

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/Å², 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 H₂O 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 isomorphous substitution) is also consistent with this idea.