

NMR SPECTROSCOPIC INVESTIGATIONS OF SURFACE AND INTERLAYER SPECIES ON MINERALS, CLAYS AND OTHER OXIDES

R. James Kirkpatrick¹, Yeongkyoo Kim¹,
Charles A. Weiss², Randall T. Cygan³

¹Department of Geology
University of Illinois
Urbana, Il 61801, USA

²U. S. Army Engineer Waterways Experiment Station
Concrete Technology Division, Structures Laboratory
Vicksburg, MS 39180, USA

³Geochemistry Department
Sandia National Laboratories
Albuquerque, NM 87185, USA

INTRODUCTION

The behavior of chemical species adsorbed on solid surfaces and exchanged into clay interlayers plays a significant role in controlling many natural and technologically important processes, including rheological behavior, catalysis, plant growth, transport in natural pore fluids and those near anthropogenic hazardous waste sites, and water-mineral interaction. Adsorption and exchange reactions have been the focus of intense study for many decades (see, e.g., references 1-6 for introductions). Only more recently, however, have there been extensive spectroscopic studies of surface species (e.g., references 7-11). Among the spectroscopic methods useful for studying surface and exchanged species (e.g., infrared, X-ray photoelectron spectroscopy [XPS] and X-ray absorption spectroscopy [XAS]), nuclear magnetic resonance spectroscopy (NMR) has the considerable advantage of providing not only structural information via the chemical shift and quadrupole coupling constant but dynamical information in the Hz - mHz range via lineshape analysis and relaxation rate measurements.^{7,12-14} It is also possible to obtain data in the presence of a separate fluid phase, which is essential for many applications. This paper illustrates the range of applications of NMR methods to surface and exchanged species through review of recent work from our laboratory on Cs in clay interlayers and Cs, Na and phosphate adsorbed on oxide surfaces. The substrate materials used for these experiments and our long-term objectives are related to problems of

geochemical interest, but the principles and techniques are of fundamental interest and applicable to a wide range of technological problems.

INTERLAYER EXCHANGED Cs

Cations exchanged into the interlayers of expandable clays (smectites)¹⁵ are comparatively easy to study with NMR methods because the cations become major components of the phase and their concentrations are often several wt %. In addition to Cs; Li, Na, K, and Cd have been studied by NMR.¹⁶⁻²¹ We have chosen to investigate ¹³³Cs because it is a significant component of nuclear waste, because it provides an end-member case as the least electronegative cation, and because it has desirable nuclear properties (100% abundance, relatively high frequency, 65.5 MHz at H₀ = 11.7 T, and small quadrupole moment).²²⁻²⁴

Clays are ubiquitous in near surface geological environments and are used in a wide range of technological applications. Because many of them have large cation exchange capacities they greatly affect cation reactivity and transport in natural and hazardous waste environments, and they have found application as, e.g., sorbants and molecular sieves. The environments and dynamical behavior of interlayer cations have proven difficult to study directly, because most clays lack long-range order and, thus, the interlayer sites are poorly probed by diffraction methods. In contrast, NMR provides a direct probe of the local cation environments and their dynamical behavior.

The ¹³³Cs NMR behavior of Cs-exchanged smectites illustrates well the kinds of information that can be obtained.²²⁻²⁴ Smectites are phyllosilicates similar in some ways to micas. They have layer structures consisting of a sheet of octahedral sites sandwiched between two sheets of tetrahedral sites, the so called TOT or 2:1 structure. In most smectites the tetrahedral sites are occupied by Si and the octahedral sites by Al, Fe, Mg, Li and other cations. The TOT layers develop net negative charge by aliovalent substitution in both the octahedral and tetrahedral sites, causing the attraction of cations and water molecules into the interlayer regions. Cation exchange can be quite rapid, because the interlayer regions are two dimensional and exposed to exterior fluids.

We have done our experiments with hectorite, which is a 2:1 smectite that develops negative layer charge by substitution of Li for Mg in the octahedral sheet.^{22,23} Samples were prepared by multiple exchange in 1.0 and 0.1 M CsCl solutions until essentially complete Cs-exchange was reached (97% of the interlayer cations). Temperature dependent data are essential to interpret the results, because there is rapid exchange of Cs among different interlayer sites at room temperature (RT).

At temperatures greater than -10°C, the ¹³³Cs NMR spectrum of a Cs-exchanged hectorite in contact with 1.0M CsCl solution (a slurry sample) consists of two peaks, one between 3.5 and

10.9 ppm and the other between -15.2 and -8.3 ppm (Figure 1). These peaks are readily assigned to Cs in the CsCl solution (positive peak) and Cs in the clay interlayer (negative peak). With decreasing temperature the peak for the solution disappears between -30 and -40°C as the solution freezes and CsCl precipitates (peak at 228.1 ppm). The peak for Cs in the interlayer begins to split into two peaks at about -20°C, which at temperatures less than -70°C have values near 27 and -29 ppm. Such peak splitting is classical behavior for dynamical averaging between two sites, and the spectra can be used to determine frequencies of exchange between these two sites via line shape analysis. The two peaks are resolved at low temperature, because Cs is either not exchanging between the two sites or is doing so at frequencies an order of magnitude or more less than the peak separation, which is in the kHz range. As Cs atoms begin to exchange between the two sites with increasing temperature their nuclei take on a chemical shift that is the abundance weighted average for the two sites. Complete averaging occurs when the exchange frequency is approximately an order of magnitude greater than the peak splitting (ca. 10 kHz here). For our samples averaging appears to begin near -70°C and to be complete for most Cs near -20°C. There is some site heterogeneity, as can be expected for a complex natural sample.

The two interlayer sites at low temperatures are assigned to Cs tightly bonded to the oxygens of the basal surface (near -29 ppm) and to Cs less tightly bonded to the basal oxygens and located more in the center of the interlayer (near 27 ppm). For both of these types of sites, the Cs is also coordinated by water molecules. The water keeps the TOT layers separated and is also undergoing site exchange. Thus, space is available for the Cs to move among sites. The frequency of this motion, however, is orders of magnitude less than typical lattice vibrational frequencies and is probably best thought of as self-diffusion coupled to the motion of the water molecules.

The dynamical behavior of the slurry sample contrasts dramatically with the rigid Cs observed for a fully dehydrated Cs-exchanged hectorite (Figure 2). In the absence of interlayer water, Cs is present in two sites coordinated only by basal oxygens. These are probably 9-coordinate (near 30 ppm) and 12-coordinate (near -120 ppm). The other peaks in the spectra are spinning sidebands, which are the result of magic angle spinning and a relatively large site asymmetry unaveraged by atomic motion.

The results for the hectorite slurry sample also contrast with those for a Cs-exchanged vermiculite. Vermiculite is a 2:1 clay mineral that develops its layer charge primarily by Al for Si substitution in the tetrahedral sheet. The total substitution is also much greater than in smectites. Thus, the amount of negative charge and the distance to the interlayer cation from the site of charge development is much less in vermiculites than in hectorite. The net effects for vermiculite are that interlayer Cs causes the interlayer region to dehydrate and collapse, forcing Cs to occur in only one site (near 57 ppm, data not shown) and preventing any dynamical behavior near room temperature.

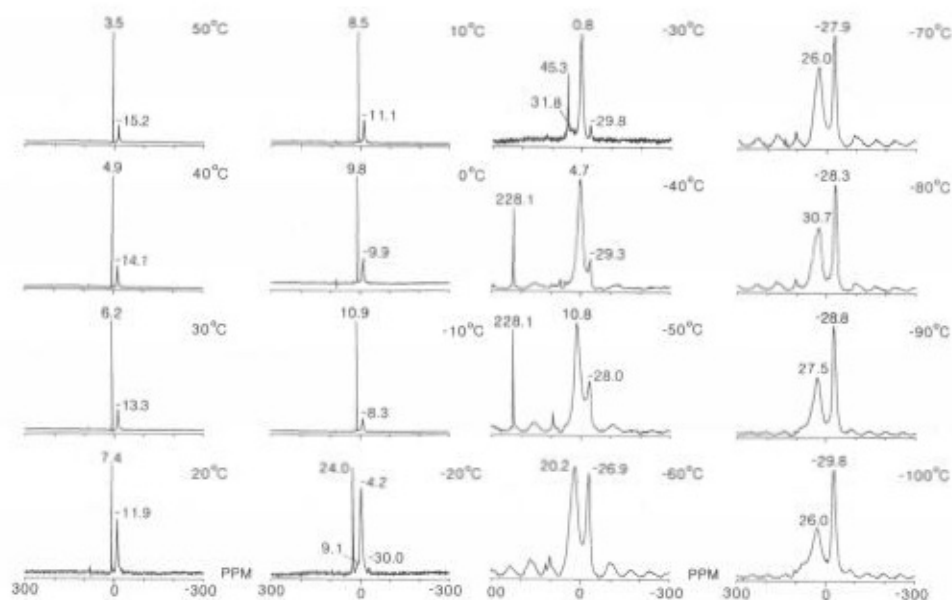


Figure 1. ^{133}Cs MAS NMR spectra of Cs-exchanged hectorite in a 1.0 M CsCl slurry at temperatures between 50 and -100°C . The H_0 field strength was 8.45 T. After reference 22.

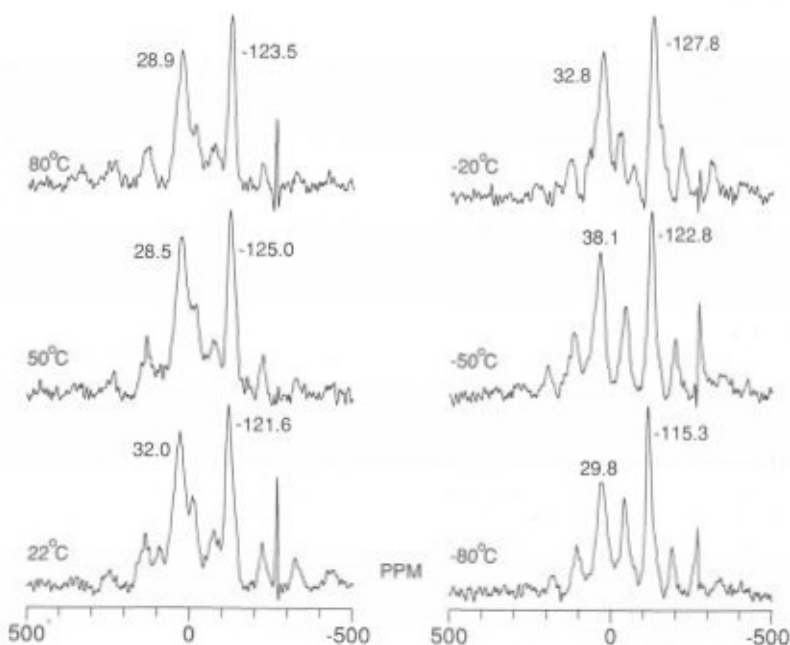


Figure 2. ^{133}Cs MAS NMR spectra of Cs-exchanged hectorite sample dehydrated at 500°C before analysis at temperatures from 80 to -80°C . The labeled peaks near -120 and $+30$ ppm are true center bands, and the other peaks are spinning sidebands. After reference 22.

Cs ADSORPTION ON SURFACES

Cations adsorb on solid surfaces for the same fundamental reason that they exchange into clay interlayers or zeolitic cavities, that is, to balance local negative charge. The molecular scale mechanisms of surface adsorption, however, can be significantly different. In clay interlayers all the oxygen atoms of the basal surface are 2-coordinate by tetrahedral cations (Si,Al). Some exterior surfaces are structurally similar to clay interlayers, e.g., the basal surfaces of clay particles, but many surfaces are very different, containing large numbers of broken bonds and locally uncompensated charge. pH dependent hydrogen adsorption/desorption greatly affects surface charge, with positive charge occurring at low pH and negative charge at high pH. The details vary greatly with bulk phase composition. For large, low-charge cations such as Cs, the presence or absence of a bulk aqueous phase and relative humidity (RH) have important effects. At low RH there are few water molecules on the surface, and the cations must interact directly with the surface oxygens. As RH increases the equilibrium number of surface water molecules increases, and at RHs approaching 100% there is a surface film many molecules thick that behaves like bulk water. For typical phyllosilicates (kaolinite and mica) there are 1, 2, and 3 statistical monolayers of adsorbed water at 10%, 60% and 80% RH respectively.^{25,26}

The ¹³³Cs NMR results for Cs on the surfaces of illite, kaolinite, boehmite and silica gel (Figure 3) show that for this large, low charge cation the surface behavior is quite similar to the interlayer behavior. They also illustrate the capabilities of NMR methods to probe surface species and the effects of RH on the structural environments and dynamical behavior of the Cs.^{24,27} The samples were prepared by immersing 0.5 gm of powdered solid in 50 ml of 0.1M CsCl solution at 25°C for 5 days. Final pHs were between 4.60 and 7.77, greater than the zero point of charge, except for boehmite, which has a ZPC of ca. 8.0.²⁸ The solution was removed from the samples by filtering through a millipore filter with no washing except when indicated. The extent of removal of the solution varies among the samples due to varying permeability and significantly affects the spectra. Silica gel is an amorphous, high surface hydrous silica. Illite is a 2:1 phyllosilicate with a composition approaching muscovite mica and little interlayer exchange capacity. Kaolinite is a 1:1 phyllosilicate with a sheet of tetrahedra occupied by Si linked to a sheet of octahedra occupied primarily by Al. Boehmite is γ -AlO(OH) and has a layer structure based on Al-O,OH octahedra.

For boehmite (Figure 3D) the solution was removed very effectively by filtering, and only those Cs atoms tightly bound to the surface (Stern layer)⁶ are preserved in the sample. The amount of adsorbed Cs is small (ca. 0.0016 atoms/Å²), as expected at pHs less than the ZPC. At ca. 0% RH (over solid P₂O₅) there is one broad peak due to Cs in asymmetrical environments coordinated by surface oxygens and what few water molecules are on the surface. At higher RHs, the peaks are much narrower, indicative of Cs in very symmetrical, time-averaged environments coordinated to both surface oxygens and water molecules and probably undergoing exchange among sites at

frequencies > ca. 10 kHz. The chemical shifts become less positive as the surface Ca/H₂O ratio decreases, paralleling the variation in bulk solutions.^{2,29}

For the silica gel (Figure 3A), the solution was removed slightly less effectively, and more Cs was left (ca. 0.0020 atoms/Å²). The spectral behavior is quite similar to that of boehmite, except that there is a peak due to surface Cs coordinated by only water molecules and not in contact with the surface oxygens (so-called outer sphere complexes)^{2,3} at 30% RH. Complete dynamical averaging among sites at frequencies greater than ca. 10 kHz occurs at 70% RH and greater.

For illite (Figure 3B) the total amount of Cs adsorbed is two orders of magnitude larger (ca. 0.26 atoms/Å²) due primarily to the permanent charge developed by substitution of Al for Si in the tetrahedral sites and to less efficient filtering of the solution caused by lower sample permeability. The maximum amount of hydrated Cs that can be accommodated on the illite surface is ca. 0.023 atoms/Å², close to the amount

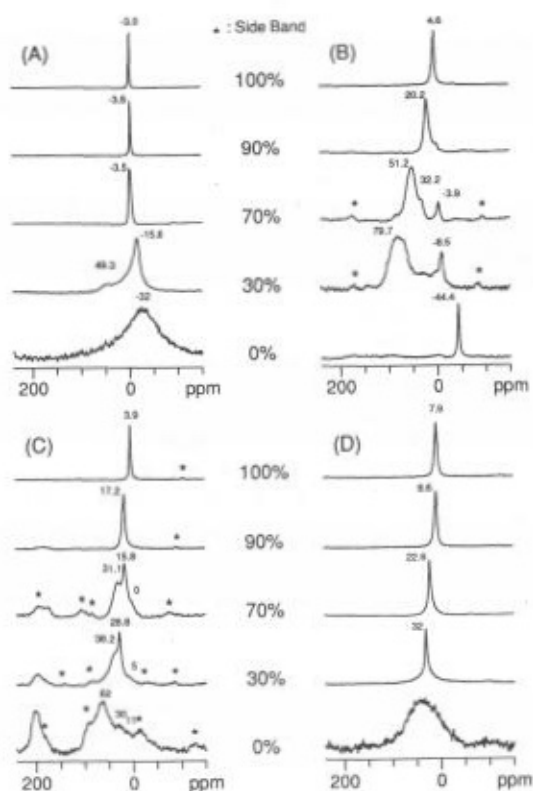


Figure 3. ¹³³Cs MAS NMR spectra of Cs-exchanged (A) silica gel, (B) illite, (C) kaolinite, and (D) boehmite collected at H₀ = 11.7 T, room temperature and the indicated relative humidities. The peaks marked by * are spinning sidebands. After reference 27.

expected if the narrow, most negative peak and its small shoulder are due to Cs in direct contact with the surface oxygens (inner sphere complexes).^{2,3} The remainder of the Cs is in outer sphere complexes and gives rise to the larger more positive peaks. The illite crystallites are blocky, allowing both inner sphere and outer sphere Cs to adsorb on the crystallite tops and bottoms and on the broken edges of the sheets at the crystallite edges. At 30% RH, the inner sphere complexes resonate at -8.5 ppm (crystallite tops and bottoms) and near 0 ppm (crystallite edges), whereas the outer sphere complexes resonate at ca. 80 ppm (broad peak, tops and bottoms) and near 30 ppm (broad peak, edges). Assignment of these peaks is based on the dependence of the chemical shifts on solid composition, solution composition, behavior on washing with DI water, and comparison with the results for smectites. As for the other samples, dynamical averaging at frequencies > ca. 10 kHz occurs at higher RHs.

For kaolinite the sample permeability was very low and the solution was poorly removed. The spectra (Figure 3C) are consequently complex, containing peaks for inner and outer sphere complexes, CsCl precipitate from residual solution (near 200 ppm) and a complex spinning sideband pattern. Spectral resolution is poorer, but at 70% RH for instance, inner sphere complexes resonate near 16 ppm and outer sphere complexes near 31 ppm. Dynamical averaging of the inner and outer sphere complexes occurs at 70% RH, and at 100% RH even the CsCl precipitate is dissolved in the water film and averaged.

Assignment of the observed peaks just described parallels that for Cs in smectite interlayers.^{22,23} Peaks that are more shielded (negative), narrower, vary less with sample condition, vary more with sample composition, and have larger sidebands

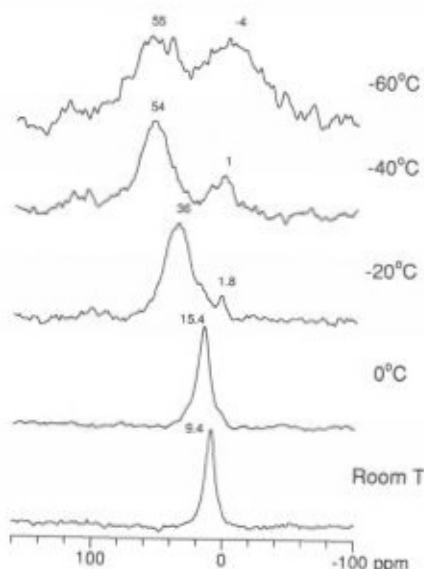


Figure 4. ¹³³Cs MAS NMR spectra of Cs-exchanged illite equilibrated at 100% relative humidity. $H_0 = 11.7$ T. Temperatures as labeled. After reference 27.

are assigned to Cs in inner sphere complexes. Peaks that are broader, less shielded, and that vary more with sample condition are assigned to Cs in outer sphere complexes.

The spectral behavior with varying temperature, sample washing and varying solution concentration provides strong confirming evidence for the assignments and also additional dynamical information. Variable temperature data for illite at 100% RH (Figure 4) show that dynamical averaging at frequencies $>$ ca. 1 kHz ceases near -20°C . At lower temperatures more Cs is transferred to inner sphere complexes (the more negative peak) as few water molecules remain on the surface due to freezing. The peaks also become broad, indicating statically asymmetric sites.

For illite and kaolinite with decreasing solution concentration (Figure 5) there are two important changes. The relative intensity for inner sphere complexes increases, and the chemical shifts become substantially less positive or more negative due to the reduced Cs/water ratio, especially for the outer sphere complexes. Washing with DI water removes most of the Cs in outer sphere complexes and causes spectral changes parallel to those caused by decreasing solution concentration (data not shown).

Na ADSORPTION ON SURFACES AND COMPETITION WITH Cs

The surface behavior of Na is similar to that of Cs, except that inner sphere complexes are not observed. Although Na has the same charge as Cs, it has a smaller ionic radius and thus a larger hydration energy. Consequently, Na retains its shell of hydration waters. For illite (Figure 6), outer sphere complexes resonate between -7.7 and -1.1 ppm and NaCl

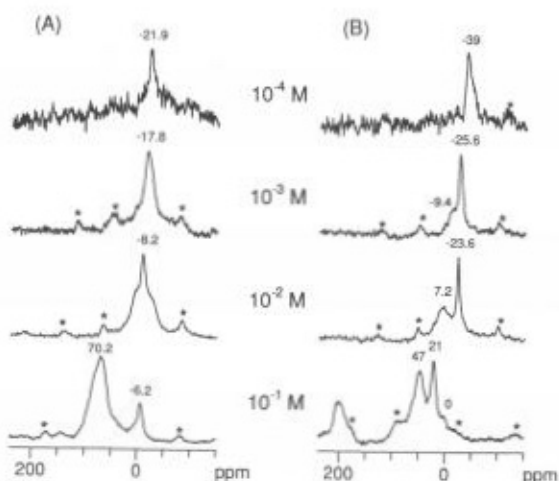


Figure 5. ^{133}Cs MAS NMR spectra of (A) illite and (B) kaolinite Cs-exchanged at the indicated CsCl solution concentrations and collected at room humidity (ca. 35% RH) and $H_0 = 11.7$ T. After reference 27.

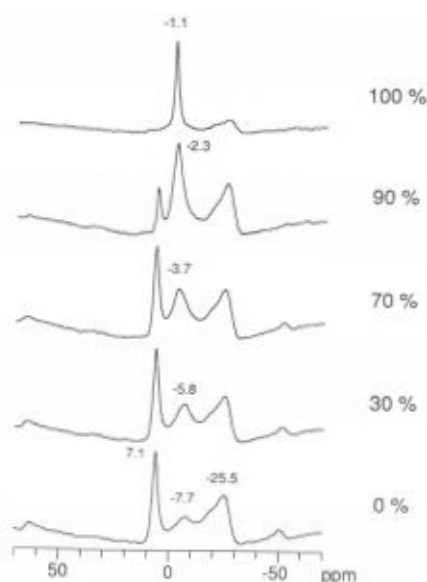


Figure 6. ^{23}Na MAS NMR spectra of illite exchanged in 0.1 M NaCl solutions at 25°C. Spectra collected at $H_0 = 11.7$ T, room temperature, and room humidity (ca. 35% RH).

precipitate from residual solution occurs at 7.1 ppm. The peak at -25.5 ppm and the shoulder near -20 ppm are due to unexchangeable Na bound in the illite, as shown by spectra for non-exchanged samples. With increasing RH at RT the relative amount of Na in the surface water film increases, and the amount of NaCl precipitate decreases, as expected for an increasing thickness of the water film. The peak for the surface Na also narrows, indicating increased dynamical averaging of sites. For mixed Cs/Na solutions, the relative amount of Cs in inner sphere sites increases with decreasing Cs/Na ratio, indicating that Cs competes for sites next to the surface (the Stern layer) more effectively than Na (data not shown).

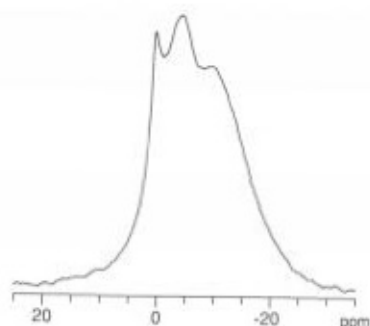


Figure 7. ^{31}P MAS NMR spectrum of a γ -alumina sample in a 0.1 M KH_2PO_4 solution at pH 5.

³¹P NMR OF SURFACE ADSORBED PHOSPHATE COMPLEXES

The structural environments and dynamical behavior of surface phosphate species contrasts strongly with those of Cs and Na described above. For Al-containing substrates, phosphate forms strongly bonded inner sphere complexes through P-O-Al linkages. Our work on the ³¹P NMR behavior of kaolinite, boehmite, and γ -alumina reacted at 25°C for 24 hrs with KH₂PO₄ solutions with concentrations from 10⁻¹ to 10⁻⁴ M and pHs from 3 to 11 are consistent with this idea but also indicate that amorphous K-H-aluminophosphate precipitates form under all conditions examined). The absence of dynamical averaging is clearly indicated by the spectrum of a moist γ -alumina sample (Figure 7). The narrow peak near +2 ppm is due to phosphate in the solution, that near -5 ppm to inner sphere complexes, and that near -12 ppm to amorphous precipitates. The chemical shifts of the inner sphere complexes become less negative with increasing pH, consistent with progressive deprotonation with increasing pH and rapid H-exchange among surface phosphate sites.

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