# $^{133}$Cs NMR STUDY OF Cs REACTION WITH CLAY MINERALS

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## ABSTRACT

To characterize the structural environments and dynamical behavior of Cs in Cs-reacted clay minerals, $^{133}$Cs NMR data were collected. Humidities ranged from ≈0% to 100% R. H., and temperatures ranged from room temperature to -100°C. For montmorillonite, all the detectable Cs is in the interlayers and there is motional averaging of Cs among two or more sites at room temperature. For kaolinite we can distinguish several different Cs sites: Cs relatively tightly bonded on the broken crystallite edges, loosely bonded in the diffuse layer on the surface and in expandable layers which occur as mixed layers in the kaolinite. Cs in the expandable layers, is tightly held compared to Cs on other sites. For all phases the surface Cs is motional averaging at $\nu \geq 100$ kHz at 100% R. H.. $^{133}$Cs NMR studies of Cs-exchanged clay minerals show that the different minerals have Cs in several different structural sites with different dynamical behavior, indicating that careful characterization of the minerals present at a particular waste site is required to predict the behavior of Cs at that site.

## INTRODUCTION

Clay minerals are ubiquitous in soils and many rocks and are used in many industrial applications. An understanding of their chemical behavior is critical for the storage of contaminants because of their surface chemical activity resulting from their small particle sizes and large surface areas. Some clay minerals can adsorb large amounts of cations in their interlayers due to the negative charge caused by the substitution of lower valent cations for higher valent ones in the tetrahedral and octahedral sheets.

$^{137}$Cs is an important component of nuclear waste and its reaction with clay

minerals is significant due to these controlling surface interactions [1]. Its chemical behavior in storage repositories and migration in natural environments are critical issues in the nuclear industry and a fundamental understanding of Cs on mineral surfaces and in clay interlayers is necessary for proper evaluation of waste disposal and retention.

[133]Cs nuclear magnetic resonance (NMR) spectroscopy provides useful information about the structural roles and atomic scale dynamics of Cs in and on clay minerals and zeolites [2, 3, 4, 5, 6, 7]. [133]Cs is readily observed because it has 100 % natural abundance and a small quadrupolar moment compared to other alkali and alkaline earth cations.

## EXPERIMENTAL

The montmorillonite is from Apache County, Arizona (Cheto variety) and the kaolinite is from Washington County, Georgia, obtained from the Source Clay Repository of The Clay Minerals Society. The boehmite was obtained from Alpha Products, and the silica gel from Brinkmann. For the Cs-exchange reactions, 0.5 g of those materials were mixed with 50 ml of 0.1 M CsCl solution for 5 days in Teflon bottles in a water bath at 25°C. The solution was vacuum filtered using a Millipore filter system and air-dried. Some of the samples were washed with different amounts of deionized water during vacuum filtering.

The [133]Cs magic-angle spinning (MAS) 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 Nicolet model 1280 computer and pulse programmer. Most of the spectra were collected at MAS frequencies of 5 to 9 kHz in silicon nitride rotors using a 5 mm probe manufactured by Doty Scientific. Low temperature spectra were collected for montmorillonite samples and washed kaolinite samples at room humidity and 100% R. H.. Those samples were spun in ceramic rotors at 4 kHz in dry $N_2$ with a different 5 mm Doty Scientific MAS probe. To identify the Cs environments in kaolinite after washing, separate samples were heated at 450°C before NMR spectra were collected. Spectra for the materials were also collected at room humidity and 100% R. H. to determine the effects of humidity on the dynamic behavior of Cs in different sites.

## RESULTS AND DISCUSSION

Our [133]Cs NMR spectra for kaolinite, montmorillonite, silica gel, and boehmite show that Cs occurs in several different environments on the surfaces of these materials. These environments include interlayer sites in the clays, relatively tightly bonded sites, loosely bonded sites in the diffuse layer in the thin film of surface water, and CsCl surface precipitates.

For kaolinite, there are at least three different environments of Cs on sam-
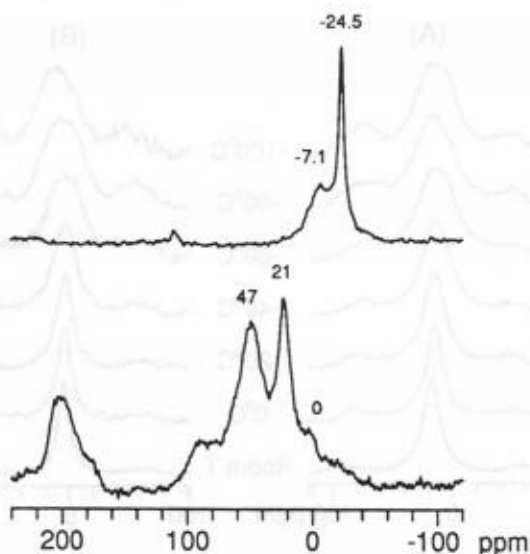
Figure 1: $^{133}$Cs MAS NMR spectra of kaolinite samples air dried after Cs exchange and vacuum filtering (bottom) and washed by deionized water during vacuum filtering and air dried (top). Room humidity.

ples dried after filtering (Fig.1). The broad peak at 200 ppm is probably due to crystalline CsCl precipitated from residual CsCl solution remaining after vacuum filtering. There are two other central peaks at 21 and 47 ppm, and probably a small peak at 0 ppm. The other peaks are spinning sidebands. We assign the peak at 21 ppm to Cs held relatively tightly on the deprotonated broken crystalline edges and the peak at 47 ppm to weakly bonded Cs in the diffuse layer. The peaks for the tightly bonded Cs are narrower and show more spinning sidebands, indicating that these Cs environments are better defined and have less motion than the other sites. At room R. H. 2 to 4 layers of surface adsorbed water are probably present [8].

For the washed kaolinite sample, there are two central peaks at -24.5 and -7.2 ppm. The peak at -24.5 ppm is assigned to Cs in the expandable layers mixed with kaolinite, probably represented by the small 0 ppm peak before washing. Natural kaolinite often contains mixed expandable layers and these defect sites are very important for the measurement of CEC in kaolinite compared to smectites [7, 9]. The -7.2 ppm peak is due to Cs relatively tightly bonded on the surface (21 ppm peak of the unwashed sample).

Cs chemical shifts are very sensitive to the Cs population and humidity. $^{133}$Cs chemical shifts in solutions become less shielded (more positive) at higher CsCl solution concentrations [10, 11]. Thus decreased Cs/H$_2$O ratio on the surface and
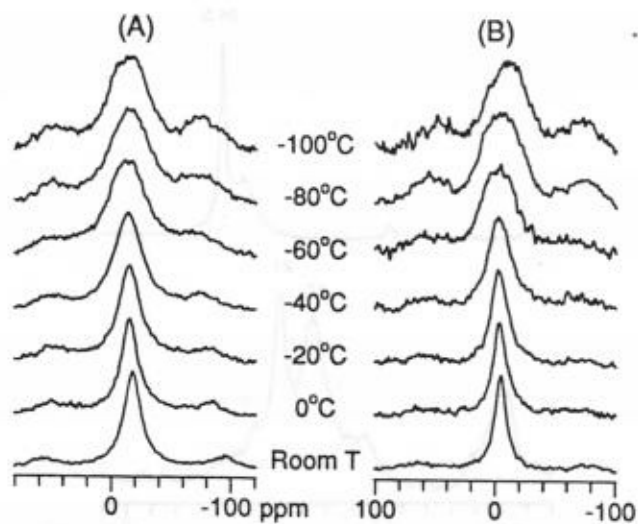
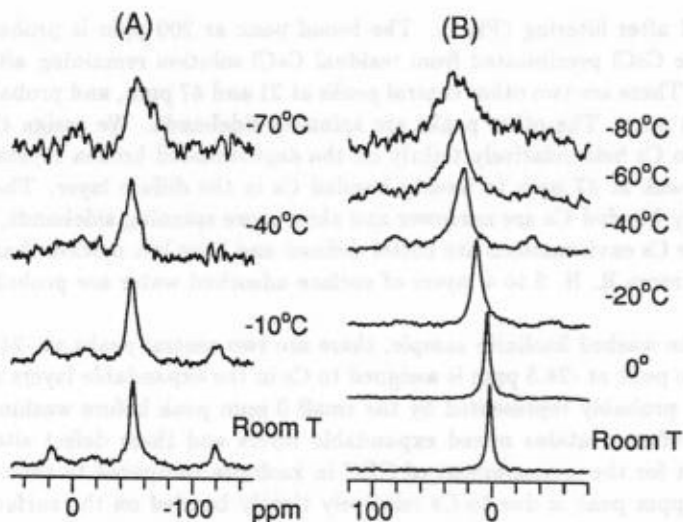Figure 2: $^{133}$Cs MAS NMR spectra of montmorillonite at room humidity (A) and 100% R. H. (B).



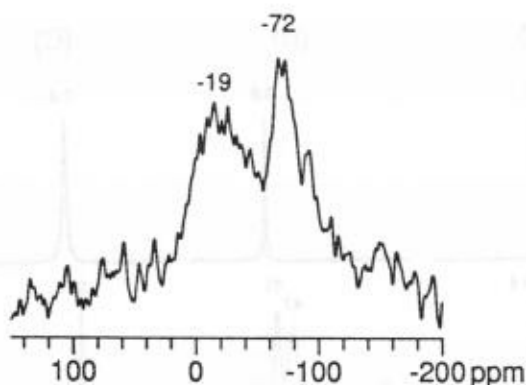Figure 3: $^{133}$Cs MAS NMR spectra of kaolinite at room humidity (A) and 100% R. H. (B).

Figure 4: $^{133}$Cs MAS NMR spectra of Cs-reacted kaolinite after heating at 450°C for 1 hr.

in the interlayer after washing makes the chemical shifts more shielded. The peak for Cs bonded tightly on the surface shows reduced intensity and a more shielded chemical shift after washing, while the peak due to Cs in the diffuse layer is lost entirely. These changes also support our assignments of those peaks. The same intensity loss and changes of chemical shift occur for boehmite and silica gel.

Most of the Cs in the montmorillonite occurs in interlayers (Fig. 2) and, as expected, the chemical shifts are in the range previously reported for smectite clays [5, 6]. The chemical shift at 100% R. H. is less shielded than at room humidity. With higher humidity, the $Cs/H_2O$ ratio in the interlayer decreases, making the $^{133}$Cs chemical shift less shielded. The peak is narrower at 100% R. H. than at room humidity, indicating that there is motion of the Cs at $\nu \geq 10$ kHz at 100% humidity. The frequency of motion decreases at lower temperatures, causing the peak widths to increase with decreasing temperature at both humidities.

The variable temperature spectra of a washed kaolinite show features similar to those of montmorillonite, supporting the occurrence of the same Cs in interlayer sites (Fig. 3). At room temperature and both room humidity and 100% R. H. there is a single narrow peak in the chemical shift range for Cs in interlayers, and the peak width increases with decreasing temperature. The chemical shifts at 100% R. H. are less shielded than those at room humidity, as for montmorillonite. After washing, most of the surface Cs is removed but the Cs in the expandable layers is more tightly held and is not removed. Spectra of washed boehmite and silica gel, which have no expandable layers, do not have this well-defined sharp peak, supporting our conclusion.

The low temperature spectra of the washed kaolinite at room humidity behave like those of montmorillonite, with peak broadening at constant chemical shift. At 100% R. H., however, the chemical shifts become less shielded at lower temper-
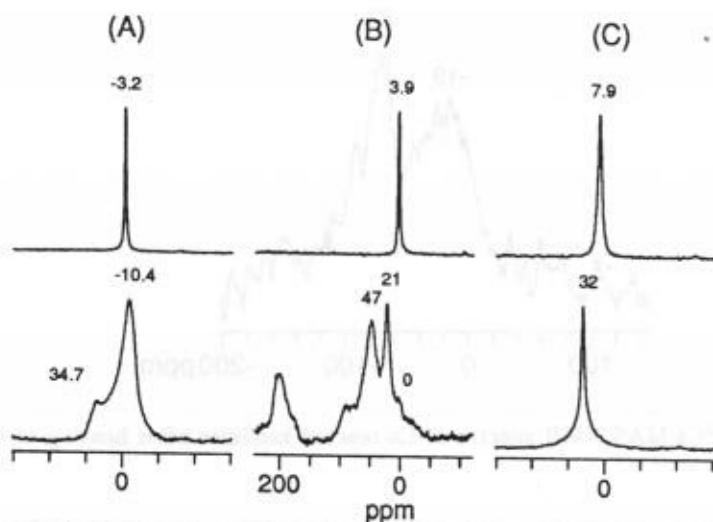
Figure 5: $^{133}$Cs MAS NMR spectra of silica gel (A), kaolinite (B), and boehmite (C) after Cs-exchange at room humidity (bottom) and 100% R. H. (top).

atures, indicating that the interlayer charge of the expandable layers is very low and that at lower temperature some of the interlayer water is frozen resulting in a higher effective Cs/H$_2$O ratio in the expandable layers. Cs in normal smectite does not show this decreased shielding, and it may be a characteristic feature of mixed expandable layers in kaolinite.

The existence of Cs in expandable layers in kaolinite is also verified by the spectra collected after heating the sample at 450°C for 1 hour. Weiss et al. [5, 6] showed that similarly heated Cs-exchanged smectites yield two $^{133}$Cs NMR peaks due to the creation of two new sites after collapse of the layers. Our samples yield two peaks at -19 and 72 ppm, consistent with this interpretation (Fig. 4).

For all phases examined, all the Cs undergoes motional averaging at 100% humidities, as indicated by the single narrow peaks near 0 ppm (Fig. 5). The frequency of this motion is $\geq$ 100 kHz.

Boehmite shows one peak at room humidity and silica gel two (Fig. 5). We assign the peaks at 32 ppm for boehmite and -10.4 ppm for silica gel to Cs relatively tightly bonded to the surface, in sites comparable to those causing the 21 ppm peak for kaolinite. The peak at 34.7 ppm for silica gel is assigned to Cs loosely bonded in the diffuse layer comparable to the 47 ppm peak in kaolinite.

The variable number of peaks and their relative intensities for these materials are due to the ability of the samples to retain water during filtration of the CsCl from the solid. Kaolinite has lower permeability, and it is difficult to filter out all the water from it. As a result, Cs in solution without any influence from the

surface charge remains after filtering and causes the CsCl peak after air-drying. In contrast, boehmite and silica gel has higher permeabilities and vacuum filtering effectively removes the water from the surface and even Cs in the diffuse layer. Only a small amount of Cs in the diffuse layer is left on the silica gel and none on the boehmite. The chemical shifts of tightly bonded Cs on the surfaces of different materials depend on the composition and structure of the surface. Cs can be adsorbed on deprotonated surface oxygens by electrostatic forces ($M-O^{(2-v)}-Cs^+$, $M$ = metal on the surface, $v$ = bond valence). For Al in boehmite $v$ is $+1/2$ and for Si in silica gel it is $+1$, causing the difference between the -10.4 ppm chemical shift for silica gel and 32 ppm chemical shift of boehmite. Kaolinite is composed of a Si tetrahedral sheet and an Al octahedral sheet, and the $^{133}$Cs chemical shift for Cs on its surface sites is near 21 ppm, between the values for the two end member surfaces.

## CONCLUSION

$^{133}$Cs MAS NMR provides useful information about Cs structural environments and dynamics on different clay minerals. Clay minerals with expandable layers and significant interlayer charge, such as montmorillonite, contain most of the Cs in the interlayer and the Cs undergoes motional averaging at room temperature at $\nu \geq 10$ kHz. However, for clay minerals without interlayer charge, such as kaolinite, surface charge caused by surface protonation and deprotonation is important. At pH's higher than the PZC, most of the Cs is adsorbed on broken crystalline edges due to this charge. Defects sites can also be important for kaolinite, and in our kaolinite sample some of the Cs is adsorbed in expandable layers mixed with the kaolinite. The interlayer charge of this expandable layer is very small compared to normal smectite.

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