus, all the ditrigonal holes may be filled with Cs. For kaolinite, however, Cs1 peaks for two different environments are not clearly resolved, probably due to less Cs1 on the crystallite tops and bottoms caused by the smaller Al[4] for Si[4] substitution in kaolinite.

The NMR peak positions for Cs2 show no consistent

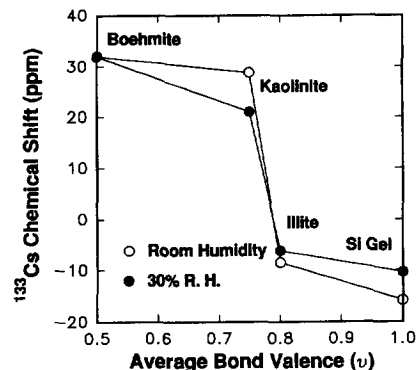


FIG. 9. ^{133}Cs chemical shifts as a function of average surface bond valence for the surface or edge sites at room humidity and 30% R. H. for the indicated phases.

changes with phase composition, because the Cs is not close to the surface. Rather these chemical shifts are more sensitive to R. H. (Fig. 2). They are also sensitive to the Cs concentration on the surface, becoming more shielded with decreasing Cs concentration. These variations parallel those of ^{133}Cs in CsCl solutions, in which the chemical shifts become more shielded with decreasing concentration (Halliday et al., 1969; Haase et al., 1977). The amount of Cs in our samples decreases in the order illite > kaolinite > silica gel > boehmite, and as expected the Cs2 chemical shifts at room humidity change from 70.2 ppm for illite to 47 ppm for kaolinite to 34.7 ppm for silica gel. For illite there is also spectral intensity near 37 ppm at room humidity and 30 ppm at 30% R. H. and a small peak at 32.2 ppm at 70% R. H. These chemical shifts are close to that of Cs2 for silica gel. We assign these peaks to Cs2 at broken edges and the 70.2 ppm peak at room humidity, 79.7 ppm at 30% R. H., and 51.2 ppm at 70% R. H. to Cs2 crystallite tops and bottoms. These differences in chemical shifts are due to differences in the Cs concentrations at these sites. On the tops and bottoms of illite crystallites we expect there to be more Cs per unit area in the water film than on broken edges, because crystallite tops and bottoms have a more negative surface charge, attracting more Cs. This larger concentration makes the chemical shift less shielded. At the edge sites the Cs density should be similar to Si gel, because there is no permanent charge on the surface, and the charge present is due to surface deprotonation. For kaolinite the charge at the crystallite tops and bottoms is smaller than for illite due to the much smaller tetrahedral Al for Si substitution, and thus the Cs2 concentration is smaller, causing a less shielded peak at 47 ppm. The chemical shift for Cs2 at the kaolinite edge sites may be the same as for crystallite tops and bottoms, although very small intensity at 37 ppm may be due to these sites. The origin of the small peak near 120 ppm at room humidity for illite is not clear.

4. Dynamical Behavior

The occurrence of a single narrow peak near 0 ppm for all samples at 100% R. H. indicates that all the Cs on the surface is undergoing motional averaging at frequencies ≥ 100 kHz, even the CsCl precipitates in the kaolinite sample (e.g., Weiss et al., 1990a). The presence of multiple peaks at lower R. H.'s, on the other hand, clearly indicates that if there is exchange between the sites represented by those peaks, the rate of exchange must be < 10 kHz. For none of the samples, however, is the chemical shift of the averaged peak equal to the mean of those at low R. H. (Fig. 2), as would be expected for dynamical averaging among sites with constant chemical shifts. This contrasts with the low temperature ^{133}Cs NMR spectra for hectorite (Weiss et al., 1990a,b), in which the dynamically averaged peaks are at the weighted average of the low temperature peaks. For our samples, the Cs1 and Cs2 chemical shifts change because changes in R. H. cause changes in the surface Cs/H₂O ratio. As a result, for silica gel the dynamically averaged peak is less shielded than the weighted average of two peaks, and for other phases they are more shielded. All have chemical shifts close to 0 ppm.

The motion of Cs on the surface is greatly affected by the amount of water on the surface. Previous studies of the R. H. dependence of the water adsorption on amorphous silica (HiSil), quartz, hematite, kaolinite, and mica show that the water adsorption density increases exponentially with increasing R. H. (Miyata, 1968; McCafferty and Zettlemoyer, 1971; Klier et al., 1973; Pashley and Kitchener, 1979; Newmann, 1987; Parks, 1990). For instance, kaolinite and mica have 1, 2, and 3 statistical monolayers of adsorbed water at ca. 10%, 60%, and 80% R. H., respectively, and very thick water films near 100% R. H. (Newmann, 1987). Thus, it appears that the 1–2 statistical monolayers of adsorbed water expected at our room humidity are not sufficient for the Cs in the Cs1 and Cs2 sites on our samples to undergo motional averaging at kHz frequencies. Water adsorbed on oxide surface is different from bulk water, and the difference decreases with increasing distance from the surfaces (McCafferty and Zettlemoyer, 1971; Parks, 1990). Molecules in the first monolayer are hydrogen bonded to adjacent SiO or AlO sites and are much less mobile than in liquid water. As R. H. increases, the additional water is adsorbed by hydrogen bonding to other adsorbed water molecules, making a continuous network. The motion of adsorbed Cs is closely related to the mobility of surface water. For a given amount of Cs on the surface, the average Cs would be closer to the surface in a thin water layer, and it would be less mobile due to the decreased mobility of the water. With increasing R. H., the average Cs distance from the surface and its frequency of motion should increase, causing motional averaging and ^{133}Cs chemical shifts near 0 ppm.

Support for this conclusion comes from the observation that with increasing R. H. both Cs1 and Cs2 peaks with negative chemical shifts become less negative and these with positive chemical shifts become less positive, all moving towards 0 ppm, the approximate chemical shift of bulk solution. Thus, as the thickness of the water film increases with increasing R. H., the effect of surface decreases, and the Cs environments become more solution-like. This result implies that if water molecules are present, Cs1 is hydrated even though it is relatively tightly bonded on the surface. The broad peaks present at $\approx 0\%$ R. H. indicate that the hydration shell is lost.

Although the room temperature spectra for all samples at 100% R. H. contain only one peak, the low temperature experiments for illite show that multiple sites are still present (Fig. 3). With decreasing temperature, the motionally averaged peak resolves into two peaks with a mean chemical shift near that of the room temperature spectrum, as expected for motional averaging. As for the room temperature spectra, the more shielded peak is due to Cs1 and less shielded one to Cs2. The chemical shift of the motionally averaged peak is not exactly the average of the two low temperature peaks, because at low temperatures partial freezing of the water probably increases the surface Cs/H₂O ratio, causing the chemical shift of the Cs2 peak to become less shielded. The chemical shift of the Cs1 peak varies less with temperature, as expected for tightly bonded Cs. The relative intensity of the Cs1 peak probably increases due to a decrease of the frequency of motional averaging and the increased Cs/H₂O ratio caused by freezing, pushing Cs cations closer to the

surface and increasing the fraction of tightly bonded Cs which does not undergo motional averaging. These effects make the spectrum collected at -20°C and that at 70% R. H. and room temperature very similar. At -60°C the Cs1 peak for illite is not as sharp as at 0% R. H., indicating that the Cs1 environments on crystallite tops and bottoms are not as well defined as at 0% R. H.

4.4. Effects of Other Experimental Factors

4.4.1. Effects of Washing

For all the samples, washing with as little as 1 mL of deionized water easily removes most of the Cs2 from the surfaces of our samples, because it is loosely bonded (Fig. 4). Washing also reduces the intensities of the Cs1 peaks and causes their chemical shifts to become 3–28 ppm more shielded. This change is as expected due to reduction of the surface Cs/H₂O ratio after washing. The spectra for silica gel clearly show this trend (Fig. 4A), with the Cs2 peak at 34.7 ppm disappearing after washing and the Cs1 peak at -10.4 ppm moving to -32.2 and -34.3 ppm.

For illite the effects of washing are more complex (Fig. 4B). The large Cs2 peak at 70 ppm disappears, the Cs1 peak at -6.2 ppm becomes more shielded at -8 ppm, and an additional broad peak appears near -30 ppm. There are several possibilities for the assignment of this third peak, but we cannot unambiguously verify any of them.

One possibility is that it is due to Cs in illite interlayers substituting for K (Evans et al., 1983; Comans et al., 1991; Comans and Hockley, 1992). Comans et al. (1991) and Comans and Hockley (1992) reported a rapid initial adsorption reaction followed by a slow continuation of Cs uptake during Cs exchange with illite, and they interpreted this to indicate Cs fixation in the illite interlayers after long reaction. For our experiments, reaction at room temperature for 54 days at 10^{-2} M CsCl causes our illite to yield a more shielded peak at -46 ppm, consistent with this idea (Fig. 7). There is, however, no significant change at 10^{-1} M CsCl after 58 days of reaction although this may be due to the small relative intensity of the peak. The observation that at 100% humidity Cs in this site becomes motional averaged with Cs1 at frequencies > 20 kHz (data not shown), however, clearly indicates that Cs on this site is mobile. It is difficult to reconcile this mobility with Cs being bonded in sites accessible only by slow reaction.

The second possible assignment for this peak is to Cs in expandable layers, as observed for kaolinite (Kim et al., 1996). After heating at 500°C for an hour, however, the sample washed with 2 ml of deionized water yields only the peak for Cs1 and a small peak at -61.6 ppm (Fig. 6). Normal smectite and the expandable layers in kaolinite yield two peaks (Weiss et al., 1990a,b; Kim et al., 1996). For our illite it is possible that one of the expected peaks for Cs in expandable layers overlaps the large peak for Cs1 at -13.5 ppm. The smaller relative intensity of the peak at -61.6 ppm after heating compared to one near -30 ppm before heating suggests that Cs is in interlayer sites, and that as for other interlayer sites (Weiss et al., 1990a,b; Kim et al., 1996) collapsing the interlayer causes one peak at -61.6 ppm and another near 0 ppm, overlapping the large peak at 13.5 ppm.

A third possibility is that the -30 ppm peak is due to Cs in frayed edge sites (Sawhney, 1970, 1972). If this idea is correct, this peak should have a larger relative intensity at lower concentrations, because Cs is thought to preferentially adsorb at such sites at lower solution concentrations and this site is easily saturated. The relative intensity for this peak does not increase at lower concentrations, probably excluding this possibility (Fig. 5). Our sample is an unweathered, hydrothermal illite, and may have fewer frayed edge sites than illite in soils and sediments, consistent with our data. Thus, although we are now unable to definitely assign this peak, it appears to be minor and may in fact be the result of washing.

The spectra for kaolinite also change significantly after washing (Fig. 4C). The peaks assigned to surface crystalline Cs1 and Cs2 are totally removed, and there is a broad peak at 7.2 ppm and a narrow peak at -24.5 ppm. The 7.2 ppm peak is due to Cs1, and the -24.5 peak is due to Cs in expandable layer in the kaolinite, as previously described by Kim et al. (1996). The peak at -24.5 ppm behaves in every way like Cs in smectite. Its chemical shift is also very sensitive to R. H., and before washing it may be represented by the intensity near 0 ppm (Fig. 1).

For boehmite, washing causes only reduction in peak intensity with a slight change in chemical shift to less positive values (Fig. 4D). These results are consistent with the idea that Cs is not strongly held on the surface compared to those other mineral phases. This difference is due to the relatively high PZC of boehmite (pH 8, Parks, 1965). After reaction with boehmite, the pH of the CsCl solution was 7.77, and at this pH the surface charge is neutral or positive preventing Cs from being strongly attracted to the surface.

4.4.2. Effects of Solution Concentrations

Bulk solution concentration also has a large effect on the spectra of illite and kaolinite, and these changes strongly support our peak assignments. At concentrations less than 10^{-2} M, the intensities of peaks due to Cs2 are generally reduced, and the spectra are similar to those of the washed samples (Fig. 5). The loss of intensity for Cs2 can be readily explained by the EDL model. If the dashed line in the top figure of Fig. 8 represents the thickness of the surface water film after filtering, Cs in the diffuse layer is removed more effectively at lower concentrations (B). In our experiments the differences in solution concentration are much greater than those represented in Fig. 8, and the change in the Cs distribution in the diffuse layer should be larger.

For illite at 10^{-2} M, in addition to the Cs1 peak at -8.4 ppm, there is a broad underlying peak due to Cs2 (Fig. 5A). This Cs2 chemical shift is more shielded than at larger concentrations due to the decreased Cs/H₂O ratio in the diffuse layer. Chemical analysis (Table 1) shows that at 10^{-2} M, the total amount of Cs in the illite sample is more than that of Cs1 (13% before washing), consistent with this assignment. At 10^{-3} M and 10^{-4} M the spectra are dominated by the peak due to Cs1, and its chemical shift becomes more shielded with decreasing solution concentration as expected due to the decreasing Cs/H₂O ratio in the water film on the surface. The S/N ratio decreases with decreasing

solution concentration because the total amount of Cs on the surface also decreases, as verified by the chemical analyses (Table 1).

Similarly, for kaolinite, the chemical shift of the Cs1 peak becomes more shielded and the S/N decreases with decreasing solution concentration, but the peak for Cs in the expandable layers shows less change (Fig. 5B). The Cs/H₂O ratio in the interlayers is, thus, less effected by the Cs concentration than the Cs/H₂O ratio on the surface. Some of the intensity more negative than -39 ppm at 10⁻⁴ M may be due to Cs1. A more negative chemical shift for Cs1 is also consistent with a decrease in Cs density on the surface with decreasing solution concentration. The presence of the expandable layers may account for much of the discrepancy in previous data, but some Al for Si substitution appears necessary. This may be below detectability limit from ²⁷Al and ²⁹Si NMR (≈1%).

4.5. Comparisons with Previous Studies

Our results provide significant results bearing directly on controversial problems about cation adsorption on kaolinite and illite. For kaolinite, the most controversial question is whether there is permanent charge on the basal surface. Although there is some evidence for a weak negative charge on the basal surface caused by tetrahedral Al for Si substitution (van Olphen, 1977; Bolland et al., 1976; Zhou and Gunter, 1992; Newmann et al., 1994), there is also evidence against it (Ferris and Jepson, 1975; Herrington et al., 1992). Our kaolinite data indicate that cation adsorption occurs not only on broken edges but on basal surfaces and in mixed expandable layers.

For illite, adsorption isotherm data indicate several sites, especially for Cs. Easily exchangeable sites called planar and surface sites, and frayed edge sites are thought to be selective for Cs (Bolt et al., 1963; Sawhney, 1970, 1972; Brouwer et al., 1983; Evans et al., 1983). These ideas are based purely on equilibrium adsorption isotherm data, and there has been no direct spectroscopic evidence for them. Except for the frayed edge sites, their actual structural environments are not normally considered.

From our data, it is clear that for illite a large portion of the Cs is adsorbed on crystallite tops and bottoms. These sites probably correspond to the planar sites of Bolt et al. (1963) and Brouwer et al. (1983). The large relative intensity of the peak for crystallite tops and bottoms in our illite corresponds well with the large amount of Cs in planar sites (96% and 96.5% from Bolt et al., 1963; Brouwer et al., 1983). Our spectra also indicate the presence of an additional adsorption site holding a small amount of Cs that we cannot positively assign. This Cs is probably not in frayed edge sites, but careful characterization of the actual minerals present at a waste site is important for understanding the behavior of exchangeable species at that site.

5. CONCLUSIONS

Our Cs NMR spectra for Cs adsorbed on illite, kaolinite, boehmite, and silica gel surfaces show that there are primarily two surface Cs environments, one relatively tightly

bonded to the surface (Cs in the Stern layer; Cs1) and the other more loosely bonded (Cs in the diffuse layer; Cs2). Detailed analysis of the illite data show that most of the Cs is adsorbed on the basal surfaces (crystallite tops and bottoms), but that edge sites are also important. A small amount of Cs may also occur in defect expandable layers or substituting for K in illite layers.

The peaks for Cs1 have many features indicating that it is tightly bonded to the surface. (1) Their chemical shifts change with surface composition, becoming more shielded with increasing Si/Al ratio. (2) They are more shielded and narrower than those of Cs2. (3) They have larger spinning side bands than Cs2. (4) They change less with R. H. and Cs surface density than Cs2.

The chemical shifts for Cs2 do not show systematic changes with Si/Al ratio, but are more sensitive to changing R. H. and Cs surface density. They are more shielded at high R. H. and low surface Cs concentration, as expected from results for CsCl solutions.

At higher R. H., Cs undergoes motional averaging between the Cs1 and Cs2 sites at frequencies > 100 kHz, and there is one narrow peak. Spectral changes observed with decreasing temperature are similar to those caused by decreasing R. H. due to a decreased frequency of Cs motion and increased effective surface Cs/H₂O ratio. The spectrum for illite at -60°C contains two peaks, one for Cs1 and the other for Cs2. The peaks due to Cs2 decrease in intensity and eventually disappear for the samples reacted with progressively lower CsCl solution concentrations, and the Cs1 chemical shifts become progressively more shielded. These changes are due to decreasing Cs surface density. Some of Cs in kaolinite is adsorbed in expandable layers which occur as mixed layers in the kaolinite.

Acknowledgments—This work was sponsored by NSF grants EAR 90-04260 and 93-15695 (RJK, PI) and the Nuclear Regulatory Commission and the U. S. Department of Energy under contract DE-AC04-94AL85000.

Editorial handling: J. Tossell

REFERENCES

- Alberts J. J. and Wahlgren M. A. (1981) Concentrations of ^{239,240}Pu, ¹³⁷Cs, and ⁹⁰Sr in the waters of the Laurentian Great Lakes. Comparison of 1973 and 1976. *Environ. Sci. Technol.* **15**, 94–98.
- Bank S., Bank J. F., and Ellis P. D. (1989) Solid-state ¹¹³Cd nuclear magnetic resonance study of exchanged montmorillonites. *J. Phys. Chem.* **93**, 4847–4855.
- Beasley T. M. and Jennings C. D. (1984) Inventories of ^{239,240}Pu, ²⁴¹Am, ¹³⁷Cs, and ⁶⁰Co in Columbia River sediments from Hanford to the Columbia River estuary. *Environ. Sci. Technol.* **18**, 207–212.
- Bolland M. D. A., Posner A. M., and Quirk J. P. (1976) Surface charge on kaolinites in aqueous suspension. *Aust. J. Soil Res.* **14**, 197–216.
- Bolt G. H., Sumner M. E., and Kamphorst A. (1963) A study of the equilibria between three categories of potassium in an illitic soil. *Soil Sci. Soc. Proc.* **27**, 294–299.
- Brouwer E., Baeyens B., Maes A., and Cremers A. (1983) Cesium and Rubidium ion equilibria in illite clay. *J. Phys. Chem.* **87**, 1213–1219.
- Comans R. N. J. and Hockley D. E. (1992) Kinetics of Cs sorption on illite. *Geochim. Cosmochim. Acta* **56**, 1157–1164.
- Comans R. N. J., Haller M., and De Preter P. (1991) Sorption of

- Cs on illite: Nonequilibrium behavior and reversibility. *Geochim. Cosmochim. Acta* **55**, 433–440.
- Chittenden II, D. M. (1983) Factors affecting the soluble-suspended distribution of strontium-90 and cesium-137 in Dardanelle Reservoir, Arkansas. *Environ. Sci. Technol.* **17**, 26–31.
- Davis J. A. and Kent D. B. (1990) Surface complexation modeling in aqueous geochemistry. In *Mineral-Water Interface Geochemistry* (ed. M. F. Hochella Jr. and A. F. White); *Rev. Mineral.* **23**, 177–260.
- Delville A., Grandjean J., and Laszlo P. (1991) Order acquisition by clay platelets in a magnetic field. NMR study of the structure and microdynamics of the adsorbed water layer. *J. Phys. Chem.* **95**, 1383–1392.
- Engelhardt G. and Michel D. (1987) *High-Resolution Solid-State NMR of Silicates and Zeolites*. Wiley.
- Evans D. W., Alberts J. J., and Clark R. A. (1983) Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediments. *Geochim. Cosmochim. Acta* **47**, 1041–1049.
- Ferris A. P. and Jepson W. B. (1975) The exchange capacities of kaolinite and the preparation of homoionic clays. *J. Colloid Interface Sci.* **51**, 245–259.
- Fripiat J. J. and Letellier M. (1984) Microdynamic behavior of water in clay gels below the freezing point. *J. Mag. Res.* **57**, 279–286.
- Güven N. (1988) Smectites. In *Hydrous Phyllosilicates* (ed. S. W. Bailey); *Rev. Mineral.* **19**, 497–559.
- Grandjean J. and Laszlo P. (1989a) Multinuclear and pulsed gradient magnetic resonance studies of sodium cations and of water reorientation at the interface of a clay. *J. Mag. Res.* **83**, 128–137.
- Grandjean J. and Laszlo P. (1989b) Deuterium nuclear magnetic resonance studies of water molecular restrained by their proximity to a clay surface. *Clays Clay Mineral.* **37**, 403–408.
- Haase A. R. et al. (1977) Nuclear magnetic shielding and quadrupole coupling of ^{133}Cs in cesium salt powders. *Zeit. Naturforsch.* **32a**, 952–956.
- Halliday J. D., Richards R. E., and Sharp R. R. (1969) Chemical shifts in nuclear resonances of caesium ions in solution. *Proc. Royal Soc. London* **313**, 45–69.
- Hecht, A.-M. and Geissler E. (1970) Nuclear magnetic resonance and relaxation of adsorbed water in synthetic fluor montmorillonite. *J. Colloid Interface Sci.* **34**, 32–35.
- Hecht A.-M. and Geissler E. (1973) Nuclear spin relaxation in single and double layer system of adsorbed water. *J. Colloid Interface Sci.* **44**, 1–12.
- Herrington T. M., Clarke A. Q., and Watts J. C. (1992) The surface charge of kaolin. *Colloids Surface* **68**, 161–169.
- Hougardy J., Stone W. E. E., and Fripiat J. J. (1976) NMR study of adsorbed water. I. Molecular orientation and protonic motions in the two-layer hydrate of a Na vermiculite. *J. Chem. Phys.* **64**, 3840–3851.
- Kim S. J., Kim Y., and Noh J. H. (1990) Mineralogy and genesis of hydrothermal deposits in the southeastern part of Korean Peninsula: (1) "Napseok" deposits in Yangsan area. *J. Miner. Soc. Korea* **3**, 44–57.
- Kim Y., Cygan R. T., and Kirkpatrick R. J. (1996) ^{133}Cs NMR and XPS investigation of Cs adsorbed on clay minerals and related phases. *Geochim. Cosmochim. Acta* **60**, 1041–1052.
- Kadi-Hanifi M. (1980) Proton nuclear magnetic resonance studies of "one-layer" hydrates of oriented hectorite. *Clays Clay Mineral.* **28**, 65–66.
- Kirkpatrick R. J. (1988) MAS NMR spectroscopy of minerals and glasses. In *Spectroscopic Methods in Mineralogy and Geology* (ed. F. C. Hawthorne); *Rev. Mineral.* **18**, 341–403.
- Klier K., Shen J. H., and Zettlemoyer A. C. (1973) Water on silica and silicate surfaces. I. Partially hydrophobic silicas. *J. Phys. Chem.* **77**, 1458–1465.
- Klopprogge J. T., Jansen J. B. H., Schuiling R. D., and Geus J. W. (1992) The interlayer collapse during dehydration of synthetic $\text{Na}_{0.7}$ -beidellite: A ^{23}Na solid-state magic-angle spinning NMR study. *Clays Clay Mineral.* **40**, 561–566.
- Koppelman M. H. and Dillard J. G. (1977) A study of the adsorption of Ni(II) and Cu(II) by clay minerals. *Clays Clay Mineral.* **25**, 457–462.
- Koppelman M. H., Emerson A. B., and Dillard J. G. (1980) Adsorbed Cr(III) in chlorite, illite, and kaolinite: An X-ray photoelectron spectroscopic study. *Clays Clay Mineral.* **28**, 119–124.
- Lambert J.-F., Prost R., and Smith M. E. (1992) ^{39}K solid-state NMR studies of potassium tecto- and phyllosilicates: The in situ detection of hydratable K^+ in smectites. *Clays Clay Mineral.* **40**, 253–261.
- Laperche V., Lambert J. F., Prost R., and Fripiat J. J. (1990) High-resolution solid-state NMR of exchangeable cations in the inter-layer surface of a swelling mica: ^{23}Na , ^{111}Cd , and ^{133}Cs vermiculites. *J. Phys. Chem.* **94**, 8821–8831.
- Luca V., Cardile C. M., and Meinhold R. H. (1989) High-resolution multinuclear NMR study of cation migration in montmorillonite. *Clay Mineral.* **24**, 115–119.
- Maiti T. C., Smith M. R., and Lau J. C. (1989) Colloid formation study of U, Th, Ra, Pb, Po, Sr, Rb, and Cs in briny (high ionic strength) groundwaters: Analog study for waste disposal. *Nuclear Technol.* **84**, 82–87.
- McBride M. B. (1994) *Environmental Chemistry of Soils*. Oxford University Press.
- McCafferty E. and Zettlemoyer A. C. (1971) Adsorption of water vapour on $\alpha\text{-Fe}_2\text{O}_3$. *Disc. Farad. Soc.* **52**, 239–255.
- Miyata K. (1968) Free energy of adsorption of water vapor on quartz. *Nippon Kagaku Zasshi* **89**, 346–349.
- Monsef-Mirzai P. and McWhinnie W. R. (1982) Spectroscopic studies of metal ions sorbed onto kaolinite. *Inorg. Chim. Acta* **58**, 143–148.
- Murray H. H. (1988) Kaolin minerals: Their genesis and occurrences. In *Hydrous Phyllosilicates* (ed. S. W. Bailey); *Rev. Mineral.* **19**, 67–89.
- Newmann A. C. D. (1987) The interaction of water with clay mineral surfaces. In *Chemistry of Clays and Clay Minerals* (ed. A. C. D. Newmann), 237–274. Miner. Soc.
- Newmann R. H., Childs C. W., and Churchman G. J. (1994) Aluminum coordination and structural disorder in halloysite and kaolinite by ^{27}Al NMR spectroscopy. *Clay Mineral.* **29**, 305–312.
- O'Day P. A., Parks G. A., and Brown G. E., Jr. (1994) Molecular structure and binding sites of cobalt(II) surface complexes on kaolinite from X-ray absorption spectroscopy. *Clays Clay Mineral.* **42**, 337–355.
- Pashley R. M. and Kitchener J. A. (1979) Surface forces in adsorbed multilayers of water on quartz. *J. Colloid Interface Sci.* **71**, 491–500.
- Parks G. A. (1965) The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.* **65**, 177–198.
- Parks G. A. (1967) Aqueous surface chemistry of oxides and complex oxide minerals. In *Equilibrium Concepts in Natural Water Systems* (ed. W. Stumm); *Advan. Chem. Ser.* **67**, 121–160.
- Parks G. A. (1975) Adsorption in the marine environment. In *Chemical Oceanography* (ed. J. P. Riley and G. Skirrow), pp. 241–308. Acad. Press.
- Parks G. A. (1990) Surface energy and adsorption at mineral-water interfaces: An introduction. In *Mineral-Water Interface Geochemistry* (ed. M. F. Hochella, Jr. and A. F. White); *Rev. Mineral.* **23**, 133–175.
- Phillips B. L., Kirkpatrick R. J., and Hovis G. L. (1988) ^{27}Al , ^{29}Si , and ^{23}Na MAS NMR study of an Al, Si ordered alkali feldspar solid solution series. *Phys. Chem. Mineral.* **16**, 262–275.
- Power W. P., Mooibroek S., Wasylishen R. E., and Cameron T. S. (1994) Cesium-133 single-crystal NMR study of cesium chromate. *J. Phys. Chem.* **98**, 1552–1560.
- Pruett R. J. and Schroeder P. A. (1995) Well- and poorly-ordered kaolinite from Georgia, U.S.A. 32nd Annual Meeting of the Clay Minerals Society, Program and Abstracts, 103.
- Santschi P. H., Bollhalder S., Zingg S., Lück A., and Farrenkothén K. (1990) The self-cleaning capacity of surface waters after radioactive fallout. Evidence from European Waters after Chernobyl, 1986–1988. *Environ. Sci. Technol.* **24**, 519–527.
- Sawhney B. L. (1970) Potassium and cesium ion selectivity in relation to clay mineral structure. *Clays Clay Mineral.* **18**, 47–52.
- Sawhney B. L. (1972) Selective sorption and fixation of cations by clay minerals: A review. *Clays Clay Mineral.* **20**, 93–100.

- Środoń, J. and Eberl D. D. (1984) Illite. In *Micas* (ed. S. W. Bailey); *Rev. Mineral.* **13**, 495–544.
- Swartzen-Allen S. L. and Matijević E. (1974) Surface and colloid chemistry of clays. *Chem. Rev.* **74**, 385–400.
- Tamura T. and Jacobs D. G. (1960) Structural implications in cesium sorption. *Health Phys.* **2**, 391–398.
- Tinet D., Faugere A. M., and Prost R. (1991) ^{111}Cd NMR chemical shift tensor analysis of cadmium-exchanged clays and clay gels. *J. Phys. Chem.* **95**, 8804–8807.
- Turner G. L., Smith K. A., Kirkpatrick R. J., and Oldfield E. (1986) Structure and cation effects on phosphorus-31 NMR chemical shift and chemical-shift anisotropies of orthophosphates. *J. Mag. Res.* **70**, 408–415.
- van Olphen H. (1977) *An Introduction to Clay Colloid Chemistry*. 2nd ed. Wiley Intersci.
- Weiss C. A., Jr., Kirkpatrick R. J., and Altaner S. P. (1990a) The structural environment of cations adsorbed onto clays: ^{133}Cs variable-temperature MAS NMR spectroscopic study of hectorite. *Geochim. Cosmochim. Acta* **54**, 1655–1669.
- Weiss C. A., Jr., Kirkpatrick R. J., and Altaner S. P. (1990b) Variations in interlayer cation sites of clay minerals as studied by ^{133}Cs MAS nuclear magnetic resonance spectroscopy. *Amer. Mineral.* **75**, 970–982.
- Woessner D. E. (1977) Nuclear magnetic relaxation and structure in aqueous heterogeneous systems. *Mol. Phys.* **34**, 899–920.
- Woessner D. E. (1980) An NMR investigation into the range of the surface effect of the rotation of water molecules. *J. Mag. Res.* **39**, 297–308.
- Woessner D. E. and Snowden B. S., Jr. (1969) A study of orientation of adsorbed water molecules on montmorillonite clays by pulsed NMR. *J. Colloid Interface Sci.* **30**, 54–68.
- Xue Y. and Stebbins J. F. (1993) ^{23}Na NMR chemical shifts and local Na coordination environments in silicates crystals, melts, and glasses. *Phys. Chem. Mineral.* **20**, 297–307.
- Yoon R. H., Salman T., and Donnay G. (1979) Predicting points of zero charge of oxides and hydroxides. *J. Colloid Interface Sci.* **70**, 483–493.
- Zhou Z. and Gunter W. D. (1992) The nature of the surface charge of kaolinite. *Clays Clay Mineral.* **40**, 365–368.