NMR T_1 relaxation study of ^{133}Cs and ^{23}Na adsorbed on illite

YEONGKYOO KIM* AND R. JAMES KIRKPATRICK[†]

Department of Geology, University of Illinois, Urbana, Illinois 61801, U.S.A.

ABSTRACT

^{23}Na and ^{133}Cs NMR T_1 relaxation data for wet paste samples made from illite and either NaCl or CsCl solutions show that there is significant adsorption of the Na and Cs onto the surface. The Na and Cs are in the NMR rapid exchange regime (exchange frequencies > approximately 10^4 Hz), allowing the T_1 values to provide useful information about surface occupancies. For ^{133}Cs, the data can be modeled to yield values for the fraction of Cs in the sample adsorbed onto surface sites and for the density of Cs surface occupancy. The maximum surface density observed for 0.1 M CsCl solutions is approximately 0.035 atoms/Å^2, essentially identical to the density of inner-sphere Cs sites determined from magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra of dried samples observed at a relative humidity of approximately 35%. The similarity of these results suggests that the relatively simple compositional dependence of the ^{133}Cs T_1 data is due to most of the surface Cs being in inner-sphere complexes with a relatively constant average T_1 when bulk H$_2$O is present. In contrast, the ^{23}Na T_1 data cannot be modeled in this way, consistent with the idea that its sorption on illite is dominated by outer-sphere complexes (Stern and/or Gouy layers) with a range of T_1 values. The similarity of the ^{23}Na T_1 behaviors of pastes made from NaCl solutions and either illite or silica gel (which has no permanent negative charge due to isomorphic substitution) is also consistent with this idea.

INTRODUCTION

Although many geochemical reactions in environments near the Earth's surface occur at mineral-water interfaces, molecular level understanding of these reactions remains limited because of the difficulty of studying surface species in situ. Among the various spectroscopic methods used to study such species (e.g., Hochella and White 1990), nuclear magnetic resonance (NMR) is one of the most effective. It can provide not only element-specific information about local structural environments but also information about dynamical behavior at the atomic scale. Most NMR studies of species adsorbed on mineral surfaces or exchanged into clay interlayers or zeolite cavities have depended primarily on the chemical shift for structural information and line-shape analysis for dynamical information (see Kim et al. 1996a, 1996b, for references). Our previous studies of Cs and Na adsorbed on mineral surfaces (Kim et al. 1996a, 1996b; Kim and Kirkpatrick 1998) have shown that multiple NMR peaks representing multiple surface environments can be detected at relative humidities less than approximately 70%, but that the presence of thick surface-water films occurring at relative humidities approaching 100% allow rapid atomic exchange among surface sites under these conditions. This behavior produces only one, time-averaged peak in the NMR spectra (e.g., Weiss et al. 1990). Because the relative propor-

tions of different sites cannot be determined from the spectra under these conditions, it has been unclear whether the proportions of different sites determined at lower relative humidities are applicable to conditions when bulk H$_2$O is present.

We present here an NMR study of the sorption of Cs and Na on illite that uses the NMR T_1 relaxation rate as the primary parameter and confirms the major conclusions of our previous results based on chemical shifts. Similar techniques based on chemical shifts have been previously used to study effects such as thallium binding to peptides in solution (Turner et al. 1982), but to our knowledge this is the first such study of exterior sorption on inorganic substrates. Our results show that the Cs surface density determined at moderate relative humidities (30–70%, equivalent to 1–3 statistical surface H$_2$O layers) are applicable to conditions when bulk H$_2$O is present. Furthermore, the results demonstrate the likely applicability of NMR T_1 methods to a wide range of studies: for example, the pH, ionic strength, and temperature dependences of the sorption behavior of organic and inorganic species of geochemical relevance.

The time constant, T_1, describes the rate at which the occupancy of nuclear spin energy levels returns to its equilibrium value after the spin system has been excited (T_1 relaxation). T_1 data are useful because this relaxation must be stimulated, providing information about the dynamical behavior of materials at frequencies near the Larmor (resonance) frequency, which is typically of the order

* Present address: Korea Environment Institute, 1049-1 Sadang-Dong, Dongjak-Gu, Seoul, 156-090, Korea.
† E-mail: kirkpat@hercules.geology.uiuc.edu

of 10^7–10^8 Hz. For all nuclei, T_1 relaxation can be accomplished by a fluctuating magnetic field at the nucleus with a Fourier component at the Larmor frequency. For quadrupolar nuclei such as ^{23}Na and ^{133}Cs, relaxation can also be accomplished by a fluctuating electric field gradient at the nucleus with Fourier components near the Larmor frequency. Thus, relaxation times for bulk solids are often long, because the power spectrum for normal lattice modes has little intensity in 10^7–10^8 Hz range. For liquids, relaxation times vary greatly, depending on viscosity and the nuclide observed.

For sorption studies of metals in aqueous solutions we take advantage of the increased rate of T_1 relaxation for atoms or molecules on the surface due to their lower rate of atomic motion relative to the bulk solution. In the simplest case of rapid exchange between the surface sites and bulk solution, the T_1 relaxation rate ($1/T_1$) is the abundance weighted sum of the T_1 values for the solution and surface (Pfeifer 1972)

$$1/T_1 = a/T_{1,sol} + (1-a)/T_{1,sur} \qquad (1)$$

where a is the fraction of the atoms in the solution and $1-a$ is the fraction on the surface. Knowledge of the T_1 value as a function of solid/solution ratio at constant initial solution concentration allows determination of a and $T_{1,sur}$ if there is a well-defined value for $T_{1,sur}$. In the present study this relationship appears to hold for Cs but not for Na in the range of solution/solid ratios observed.

EXPERIMENTAL METHODS

Most samples for this study were pastes consisting of a few milligrams of Yangsan illite in the appropriate amount 0.1 or 0.01 M CsCl or NaCl solution to fill a 5 mm OD sample tube. Stable pastes of illite could be prepared for solid/solution ratios from about 0.05 to 3.5 mg/ml. At lower solid contents the illite settled to the bottom of the tube, and the necessary conditions of rapid exchange between solution and surface could not occur because of the long diffusion distance between overlying solution and the particle surfaces. At larger solids contents there was insufficient solution to uniformly wet the illite. Similar samples using commercial silica gel (Brinkmann) in 0.1 and 0.01 NaCl solutions could only be prepared up to solid/solution ratios of about 1.4 mg/ml.

Sericitic Yangsan illite was used in this and previous studies because it has a very low Fe content and almost no expandable layers (Kim et al. 1996b). Thus, it is ideally suited for NMR studies of surface sorption processes. It has a N_2 BET surface area of 7.8 m²/gm and a tetrahedral Al/(Al+Si) ratio of 0.22.

NMR spectra were obtained at room temperature (approximately 23 °C) under static conditions at an H_o field strength of 11.7 T using a spectrometer based on a Tecmag Aries data-processing system. Freshly prepared paste samples were held in 5 mm OD silica glass tubes sealed with a rubber stopper and examined with a homebuilt static NMR probe without spinning. T_1 values were determined with a standard inversion-recovery pulse sequence.

RESULTS AND DISCUSSION

^{133}Cs

The most striking results are for the ^{133}Cs experiments (Fig. 1A). Here the T_1 values drop dramatically from approximately 10 s for the pure solutions to approximately 0.1 s at the higher solid/solution ratios. This two order of magnitude change and the nearly constant T_1 values at large solid/solution ratios allow accurate analysis of the data in terms of Equation 1 using the observed $T_{1,sol}$ values of 10.1 and 10.45 s and the observed nearly constant T_1 value of 0.10 s at large solution-solid ratios for $T_{1,sur}$. T_1 values determined for Cs adsorbed on illite at relative humidities of 90% and approximately 100% are in the range of 0.08–0.1 s, consistent with this latter value. These calculations yield the values of Cs(surf)/Cs(total) shown in Figure 2A and, using the measured BET surface area of 7.8 m²/gm and the known amount of solution in each sample, the surface Cs densities (atoms/Å²) shown in Figure 2B.

Except for those samples in which settling of the illite occurred (see Fig. 2 caption), the ^{133}Cs NMR spectra of these samples contain a single peak, consistent with dynamical exchange between the surface and solution at frequencies > 10^4 Hz. The width of this single peak increases with increasing solid/solution ratio (Fig. 3A). Because the various possible contributions to the line width (e.g., dynamical effects, chemical shift anisotropy, first and second order quadrupole interaction, site heterogeneity) are not quantitatively understood, we do not use these values to determine Cs surface occupancy.

The rapid decrease and then leveling off of the T_1 values with increasing solid/solution ratio observed here is consistent with the strong preference of Cs for inner-sphere sorption sites determined from our previous NMR work (Kim et al. 1996a, 1996b; Kim and Kirkpatrick 1998). Indeed the observed Cs surface site density of approximately 0.035 atoms/Å² observed at solid/solution values of 1.36 and less for the 0.1 M CsCl solution is essentially identical to the value of 0.033 atoms/Å² for the fully saturated concentration of inner-sphere Cs on this illite determined for this solution concentration from the relative intensities of the center bands in ^{133}Cs MAS NMR spectra of dried samples observed at approximately 35% relative humidity (Kim et al. 1996b). As noted in this previous paper, this surface concentration is approximately the same as the maximum possible Cs surface density expected assuming a hydrated radius for Cs of 3.29 Å. We interpret this agreement between the values determined by the two different methods to indicate that Cs sorption on illite in the presence of bulk solution is dominated by inner-sphere sites with a constant average T_1 value. This result also strongly supports the idea that MAS NMR study of surface species at low relative humidities, where multiple sites can be observed, may use-
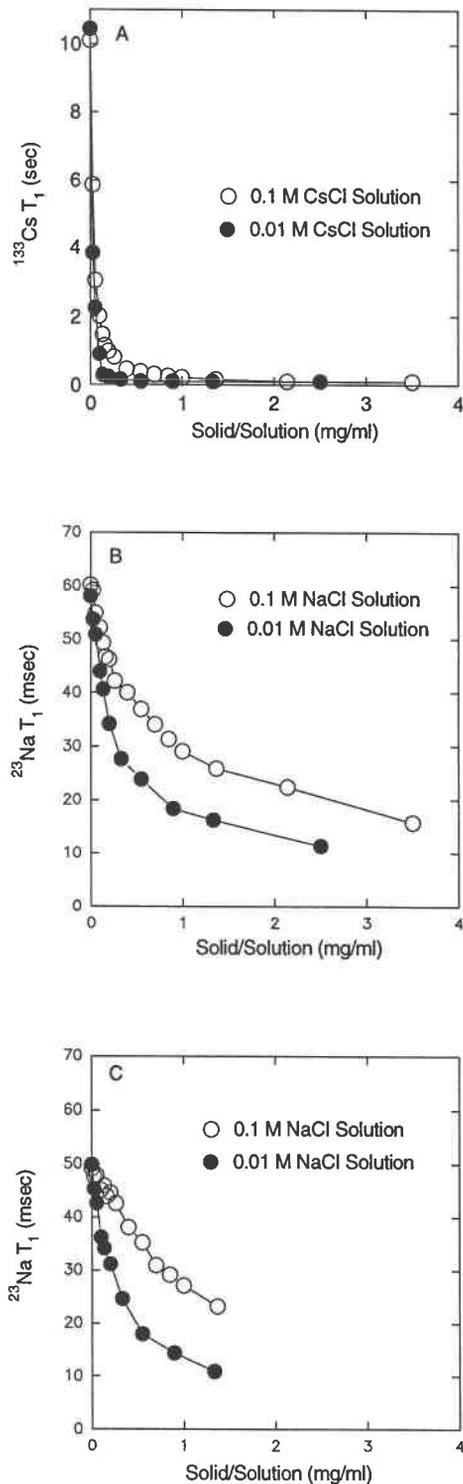
FIGURE 1.   NMR T_1 relaxation times vs. solid/solution ratio for (A) ^{133}Cs in illite-CsCl solution mixtures, (B) ^{23}Na in illite-NaCl solution mixtures, and (C) ^{23}Na in silica gel-NaCl solution mixtures.
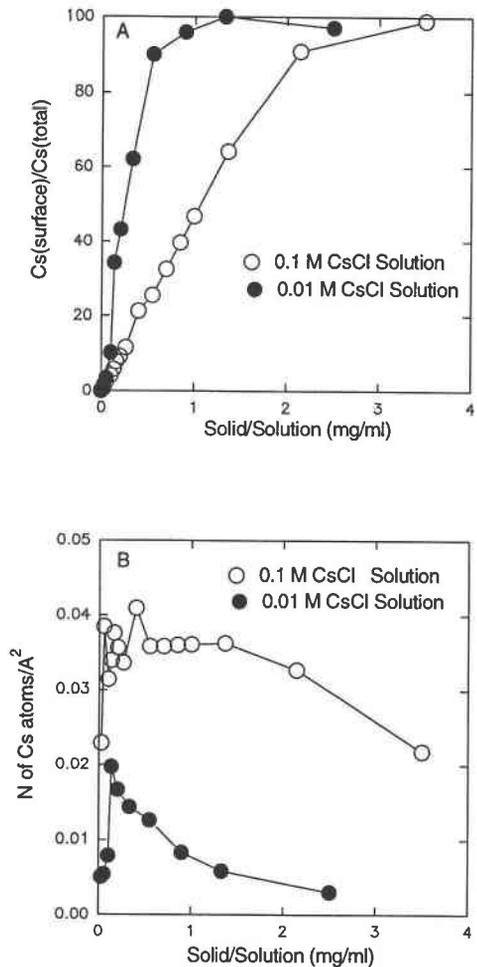
FIGURE 2.   (A) Calculated surface Cs/total Cs ratio vs. solid/solution ratio for illite/CsCl solution mixtures. (B) Calculated Cs surface density on illite (atoms/Å²) vs. solid/solution ratio for illite-CsCl solution mixtures. The first three data points in B and the first data point in A are for samples in which the solids settled to the bottom of the sample tube. For these samples the observed T_1 represents a larger but unknown solid/solution ratio.

fully probe the sorption behavior under H₂O saturated conditions.

Thus, for the samples made with 0.1 M CsCl solution, the surfaces become essentially fully saturated with Cs (each Cs and its associated H₂O molecules occupying approximately 28 Å²) until the total amount of available Cs is less than the surface can hold. At larger solution/solid ratios, nearly all the Cs is on the surface at any instant, and the Cs surface concentration decreases with increasing solid/solution ratio (decreasing total amount of Cs in the sample).

For the samples made with 0.01 M CsCl solution, the T_1 values decrease more rapidly than for the 0.1 M CsCl samples due to the order of magnitude smaller amount of Cs available at a given solid/solution ratio. Thus, the Cs becomes nearly fully removed from solution at a lower
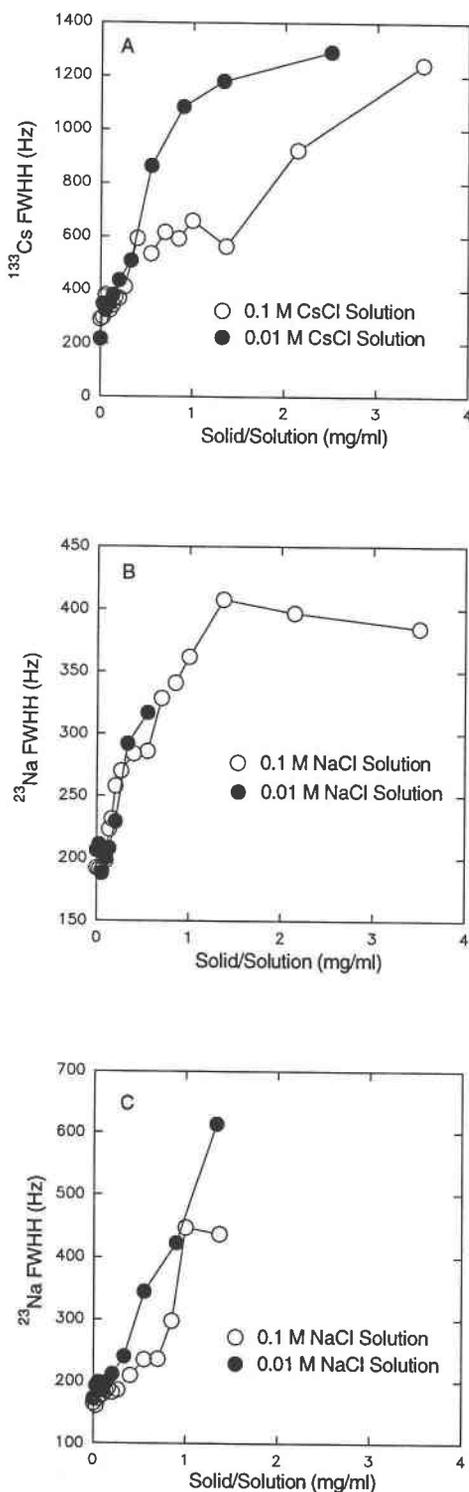
FIGURE 3. NMR peak full-widths at half-height (FWHH) vs. solid/solution ratio for (**A**) [133]Cs in illite-CsCl solution mixtures, (**B**) [23]Na in illite-NaCl solution mixtures, and (**C**) [23]Na in silica gel-NaCl solution mixtures.

solid/solution ratio (Fig. 2A). The maximum surface concentration is substantially less (approximately 0.02 atoms/Å^2) and does not maintain a constant value in the range of solution/solid ratios examined. These observations suggest that experiments similar to those described here but performed at lower solution concentrations and with variable temperature, pH, and concentration may provide useful information about the surface site energetics of illite and other minerals.

[23]Na

In contrast to Cs, Na is thought to sorb onto illite and similar minerals primarily as outer-sphere complexes due to its larger hydration energy (Ohtika and Radnai 1993; McBride 1994). Our previous ^{23}Na MAS NMR studies demonstrate that Cs effectively out-competes Na for surface sites on illite and are, thus, consistent with this interpretation (Kim and Kirkpatrick 1998). The [23]Na T_1 results presented here further confirm that Na behaves significantly differently on illite surfaces than Cs, and likewise the results are consistent with previous interpretations. As for [133]Cs, the [23]Na T_1 values decrease with increasing solid/solution ratio (Fig. 1B), but not as rapidly and only about a maximum of a factor of 6, rather than 10^2. In addition, the T_1 values do not become constant at large solid/solution ratios in the observable range of solid/solution ratios. The decreasing T_1 values and more rapid decrease for the experiments with samples made with 0.01 M NaCl solution demonstrate that surface sorption is occurring, but the absence of a well-defined value for $T_{1,\text{sur}}$ makes determination of surface occupancies by means of Equation 1 impossible. As for [133]Cs, the [23]Na peak width increases with increasing solid/solution ratio, but not nearly as dramatically (a factor of 2; Fig. 3B). The nearly constant value for the peak width of the 0.1 M NaCl solution samples at solid/solution ratios greater than 1.35 mg/ml suggests, however, that essentially all the Na is associated with the surface under these conditions.

The simplest explanation for the [23]Na T_1 behavior observed here is that the Na is being attracted toward the surface (and having its T_1 value there reduced somewhat) but that because all or much of it is held in the diffuse (Gouy) layer or as outer-sphere complexes in a Stern layer, its local environments have a significant range of T_1 values due, for example, to being at different distances from the surface in the Gouy layer. Thus, in this model there is no single, average T_1 value for surface Na, and even if essentially all the Na in the sample were associated with the surface, as suggested by the peak widths at large solid/solution ratios, the value of $T_{1,\text{sur}}$ would change with solid/solution ratio as the distance of the average Na atom from the surface changes.

The observation that [23]Na T_1 behavior of paste samples made with silica gel and NaCl solutions is essentially identical to that of the illite/NaCl solution samples (Fig. 1C and 3C) supports this interpretation. At the near-neutral pHs of NaCl solutions, silica gel is expected to have

a small net negative surface charge due to the extent of surface protonation (Parks 1967; Sposito 1984; Brady et al. 1996) and thus to weakly sorb cations. Unlike illite, it has no permanent negative charge due to isomorphic substitution. The nearly identical behavior of the illite and silica gel systems, including very similar absolute T_1 values at large solid/solution ratios, thus shows that the composition of the solid has little effect here. Again, the simplest explanation is that most of the Na sorbed onto both illite and silica gel is not directly coordinated to the surface O atoms, but instead occurs as outer-sphere complexes separated from the surface by H_2O molecules or in the Gouy layer. This conclusion is also consistent with the ^{23}Na MAS NMR results for illite (Kim and Kirkpatrick 1998).

REFERENCES CITED

Brady, P.V., Cygan, R.T., and Nagy, K.L. (1996) Molecular controls on kaolinite surface charge. Journal of Colloid and Interface Science, 183, 356–364.

Kim, Y. and Kirkpatrick, R.J. (1997) ^{23}Na and ^{133}Cs NMR study of cation adsorption on mineral surfaces: local environments, dynamics, and effects of mixed cations. Geochimica Cosmochimica Acta, 61, 5199–5208.

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

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

McBride, M.B. (1994) Environmental Chemistry of Solids. Oxford University Press, U.K.

Ohtika, H. and Radnai, T. (1993) Structure and dynamics of hydrated ions. Chemical Review, 93, 1157–1204.

Parks, G.A. (1967) Aqueous surface chemistry of oxides and complex oxide minerals; isoelectric point and zero point of charge. In W. Stumm, Ed., Equilibrium Concepts in Natural Water Systems, p. 121–160. American Chemical Society, Washington, D.C.

Sposito, G. (1984) The surface chemistry of solids. Oxford University Press, New York.

Turner, G.L., Hinton, J.F., and Millett, F.S. (1982) Thallium-205 nuclear magnetic resonance study of the thallium(I)-gramicidin A association in trifluoroethanol. Biochemistry, 21, 646–651.

Weiss, C.A., Jr., Kirkpatrick, R.J., and Altaner, S.P. (1990) The structural environments of cations adsorbed onto clays: ^{133}Cs variable temperature MAS NMR spectroscopic study of hectorite. Geochimica Cosmochimica Acta, 54, 1655–1669.