^{113}Cd, ^{1}H MAS NMR AND FTIR ANALYSIS OF Cd^{2+} ADSORPTION ON DIOCTAHEDRAL AND TRIOCTAHEDRAL SMECTITE

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Abstract—Dioctahedral and trioctahedral smectites of very low Fe contents were exchanged with Ca (0.8 N CaCl$_2$) and then with Cd (0.004 –0.2 N CdCl$_2$), resulting in the approximate Ca/Cd interlayer compositions 100/0, 75/25, 50/50 and 0/100. The samples were analyzed using ^{113}Cd and ^{1}H MAS NMR spectroscopy, at different hydration states, and by FTIR using films oriented at 90 and 45° to the infrared beam. When adsorbed from low-concentration CdCl$_2$ solutions, as in this study, Cd is in the smectite interlayer as Cd^{2+}, surrounded by water molecules. In smectite specimens with no tetrahedral charge, Cd occupies one single site in the center of the interlayer along the *c* axis but in smectite with tetrahedral charge, the basal oxygen atoms with excess negative charge interact with some of the Cd atoms more strongly, generating a second site in which Cd is displaced from the center of the interlayer and closer to those oxygen atoms. The ^{1}H NMR study showed protons from hydration water and smectite hydroxyls and showed that both have more than one component. The FTIR and ^{1}H NMR experiments indicate that Cd interacts with hydroxyl groups through one of the solvating water molecules in the first coordination sphere. Cadmium retains water molecules bridging Cd and OH groups even at low hydration states. Comparison with previous studies shows that, when adsorbed from high-concentration CdCl$_2$ solutions, Cd species other than Cd^{2+} are present in sufficient quantities to enter the interlayer and create a different Cd-water complex, seemingly displacing Cd^{2+} from the center of the interlayer.

Key Words—Cation Exchange, FTIR, MAS NMR, Smectite.

INTRODUCTION

Smectite is widely used as an adsorbent/absorbent in a variety of applications, including spillage control and the safe disposal of toxic waste (Hall, 1987). The need for environmental remediation has increased interest in obtaining a fundamental understanding of the sorption mechanism for heavy metals on clay minerals. Information on how species bind to layer silicates, on the chemical environment of the adsorbed species, and whether mobility is affected by processes such as complexation can be obtained using solid-state nuclear magnetic resonance (NMR) spectroscopy (*e.g.* Kim *et al.*, 1996a, 1996b; Grandjean and Robert, 1997; Sullivan *et al.*, 1998; Di Leo and O'Brien, 1999; Di Leo, 2000 and references therein).

In particular, Cd-montmorillonite interaction has been investigated in detail, using solid-state NMR spectroscopy, by several authors. ^{113}Cd is indeed a suitable candidate for NMR measurements. Unlike other probes, such as Co, Cd^{2+} possesses a filled *d* orbital and thus its coordination geometry is not subject to ligand-field effect. In addition, ^{113}Cd has a spin of ½ (and thus, no quadrupolar contribution to NMR relaxation, which broadens the NMR signal), a reasonable magnetogyric ratio of −0.947 kHz gauss^{-1} (for comparison, the value for ^{13}C is 1.07 kHz gauss^{-1}), and a natural abundance of

12.26%. Finally, ^{113}Cd has a demonstrated chemical shift range of >900 ppm, and the value of the chemical shift has been shown to depend on the nature, number and geometric arrangement of the atoms coordinated to Cd.

Bank *et al.* (1989), studying Cd-montmorillonite by solid-state NMR, found two components with the same chemical shift but different peak widths in their ^{113}Cd magic-angle spinning (MAS) NMR spectra and interpreted them as due to the heterogeneity of the Cd sites in the montmorillonite structure: charged Brönsted base sites along the edges and interlayer sites where Cd is more mobile and closer to Fe in the octahedral sheets. In contrast with the conclusions of Bank *et al.* (1989) are the results from Tinet *et al.* (1991) who, using static NMR analysis, observed ^{113}Cd NMR peaks with two components and interpreted them as signal anisotropy rather than a multisite effect. The anisotropy was considered to be due to Cd interaction with the smectite OH groups. Di Leo and O'Brien (1999) found one adsorption site for Cd^{2+} on montmorillonite when the amount of Cd in the exchanging solution (used to obtain Cd-montmorillonite) was small. With highly concentrated Cd solutions, three components were detected and interpreted as a combination of two species on two adsorption sites, fully hydrated Cd^{2+} in the interlayer, partially hydrated Cd^{2+} on the external surface of smectite lamellae and CdCl$^+$ in the interlayer. Sullivan *et al.* (1998, 2000) observed that, in dehydrated Cd-smectite, Cd mobility was very low and that the cation

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was located inside the pseudotrigonal cavities of the interlayer.

Although a number of papers dealing with [111]Cd and [113]Cd solid-state NMR spectroscopy of smectite are available at present, little work has been done on the ^{1}H solid-state NMR spectroscopy of such minerals. Solid-state ^{1}H MAS NMR at high magnetic fields and high spinning speeds is a powerful probe for identifying the different proton sites in smectite and provides information on the di- or trioctahedral nature of smectite, the octahedral charge and the charge of the cations residing in the interlayer space (Alba *et al.*, 2000, 2001).

In the present study, we clarify the controversy on the interpretation of the [113]Cd NMR signal from Cd-smectite and integrate it with information from ^{1}H solid-state NMR and Fourier transform infrared (FTIR) spectroscopies. Two smectites, one dioctahedral (montmorillonite) and another trioctahedral (hectorite), were used to investigate two interlayer chemical environments.

MATERIALS AND METHODS

The smectites used are a montmorillonite provided by English China Clay from St. Austell, Cornwall, UK, termed Gelwhite L, and the SHCa-1 hectorite from Hector, California, USA. They were selected for their very low Fe content (1.02 and 0.5 wt.% Fe_2O_3, respectively, for montmorillonite and hectorite, in the bulk samples) which prevents NMR line broadening (Kirkpatrick, 1988).

The <2 µm fraction was separated by centrifugation. X-ray diffraction (XRD) analysis was performed using an Enraf-Nonius PSD 120 with a curved position-sensitive detector with a 2θ detection range of 0–120º, a Ge 111 monochromator and CuKα radiation, and operated at 45 kV and 32 mA. The analyses were performed at an angle of 6º to the incident beam. The patterns showed the presence of significant amounts of opal in the montmorillonite and calcite in the hectorite.

In order to remove opal, the montmorillonite was treated with a 5% Na_2CO_3 water solution (pH 11.6 at 20ºC) as follows. Two grams of clay were placed in 100 mL of the solution and boiled for 20 min. After this, the fluid was separated. The process was repeated 27 times. Then, the solid was washed repeatedly to remove Na_2CO_3 with deionized water and acetone, to favor flocculation, until neutral pH. Finally, the solid was dried in an oven, disaggregated and ground.

The removal of calcite present in the <2 µm size-fraction of hectorite was carried out by the following procedure. The clay was dispersed in 1 L of deionized water and HCl (1 M) was added to the suspension up to a pH of 4. The suspension was stirred during calcite dissolution and decomposition and the pH was monitored continuously and kept at 4 by adding new acid. The process was continued until no pH increase was observed (~2 h), indicating complete removal of calcite.

The suspension was then centrifuged and the solid was collected and repeatedly washed with deionized water to completely remove $CaCl_2$.

The smectites were then Ca exchanged to have a better control on the extent of the subsequent Cd exchange. The Ca exchange was performed by dispersing ~1.7 g of the smectites in 40 mL of 0.8 N $CaCl_2$ and leaving the dispersion overnight. The process was repeated twice. The solids were washed repeatedly with deionized water by centrifugation until no Cl^- was detected with $AgNO_3$. Then, the samples were dried and ground.

The Ca-exchanged samples were analyzed by XRD as powder samples as indicated previously (Figure 1). In this case, the time of analysis was 13 h for the montmorillonite and 5.5 h for the hectorite. Both smectites contained small amounts of other mineral phases that were quantified by the method of profile stripping developed by Cressey and Schofield (1996) and Batchelder and Cressey (1998). Briefly, the procedure consists of subtracting from the sample pattern the patterns of the pure phases that are present in the sample, in requisite proportion. Sample and pure phases are analyzed in identical conditions and, in our case, all of them were calibrated for peak position with Si as external standard. The calculated proportions, expressed as wt.%, are the following: montmorillonite – 88% smectite, 5% calcite, 5% opal, 2% orthoclase, and traces of albite and quartz; hectorite – 98% smectite and traces of orthoclase, albite, quartz and analcime. Calcite in the montmorillonite was generated during sample preparation. Seemingly, not all Na_2CO_3 was removed after opal extraction and calcite precipitated during Ca exchange.

The Ca-exchanged samples were analyzed chemically for major elements (Si, Al, Ti, Fe, Mg, Mn, K, Na, Ca and P) by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results were corrected for the non-smectitic mineral phases, using ideal compositions (for opal, 75% SiO_2 and 25% H_2O), and the following structural formulae were calculated. Montmorillonite: $Si_{3.92}{}^{IV}Al_{0.08}{}^{VI}Al_{1.35}{}^{VI}Mg_{0.32}Ti_{0.03}Fe^{3+}_{0.13}Ca_{0.43}O_{10}(OH)_2$. Hectorite: $Si_{4.05}{}^{VI}Mg_{2.19}{}^{VI}Al_{0.11}{}^{VI}Li_{0.33}Ti_{0.01}Fe^{3+}_{0.06}Ca_{0.27}O_{10}(OH,F)_2$. Fluorine and Li were not analyzed and the assigned octahedral Li in hectorite is taken from the formula derived by Ames *et al.* (1958) for the same SHCa-1 hectorite. Other analyses in the literature show lower Li values but the present one was selected because it matches well with the rest of the element abundances (total octahedral occupancy is 2.7). The value for Si is slightly >4, indicating that some of the other mineral phases, especially quartz perhaps, were slightly underestimated. This is the reason for the different layer charge indicated by the exchangeable cations (0.55) and by the structural cations (0.76). The real value must be between the two. For the montmorillonite, the total octahedral occupancy is low (1.83) and the layer charge high (0.87), indicating a Ca excess

in the formula, probably because calcite abundance was slightly underestimated.

The Ca-smectites were exchanged with Cd in the approximate proportions of 25, 50 and 100%. Aliquots of the clay samples were weighed and their dry weights were determined by thermogravimetry. We assumed a cation exchange capacity (CEC) of 1 meq g^{-1} (Newman, 1987) for both smectites and used the following CdCl$_2$ solution concentrations: 0.004 N for the 25% exchange, 0.013 N for the 50% exchange, 0.2 N for the 100% exchange. The CdCl$_2$ concentrations were kept at or lower than 0.2 N so that Cd^{2+} was the dominant species adsorbed (Di Leo and O'Brien, 1999). The exchange was performed once for 25 and 50% and twice for 100%. The solids were washed repeatedly with deionized water by centrifugation until no Cl$^-$ was detected using the AgNO$_3$ test. The supernatant liquids were collected and analyzed for Ca by atomic absorption. These values allowed us to determine the exact CEC of the smectites (100% exchange) and the exact extent of the 25% and 50% exchanges (Table 1). The high CEC of the hectorite resulted in a smaller percentage of Cd exchanged. The XRD patterns of the Cd-exchanged smectites were

Table 1. CEC of the smectites and the corresponding fraction exchanged with Cd, determined from the Ca displaced in the Cd exchange.

Sample	CEC (meq g^{-1})	% Exchanged
Mont 25%		25.4
Mont 50%		47.9
Mont 100%	1.02	100
Hect 25%		16.8
Hect 50%		34.6
Hect 100%	1.32	100

similar to those recorded for the Ca-exchanged samples (see Figure 1).

NMR analysis

The [113]Cd and ^{1}H NMR spectra were recorded in the Instituto de Ciencia de Materiales, Madrid, Spain, on a Bruker MSL-300 spectrometer using single-pulse excitation (SP) and MAS. All spectra were obtained using typical π/2 pulse widths of 5 μs for [113]Cd and 6.5 μs for [1]H. The relevant experimental parameters were: spinning speeds 4–6 kHz and recycle delays of 2 s. The
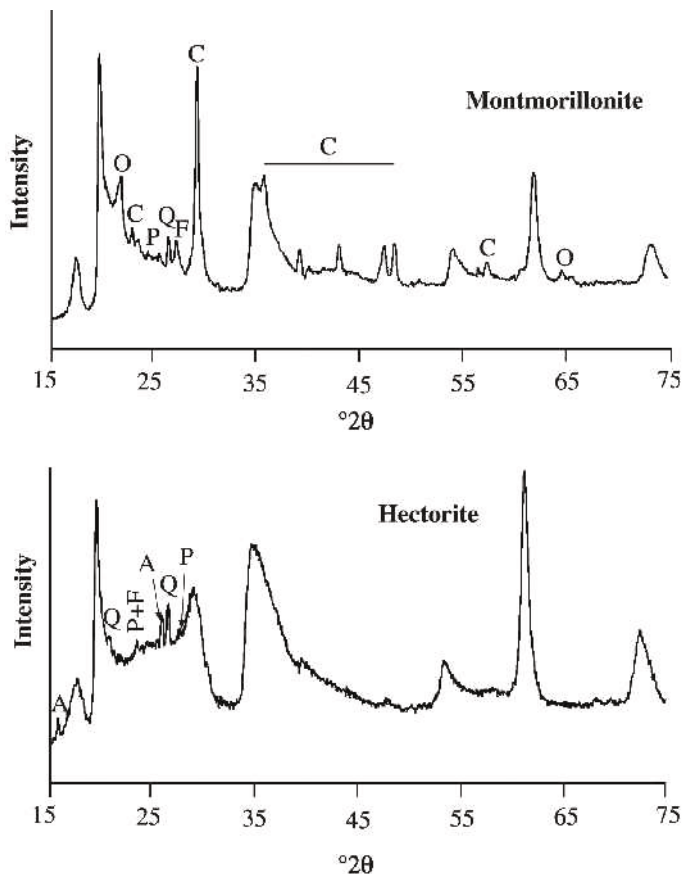

Figure 1. XRD patterns of the <2 μm fraction of montmorillonite and hectorite. The peaks of non-smectitic phases are marked. Symbols are: O – opal, C – calcite, A – analcime, Q – quartz, F – feldspars and P – plagioclase. In the montmorillonite, the 005 smectite peak and the main calcite peak overlap at 29.5°2θ.

number of scans per spectrum was 29,000–31,000 for [113]Cd and 400–800 for [1]H. The [113]Cd and ^{1}H spectra are referred to a 0.1 M $Cd(ClO_4)_2$ solution (Nolle, 1978) and acetone, respectively. The ^{1}H spectra were recorded from samples with different water contents. The smectites were first analyzed for [113]Cd and ^{1}H in equilibrium with the ambient relative humidity (28–38%). At such relative humidity, a two-water-layer complex is present in the interlayer of Cd-exchanged smectite (Di Leo and O'Brien, 1999). Then, they were dehydrated overnight at 200ºC in the rotor, left to cool down in a dry atmosphere (desiccator with Na_2CO_3) for a few minutes and analyzed for [1]H. Finally, they were transferred to a low-humidity atmosphere (11% relative humidity, saturated $LiCl·H_2O$ solution) and analyzed for ^{1}H after a few hours. Two more analyses were performed later to check any possible effect of proton-proton dipole interaction on the ^{1}H MAS NMR spectra. For these, the fully Cd-exchanged mont-morillonite and one of the partially Cd-exchanged hectorite samples (16.8% Cd, see Table 1) were exchanged with D_2O. They were heated at 170ºC in an oven for 2 h and immediately placed in a beaker with paper tissue soaked in D_2O. The beaker was sealed with paraffin film and a screw top and kept closed for several days. The samples were taken from the beaker and loaded in the rotor immediately before the analyses. These were performed at the Chemistry Department in the University of Cambridge with a Chemagnetics CMX400 spectrometer using SP and MAS. The pulse widths were 7.5 and 6.5 µs, spinning speeds 12 and 15 kHz, recycle delays 50 and 10 s and the number of scans per spectrum were 38 and 12.

FTIR analysis

The Ca/Cd-exchanged smectites were analyzed by transmission FTIR as oriented films at different angles to the incident IR beam. Ten milligrams of sample were dispersed using a sonication probe in 3.3 mL of deionized water and 50 µL of the dispersion were placed on a CaF_2 window and allowed to dry. CaF_2 is transparent to infrared (IR) radiation between 1000 and 66,000 cm^{-1}. The samples were analyzed at 90º and 45º of the window surface to the incident beam. Blank spectra for background subtraction were collected at both angles. Three hundred acquisitions were collected for each analysis, with a resolution of 8 cm^{-1}. The spectra were analyzed in the OH-stretching region (4000–2500 cm^{-1}).

NMR and FTIR spectra deconvolution and decomposition

The NMR and IR spectra were analyzed using the GRAMS 32 package from Galactic Industries Corporation. First, they were deconvoluted mathemati-cally, which results in a sharpening of the spectrum features so that overlapping bands are made conspicuous

and we could then observe the components within a band and localize their positions. These positions were then used as input values in the decomposition process. The band positions were fixed during a first step of the calculations and left free in the final calculation. The decompositions were tested for reproducibility by repeating them using different input values for the intensity and width of the bands. These repeated calculations produced similar results for the bands relevant for our study (OH stretching in FTIR spectra and hydroxyl proton in ^{1}H NMR data).

In the IR montmorillonite spectrum, the OH-stretch-ing band was decomposed into three bands, two which were more intense, observed at 3625 and 3649 cm^{-1}, corresponding roughly to AlOHAl, and one of very low intensity, observed at 3694 cm^{-1}, corresponding roughly to AlOHMg (Madejová et al., 1994). The OH-stretching system from adsorbed water between ~3570 and 3200 cm^{-1} was decomposed into three bands, following the location of the more intense maxima. The total intensity of this system was low and it did not affect the calculation of the bands of interest (OH stretching from smectite). For hectorite, the OH-stretching band is located at 3670 cm^{-1} and is narrower than the mont-morillonite OH-stretching system (Russell and Fraser, 1994). It was calculated with only one component, as only one maximum was detected. The intensity of the OH-stretching band of trioctahedral smectite is lower than that of dioctahedral smectite, and the relative intensity of our OH-hectorite band was lower than that from the adsorbed water. In spite of this, the hectorite-OH band was always calculated consistently (similar position and width) in the decomposition procedure, both in the different spectra and in different calculations of the same spectrum. The system of OH stretching from adsorbed water in hectorite was decomposed into five bands from 3630 to ~3200 cm^{-1}, corresponding to the maxima observed. These and those in montmorillonite are to be regarded only as a simulation and they do not necessarily have a physical meaning. The intensities of the smectite OH-stretching bands were measured using their areas.

RESULTS

NMR

Figure 1 shows the XRD patterns of the Ca-smectites obtained at an ambient relative humidity of 30%, which are similar to those of the Cd-exchanged samples (not shown). The d_{003} and d_{005} values of 5.0 Å (17.7º2θ) and 3.05 Å (29.2º2θ) correspond to a d_{001} of 15.1 Å, indicating the presence of the usual 2-water layer complex in the interlayer. Given the equal charge and similar ionic radius of Ca^{2+} and Cd^{2+}, the Cd-smectites will have a similar water content and interlayer configuration. Figure 1 also shows the other mineral phases present.

The ^{113}Cd (SP) MAS NMR spectra of the completely Cd-exchanged montmorillonite and hectorite are dominated by a narrow peak at ~−11 ppm (Figure 2). The decomposition of the montmorillonite spectrum shows a small component at −25 ppm, although this might not be the precise location and shape of this component because the low intensity of the signal makes the decomposition calculation difficult.

The ^{1}H MAS NMR spectra of hectorite equilibrated at ambient relative humidity show two main components, a broad signal centered at ~4 ppm and a narrow peak at ~0.5 ppm (Figure 3a,b). The first corresponds to protons in hydration water (water peak in Figure 3a) and the second to the hydroxyl protons (hydroxyl peak in Figure 3a) in hectorite (Alba *et al.*, 2001). The ^{1}H NMR spectrum of the deuterated sample (Figure 4a) shows this water-proton peak, indicating that D$_2$O for H$_2$O exchange was not complete, although the peak is much reduced. The ~0.5 ppm peak, *i.e.* the hydroxyl-proton peak, is composed of two others at ~0.6 ppm and

Figure 2. ^{113}Cd MAS NMR spectra of the completely Cd-exchanged smectites; ssb indicates spinning side bands.

−0.3/−0.1 ppm (Figure 3a,b). The Cd concentration in hectorite seems to affect the hydroxyl peaks so that their relative intensities change and also one of them seems to shift from −0.3 ppm at 17% Cd content (Figure 3a) to −0.1 ppm at 35 and 100% Cd (Figures 4a and 3b). The relative intensity of the two hydroxyl components remains unaffected by the decreasing water content, while the water peak reveals many components, which change non-uniformly in intensity with water content (Figure 3c,d).

The ^{1}H MAS NMR spectrum of Cd-montmorillonite at room humidity (100% Cd, Figure 5a) also shows an intense and broad signal centered at ~4 ppm, corresponding both to water protons, whose contribution becomes much smaller after deuteration, and to hydroxyl protons (Figure 4b). The peak has several components and our decomposition procedure could detect three water-proton peaks in the range 8.9–4.3 ppm (Figure 5a). Dehydration (Figure 5b) revealed further complexity, with five peaks within 7.8–2.7 ppm. The hydroxyl-proton peak appears, in the sample at room humidity conditions, at 1.8 ppm (Figure 5a), less resolved from the water-proton peak than in hectorite (Alba *et al.*, 2001). The spectra obtained after overnight dehydration (Figure 5b) and after deuteration (Figure 4b) show this peak in more detail, with two components at 1.7/1.8 and 0.4 ppm. The components do not have the exact same shape and relative heights in the dehydrated and deuterated samples probably due to error introduced in the decomposition process by the overlapping with water-proton peaks. The intensity of the hydroxyl-proton peaks in montmorillonite is much lower than in hectorite (compare Figure 5b with Figure 3c and d, which were obtained with the same number of scans) and they are wider (2.7–3.0 ppm in montmorillonite and 0.7–1.1 ppm in hectorite). The attempt to obtain a Cd-montmorillonite spectrum with intermediate water content, as in hectorite, failed because the rehydration was faster and the resulting spectrum was similar to that of the montmorillonite equilibrated at room humidity (Figure 5a).

Opal should contribute a signal to the ^{1}H NMR spectrum at −2.4 ppm (Klinowski *et al.*, 1998; they used tetramethylsilane as a reference and their spectrum needs to be transformed to the acetone-reference). Our deconvolution-decomposition procedure detected this peak at −2.4 ppm in the spectrum of the partially dehydrated Cd-montmorillonite (Figure 5b), of little intensity, although it was not detected in the hydrated and deuterated samples (Figures 5a and 4b), probably because of the presence of more intense water-proton peaks.

FTIR

Figure 6 shows the OH-stretching region of some of the spectra of the Ca- and Cd-smectites. The montmorillonite OH band was decomposed in three components (marked with a triangle), one of them (3694 cm^{-1})
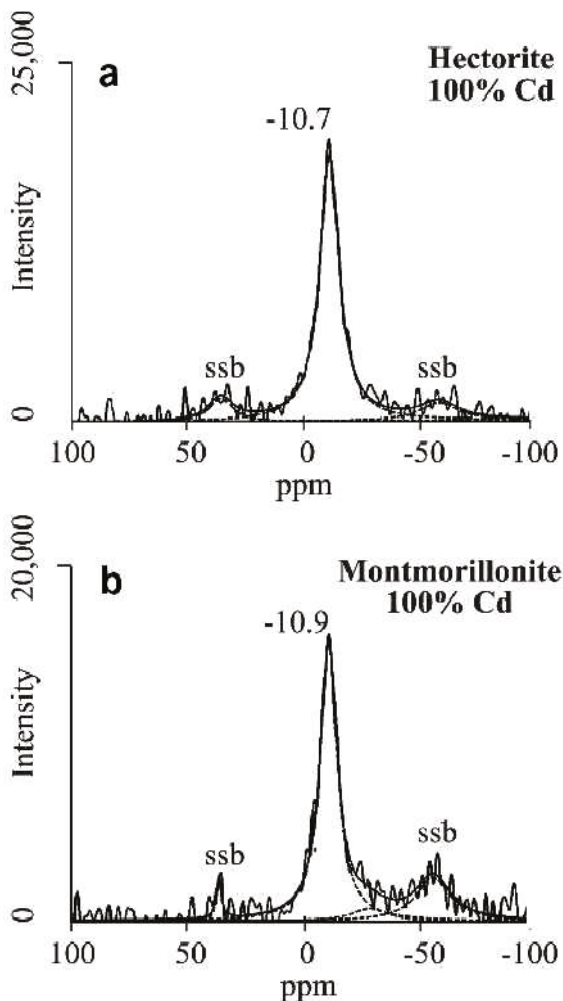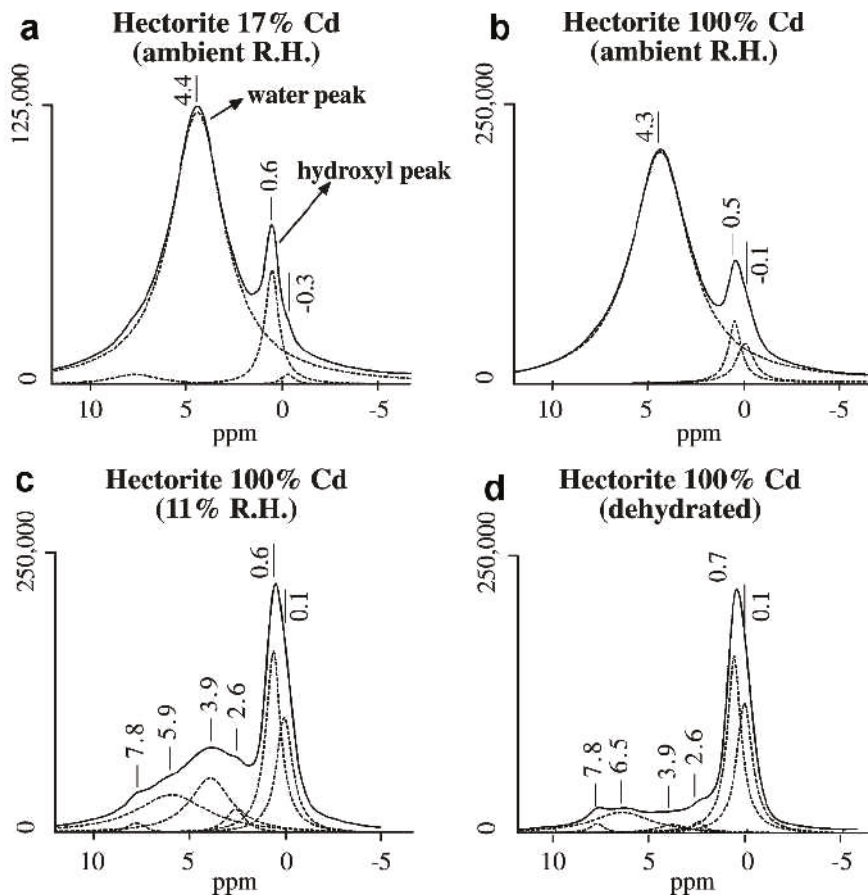
Figure 3. ^{1}H MAS NMR spectra of hectorite with different Cd and water contents, and their calculated components.

very small. The hectorite OH band has only one component. In order to test possible interactions between Cd and the OH groups, the positions of the band maxima and their intensities (areas) were analyzed with respect to Cd content and the angle between the sample film and the incident IR beam. Band positions varied only within the resolution limit of 8 cm^{-1} (typically 3–4 cm^{-1}), indicating little or no effect of the interlayer cation on the strength of the O–H bond. However, the intensity of the OH-stretching band seems to be affected. In Figure 7, the intensity of the OH-stretching band (sum of all components) is represented *vs.* the percentage of Cd exchange, for the two angles of analysis. The intensity values are higher for 45° in both smectite specimens. This is expected in hectorite because the orientation of the O–H vector is perpendicular to the *ab* crystallographic plane and, hence, at 45° the O–H vector has a larger component in the direction of the electric vector of the IR beam. For montmorillonite, the O–H vector orientation at ~16° from the *ab* plane makes the analysis of the effect of the sample orientation on the intensity of the OH-stretching band complex and, in fact, little dependence between the two variables is usually observed. In our data, the montmorillonite intensity

values for 45° are dispersed with no apparent trend, but for 90°, there is a steady decrease with increasing interlayer Cd. In hectorite, there is also an intensity decrease with increasing Cd for 45°, and for 90° the decrease is only observed for the completely Cd-exchanged specimen. The intensity changes in montmorillonite (up to 0.9 absorbance units) are larger than those in hectorite (up to 0.4 absorbance units) but, because of the lower absolute values in hectorite, the relative intensity changes in the latter are larger (53% for 45°).

The contribution by opal to the IR spectrum is assumed not to affect the montmorillonite OH-stretching bands significantly because opal has a broad OH-stretching band most of which lies below 3600 cm^{-1} (Graetsch, 1994) and, hence, it is included within the calculated hydration-water bands.

DISCUSSION

Cd-hectorite

The presence of only one peak in the [113]Cd MAS NMR spectrum of the Cd-exchanged hectorite and the symmetry of the spinning side band pattern (Figure 2a)
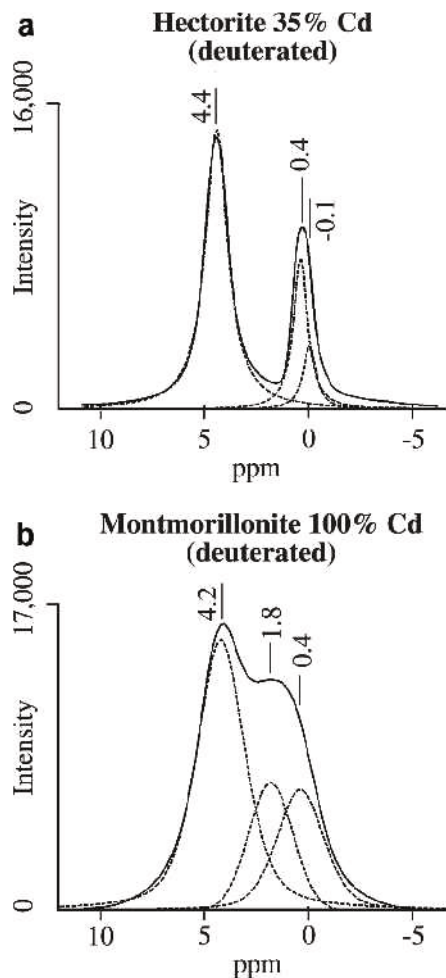
Figure 4. ^{1}H MAS NMR spectra of deuterated hectorite, with 35% Cd content, and montmorillonite, with 100% Cd content, and their calculated components.

Figure 5. ^{1}H MAS NMR spectra of montmorillonite with 100% Cd content and two hydration states, and their calculated components.

indicates a single adsorption site for Cd, probably with an isotropic environment. The XRD patterns of Cd hectorite show a *d* value similar to that of Ca-hectorite, which is of a 2-water layer complex in the interlayer, characteristic of Ca above ~20% relative humidity (MacEwan and Wilson, 1980; Sposito and Prost, 1982; Sposito *et al.*, 1999). Considering this and the similar charge/radius ratio of Cd^{2+} and Ca^{2+}, it is likely that the Cd-hectorite interlayer complex is also a 2-water layer system. On the basis of this speculation and the information from ^{113}Cd MAS NMR in this study, all Cd ions are in the center of the interlayer space surrounded, in the first coordination sphere, by six water molecules in octahedral coordination. The chemical shift of the band at ~ –11 ppm suggests a chemical environment where Cd is not in contact with the charged oxygen atoms in the smectite surface (Ellis, 1983). Di Leo and O'Brien (1999) discussed ^{113}Cd MAS and H-Cd cross-polarization-MAS NMR spectra of Cd-montmorillonite and also interpreted their peak at ~ –10 ppm
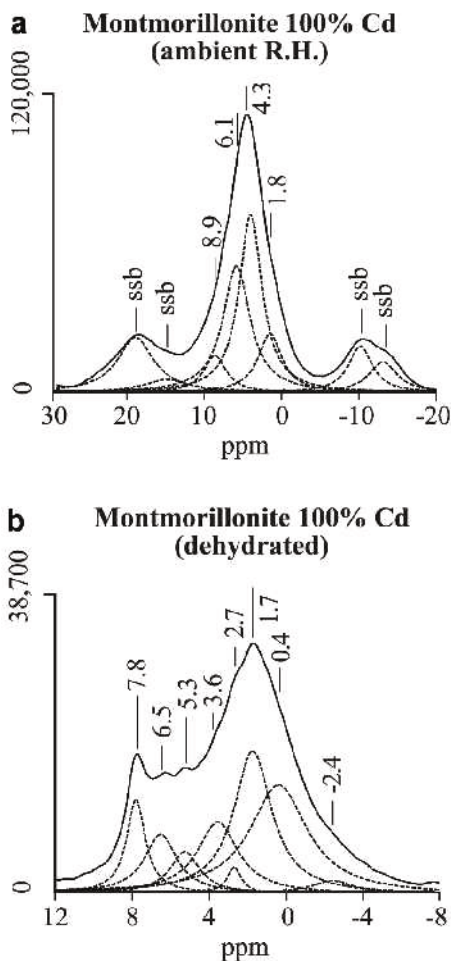
as due to interlayer Cd separated from the basal oxygen atoms by water molecules. They also studied the dynamics of their peak at ~ –10 ppm that showed a quick relaxation, indicating a relatively free motion, which also indicates that Cd is fully coordinated by water molecules rather than adsorbed on immobile oxide ions. Sullivan *et al.* (1998) performed spin-echo double resonance experiments in an attempt to couple the interlayer Cd with octahedral Al and only found coupling in completely dehydrated smectite, indicating that Cd is not in contact with the clay surface if there is hydration water. These results agree with our interpretation.

The experiments in the present work do not provide direct information about Cd mobility in the adsorption site but Tinet *et al.* (1991) showed that smectite layers cause some restriction to it because the ^{113}Cd NMR peak in their experiments became narrower with increasing water/smectite ratios.

In the ^{1}H MAS NMR spectra from hectorite equilibrated at room humidity (Figure 3a,3b) the
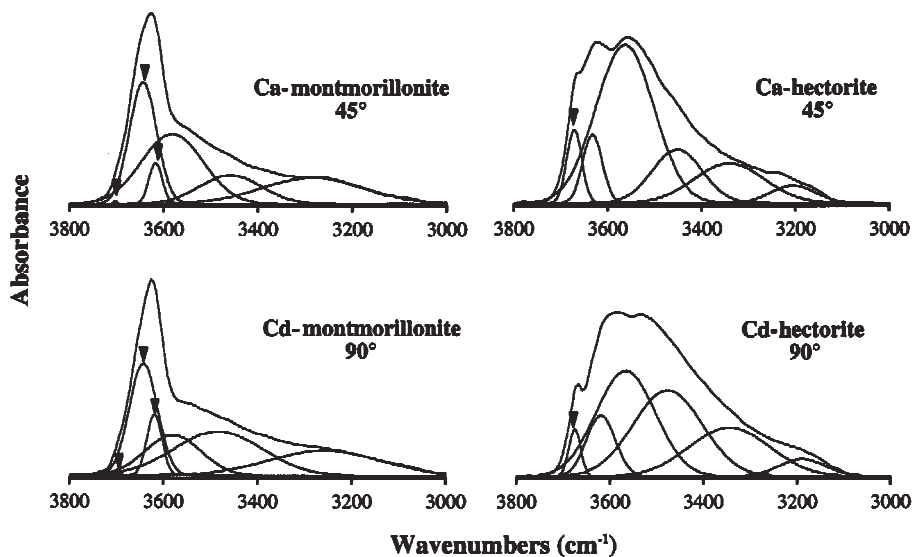
Figure 6. FTIR spectra of Ca- and Cd-exchanged smectite films at 45° and 90° to the incident beam, and their calculated components. The smectite OH-stretching bands are marked with a triangle.

component corresponding to water is quite broad. The broad peak is probably caused partly by the presence of multiple components, *i.e.* of water molecules in different chemical environments, clearly observed when the water

Figure 7. IR OH-stretching band absorbance *vs.* % of adsorbed Cd on smectite measured on films at 45° and 90° to the incident beam.

content decreases (Figure 3c,d), and partly by H–H dipole interaction, which often causes peak broadening (Kirkpatrick, 1988). The latter effect is much reduced after deuteration and the water-proton peak is narrower than in non-deuterated samples (compare Figure 3a with Figure 4a), although this could, in addition, be caused by the disappearance or reduction of some of the components of the overall peak. The fact that the several ^{1}H components are revealed in the more dehydrated samples (Figure 3c,d) could be due simply to the lower intensity of the component at ~4 ppm, which allows the spectrum to be better resolved, or could be due to sites not in rapid exchange on an NMR time scale. There is no information yet about the chemical environments to which these sites correspond and they cannot be used to constrain the structure of the Cd-water complex in the interlayer. Presumably, however, the component at ~4 ppm (Figure 3c,d) corresponds to protons in somehow 'looser' water because its intensity is very low in the least hydrated sample and increases very quickly with water content to become the dominant component. Alba *et al.* (2000) found a relationship between the chemical shift of the overall water-proton peak value and the charge of the interlayer cation in which the peak is shifted to more positive values as the charge of the cation increases. This is explained by a greater proton activity (increased acidic character of water) caused by the higher cation charge. Specifically, they found a chemical shift for the water protons of 4.60 to 4.55 ppm in the presence of trivalent cations, 4.36 ppm for divalent cations, and 4.10 ppm for monovalent cations (Alba *et al.*, 2000 and references therein). The chemical shift of the water-proton peak in the samples equilibrated at ambient relative humidity and those deuterated (Figures 3a,b, 4 and 5a) in this study seem to be in
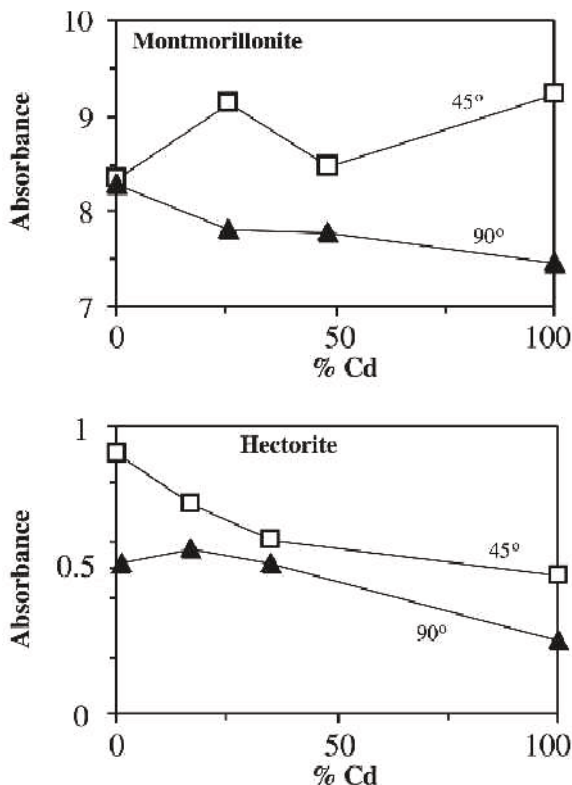
agreement with these results in both hectorite (4.4–4.3 ppm) and montmorillonite (4.2–4.3 ppm).

The hydroxyl-proton signals of hectorite have two components (Figure 3). The experiments using largely deuterated samples (Figure 4) show that the peaks and their components are not affected by H–H dipole interaction with water protons and, hence, the components are intrinsic features. These components change their relative intensities consistently as the Cd-Ca interlayer composition changes from 17 to 100% Cd (see Figures 3a, 4a and 3b). This suggests an interaction between interlayer cations and hydroxyls, and that such interaction depends on the nature of the cation. At the same time, the spectra of the Cd-hectorite with different water contents (Figure 3c and d) show that the two hydroxyl-proton components are not affected by the amount of interlayer water, *i.e.* Cd-hydroxyl interaction remains the same within a wide range of interlayer water content. This is possible if Cd retains water molecules even at the lowest hydration state recorded here so that Cd-hydroxyl interaction occurs always 'through' the surrounding water. Notice also that the number of water molecules between one Cd ion and one OH group must be similar in all hydration states to preserve the relative intensities of the two components. Hence, there must be only one water molecule 'connecting' each Cd ion with one corresponding OH group, which is compatible with both the octahedral structure of the water-Cd complex in the fully hydrated smectite (Sposito *et al.*, 1999) and the low water availability of the mostly dehydrated specimen. According to Figures 3a, 4a and 3b (17, 35 and 100% interlayer Cd content, respectively), Cd causes some hydroxyl protons to resonate at more negative ppm values (−0.3/−0.1 ppm) because this peak grows in intensity from 17 to 100% Cd occupancy. The structural formula indicates that there are only 0.27 (or some more, see materials and methods) Cd atoms per $(OH, F)_2$, where F should be a minor component, and thus not all OH groups can be affected by neighbor Cd ions. This could be the reason why the OH peak component at more positive ppm values remains in the 100% Cd-exchanged hectorite. The relative intensity of the components in Figure 3b, c and d indicates that ~40–50% of the hydroxyls are affected, which is possible if every Cd ion is bridged by a water molecule to one OH group in the upper layer and one in the lower layer. Specifically, considering ~0.3 Cd ions per $(OH, F)_2$, they would be affecting 0.6 OH groups, which can be roughly within 40–50% of the total, depending on the amount of F. Similarly, for the sample containing 17% Cd (see Figure 3a), the intensity of the peak at more negative ppm values (*i.e.* −0.3 ppm) is 7% of the total. In this case there would be ~0.05 Cd ions per $(OH,F)_2$ affecting ~0.1 hydroxyls, which is ~7%. However, the same relation does not seem to hold as precisely for the sample with 35% Cd because the area of the peak at more negative ppm values is 26% of the total area

whereas the ~0.11 Cd atoms per $(OH,F)_2$ would be affecting only 11–15% of the OH groups.

Splitting of the ^{1}H NMR hydroxyl-proton peak can also be produced by Fe location in different neighboring octahedral positions, as reported by previous experiments with static and oriented specimens of trioctahedral micas (Sanz, 1990 and references therein) but this would be negligible here due to the very low Fe content. In any case, splitting of the ^{1}H NMR signal caused by different octahedral cation configurations can be ruled out here because it would be permanent and not vary with interlayer Cd content, as in this study.

The IR data of the OH-stretching band of hectorite supply some complementary information to NMR. The position of the band is not altered by the extent of Cd exchange, which means that whatever the interaction between the two it is not strong enough to affect the O–H bond. This is compatible with the interpretation that Cd–OH interaction is mediated by a water molecule, and thus not strong. However, Cd content does affect the intensity of the OH-stretching band (Figure 7), which supports the existence of a Cd–OH interaction. It is not clear by which mechanism the intensity loss is produced. A simple mechanism would be the change of the O–H vector orientation but it is not evident how such a change would result in the patterns in Figure 7. Here also we have to expect that only a fraction of the OH groups will be affected by a nearby interlayer Cd and contribute to the intensity decrease.

Cd-montmorillonite

The main features of the ^{113}Cd MAS NMR spectrum of Cd-montmorillonite are the same as for Cd-hectorite, indicating the same types of adsorption site and environment, except for a low-intensity component at ~ −25 ppm. The presence of larger amounts of non-clay mineral phases (5% calcite and 5% opal) as compared with hectorite may suggest that the low-intensity component is due to Cd adsorption on these phases. However, we ruled out this interpretation for two reasons. First, because those very small amounts of calcite and opal, with very low adsorption capacity, will have a negligible contribution to Cd adsorption, and are not detectable by NMR (Sommers, 1988). Second, the shape of the spectrum is similar to that obtained by Bank *et al.* (1989; MAS spectra in Figures 1–3 in their article) for Cd-montmorillonite, with a higher background and spinning-side band on the right of the central peak, which suggests an intrinsic characteristic of Cd adsorbed on montmorillonite.

A possible interpretation of the component at ~ −25 ppm is that it corresponds to a small amount of Cd adsorbed on edges of montmorillonite crystals, where Cd interacts strongly with the oxygen ions and therefore has a more negative chemical shift (Di Leo and O'Brien, 1999). However, even if some Cd ions can adsorb in the edges, this cannot account for the peak at −25 ppm

because the hectorite also has crystal edges and there is no −25 ppm component in its Cd NMR spectrum. It appears that the concentration of the exchange solution affects the type of Cd species and their adsorption site, and Di Leo and O'Brien (1999) suggested that high concentrations (2 N $CdCl_2$ in their study) cause some Cd to adsorb on the edges of montmorillonite, whereas only interlayer Cd is detected for low-concentration solutions (0.2 N $CdCl_2$ in their study). According to this, our maximum $CdCl_2$ concentration of 0.2 N should not cause detectable edge adsorption. Thus, the small peak at ~−25 ppm may be interpreted as Cd in closer interaction with basal oxygen atoms where there is an excess of negative charge produced by Al for Si substitution. This may explain why Cd-hectorite, which has no tetrahedral substitution, does not produce such a [113]Cd MAS NMR peak. This interpretation is supported by the results from Laperche *et al*. (1990) who analyzed Cd-vermiculite and found that the [113]Cd MAS NMR peak moved to more negative ppm values with decreasing interlayer water content, *i.e.* with increasingly favored Cd–basal oxygen interaction.

The ^{1}H MAS NMR spectrum of hydrated Cd-montmorillonite (Figure 5a) does not show as much detail as those of Cd-hectorite because the hydroxyl-proton peak is closer to the water-proton peak and is not well resolved. However, the spectra with low water content and after deuteration (see Figures 5b and 4b, respectively) allowed decomposition of the hydroxyl-proton peak and showed the presence of two components, similar to those in Cd-hectorite. However, their relative intensities are inverted, with 40–47% of the total intensity for the component at ~1.7 ppm and 60–53% for that at 0.4 ppm. Since the error involved in this decomposition is larger because of the overlap with the water-proton peaks and the relative area values are still similar to those in hectorite, the features may be interpreted, as in hectorite, as being due to Cd–OH interaction mediated by a water molecule.

The FTIR experiments with a 90° angle between the clay film and the IR beam (Figure 7) may suggest, as in hectorite, that Cd somehow affects OH-stretching intensity, although the erratic values at 45° do not help the interpretation of data. The fact that Cd affects OH-stretching intensity to a lesser extent in montmorillonite than in hectorite may be related to the different orientation of the OH vector that brings the OH proton closer to the interlayer space in hectorite.

Reinterpretation of previous results

In some of the previous works there is inconsistency in the location and interpretation of the [113]Cd NMR (both static and MAS) signature of Cd-smectite. Di Leo and O'Brien (1999) observed that the concentration of the $CdCl_2$ solution used to exchange smectite affects both the type of Cd species sorbed and the adsorption sites. Below a 0.2 N concentration, the major Cd species

is Cd^{2+}, which is replaced by $CdCl^+$ above this value and with still higher concentrations $CdCl_{2solv.}$ and $CdCl_4^{2-}$ become increasingly present. For sufficiently low concentrations, Cd^{2+} is the only species adsorbed and enters the interlayer of smectite occupying the center of the water-cation complex and causing a single peak at ~−11 ppm in [113]Cd MAS NMR spectra. This or a similar peak was also found in our work (0.004–0.2 N $CdCl_2$), Bank *et al*. (1989, 0.05 N $CdCl_2$), Jun *et al*. (1996, 0.08 N $CdCl_2$) and Sullivan *et al*. (1998, $CdCl_2$ concentration not specified). Bank *et al*. (1989) reported the [113]Cd MAS NMR peak at ~10 ppm rather than −11 ppm, but this could be due to the fact that Cd is in low concentration in an NH_4^+-dominated interlayer. In contrast, Tinet *et al*. (1991) used a 2 N $CdCl_2$ solution and static experiments and found an asymmetric [113]Cd NMR signal spanning from 92–42 to 10 to −8 ppm, depending on the sample (two smectites and vermiculite). They also performed analyses with oriented smectite films at different angles to the magnetic field and obtained a single, somewhat asymmetric peak whose maximum moved within the above ranges from more negative to more positive ppm values with decreasing angles, indicating an anisotropic chemical shift that they interpreted as due to Cd interaction with the clay surface. However, Di Leo and O'Brien (1999) showed that using a 2 N $CdCl_2$ solution causes a large amount of the $CdCl^+$ species to be adsorbed in the interlayer, observed as a very wide peak centered at ~116 ppm in [113]Cd MAS NMR spectra. The CP MAS experiments of these samples showed that this wide peak has two main components, occurring at ~106 and 71 ppm. The first corresponds, following the assignment of Ackerman *et al*. (1979), to interlayer Cd chloride resonating between $CdCl^+$, with a chemical shift of 89 ppm, and $CdCl_2$, with a chemical shift of 114 ppm. According to this, the anisotropic chemical shift observed by Tinet *et al*. (1991) could have been produced by the presence of $CdCl^+$ in the interlayer and the disturbance of the Cd^{2+}-water complex. The chemical shift of 89 ppm for $CdCl^+$ found by Ackerman *et al*. (1979) is close to the value of the parallel component of the chemical shift tensor observed for the montmorillonite sample by Tinet *et al*. (1991). On this basis, the $CdCl^+$ ions may have oriented themselves in the interlayers of smectite crystals (probably with the Cd-Cl axis normal to the c^* direction) in such a way that the parallel component of the signal observed by Tinet *et al*. (1991) was strong and the normal component weak. Then, the chemical shift anisotropic tensor values recorded by the authors could be due to Cd^{2+} interacting with the clay surface and to $CdCl^+$ ions. In this way, the static [113]Cd NMR spectrum of a powder sample shows the contribution of both Cd species, resulting in a broad asymmetric peak in which two main components are observed, while analysis of an oriented film at any angle is dominated by the corresponding strong component, at that angle, of one

of the Cd species. Specifically, at 90º, only Cd^{2+} is observed (10 to −8 ppm, strong normal component), whereas at 0º only $CdCl^{+}$ is observed (92−42 ppm, strong parallel component) and at intermediate angles the peak position moves between the two.

CONCLUSIONS

The ultimate aim of this study is to gain information on how Cd, one of the most widespread heavy metal contaminants, is adsorbed on smectite. Cadmium concentration in surface waters and groundwaters is very low. In these conditions, and in the absence of strong complexing agents, free Cd^{2+} is the dominant species. This study confirms Di Leo and O'Brien's (1999) findings that in these conditions Cd^{2+} adsorbs on smectite mainly in the interlayer, with any possible edge-adsorption remaining undetectable by NMR. Furthermore, the present study shows that Cd occupies the center of the interlayer (along the $c*$ direction) surrounded by water molecules, probably in octahedral coordination as happens with Ca. In the absence of tetrahedral substitution in the smectite, all Cd ions maintain this disposition. If the smectite has tetrahedral substitution, some Cd ions, those near oxygen atoms with excess negative charge, seem to be attracted towards them and interact more strongly with them. This interaction causes a second ^{113}Cd NMR peak at more negative ppm values than the main peak. The Cd interaction with the smectite basal surfaces is also manifested in that Cd affects the OH groups. This is observed by ^{1}H NMR (Cd causes a second ^{1}H NMR component to appear) and FTIR spectroscopies (OH vibration intensities are affected by Cd). The interaction, however, must not be strong because it does not alter the strength of the O−H bond. This weak interaction is consistent with the above description of the Cd−water complex, in which there is one water molecule (apical water molecules in the octahedron) between the Cd ion and the smectite basal surface. The Cd ions retain the water molecules linking them to the OH groups even at very low hydration states, as shown by the fact that the hydroxyl-proton ^{1}H NMR peaks are not altered by dehydration. The ^{1}H NMR spectra in this study show water molecules in different environments, although these cannot be identified.

ACKNOWLEDGMENTS

REFERENCES

Ackerman, J.J.H., Orr, T.V., Bartuska, V.J. and Maciel, G.E. (1979) Effect of halide complexation of cadmium(II) on cadmium-113 chemical shift. *Journal of the American Chemical Society*, **101**, 341−347.

Alba, M.D., Becerro, A.I., Castro, M.A. and Perdigón, A.C. (2000) High-resolution ^{1}H MAS NMR spectra of 2:1 phyllosilicates. *Journal of the Chemical Society, Chemical Communications*, 37−38.

Alba, M.D., Becerro, A.I., Castro, M.A. and Perdigón, A.C. (2001) Hydrothermal reactivity of Lu-saturated smectites: Part II. A short-range order study. *American Mineralogist*, **86**, 124−131.

Ames, L., Sand, L. and Goldrich, S. (1958) A contribution on the Hector, California, bentonite deposit. *Economic Geology*, **53**, 22−37.

Bank, S., Bank, J.F. and Ellis, P.D. (1989) Solid-state ^{113}Cd nuclear magnetic resonance of exchanged montmorillonites. *Journal of Physical Chemistry*, **93**, 4878−4855.

Batchelder, M. and Cressey, G. (1998) Rapid, accurate phase quantification of clay-bearing samples using a position-sensitive X-ray detector. *Clays and Clay Minerals*, **46**, 183−194.

Cressey, G. and Schofield, P.F. (1996) Rapid whole-pattern profile-stripping method for the quantification of multiphase samples. *Powder Diffraction*, **11**, 35−39.

Di Leo, P. (2000) A nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) study of glycine speciation on a Cd-rich montmorillonite. *Clays and Clay Minerals*, **48**, 495−502.

Di Leo, P. and O'Brien, P. (1999) Nuclear magnetic resonance (NMR) study of Cd^{2+} sorption on montmorillonite. *Clays and Clay Minerals*, **47**, 761−768.

Ellis, P.D. (1983) Cadmium-113 magnetic resonance spectroscopy. *Science*, **221**, 1141−1146.

Graetsch, H. (1994) Structural characteristics of opaline and microcrystalline silica minerals. Pp. 209−232 in: *Silica. Physical Behavior, Geochemistry and Materials Applications* (P.J. Heaney, C.T. Prewitt and G.V. Gibbs, editors). Reviews in Mineralogy, **29**. Mineralogical Society of America, Washington, D.C.

Grandjean, J. and Robert, J.L. (1997) Multinuclear magnetic resonance studies on aqueous suspensions of synthetic saponites. *Journal of Colloid Sciences*, **187**, 267−273.

Hall, P.L. (1987) Clays − their significance, properties and origins. Pp. 1−25 in: *A Handbook of Determinative Methods in Clay Mineralogy* (M.J. Wilson, editor). Blackie, Glasgow and London.

Jun, S., Chung, K.H. and Moon, C.H. (1996) Adsorption of cadmium on montmorillonite investigated by ^{113}Cd NMR spectroscopy. *Environmental Technology*, **17**, 655−660.

Kim, Y., Cygan, R.T. and Kirkpatrick, R.J. (1996a) ^{133}Cs NMR and XPS investigation of cesium adsorbed on clay minerals and related phases. *Geochimica et Cosmochimica Acta*, **60**, 1041−1052.

Kim, Y., Kirkpatrick, R.J. and Cygan, R.T. (1996b) ^{133}Cs NMR study of cesium adsorbed on the surface of kaolinite and illite. *Geochimica et Cosmochimica Acta*, **60**, 4059−4074.

Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. Pp. 341−404 in: *Spectroscopic Methods in Mineralogy* (F.C. Hawthorne, editor). Reviews in Mineralogy, **18**. Mineralogical Society of America,

Washington, D.C.

Klinowski, J., Cheng, C., Sanz, J., Rojo, J.M. and Mackay A.L. (1998) Structural studies of tabasheer, an opal of plant origin. *Philosophical Magazine* A, **77**, 201–216.

Laperche, V., Lambert J.F., Prost, R. and Fripiat, J.J. (1990) High-resolution solid-state NMR of exchangeable cations in the interlayer surface of swelling mica: ^{23}Na, ^{111}Cd, and ^{133}Cs vermiculite. *Journal of Physical Chemistry*, **94**, 8821–8831.

MacEwan, D.M.C. and Wilson, M.J. (1980) Interlayer and intercalation complexes of clay minerals. Pp. 197–248 in: *Crystal Structures of Clay Minerals and their X-ray Identification* (G.W. Brindley and G. Brown, editors). Monograph **5**, Mineralogical Society, London.

Madejová, J., Komadel, P. and Kihel, B. (1994) Infrared study of octahedral site populations in smectites. *Clay Minerals*, **29**, 319–326.

Newman, A. (1987) The interaction of water with clay mineral surfaces. Pp. 237–274 in: *Chemistry of Clays and Clay Minerals* (A.C.D. Newman, editor). Monograph **6**, Mineralogical Society, London.

Nolle, A. (1978) Isotropic and anisotropic nuclear magnetic shielding of ^{113}Cd in cadmiumhalides, cadmium chalcogenides and in cadmiumcarbonate. *Naturforsch*, **6**, 666–671.

Russell, J.D. and Fraser, A.R. (1994) Infrared methods. Pp. 11–67 in: *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods* (M.J. Wilson, editor). Chapman &

Hall, London.

Sanz, J. (1990) Distribution of ions in phyllosilicates by NMR spectroscopy. Pp. 103–144 in: *Absorption Spectroscopy in Mineralogy* (A. Mottana and F. Burragato, editors). Elsevier, Amsterdam.

Sommers, M.F. (1988) ^{113}Cd NMR spectroscopy of coordination compounds and proteins. *Coordination Chemistry Reviews*, **86**, 43–134.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites. *Chemical Reviews*, **82**, 553–573.

Sposito, G., Skipper, N., Sutton, R., Park, S.-H., Soper, A. and Greathouse, J. (1999) Surface geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences of the USA*, **96**, 3358–3364.

Sullivan, D.J., Shore, J.S. and Rice, J.A. (1998) Assessment of cation binding to clay minerals using solid-state NMR. *Clays and Clay Minerals*, **46**, 349–354.

Sullivan, D.J., Shore, J.S. and Rice, J.A. (2000) ^{113}Cd double-resonance NMR as a probe of clay mineral cation exchange sites. *American Mineralogist*, **85**, 1022–1029.

Tinet, D., Faugere, A.M. and Prost, R. (1991) ^{113}Cd NMR chemical shift tensor analysis of cadmium-exchanged clays and clay gels. *Journal of Physical Chemistry*, **95**, 8804–8807.