

0.0.21**Mineralogical Society of America - Dana Medal Lecture****Structure and dynamics at mineral surfaces: an NMR and molecular modeling approach**

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Nuclear magnetic resonance spectroscopy (NMR) is the only spectroscopic method that simultaneously probes molecular-scale structure and relatively slow atomic and molecular dynamics and is thus often highly effective for investigating chemical behavior at mineral-water interfaces and in interlayer galleries. Computational molecular modeling is often an effective, parallel tool for interpreting the NMR data in terms of detailed structure and motion. This presentation will review application of NMR chemical shifts, quadrupolar couplings, line shapes, and T_1 relaxation rates to investigating mineral surfaces and interlayers and the use of molecular modeling in detailed interpretation of the NMR data. For reactions that produce surface precipitates and for rigidly held interlayer species, dynamical behavior has little direct effect on the observed resonances, and for these situations the experimental and computational approaches used to study mineral, glass and gel structure are often effective. These situations will be illustrated by results for aluminophosphate and aluminocarbonate surface precipitates and a variety of anions and cations in the interlayers of clays and hydroxides. Many surface and interlayer species undergo molecular scale motion, and this motion often occurs at

frequencies in the $10^1 - 10^5$ Hz range. In these cases the structural environments and the frequencies of motion can often be investigated by dynamical effects on the NMR line shape and with molecular modeling. In such cases, it is often essential to obtain the NMR data over a range of temperature and relative humidity. Such behavior will be illustrated by results for alkali cations in and on clay minerals and anions in and on layered hydroxides. In mineral-water systems, interaction of the water and solute species with the mineral surface normally leads to increased NMR $1/T_1$ relaxation rates due to increased correlation times (decreased dynamical frequencies) at the surface. If these species are in dynamical exchange between the surface and bulk fluid at frequencies greater than the static line widths, changes in the average chemical shift can be used to probe the molecular-scale structure at the surface, and the $1/T_1$ relaxation rates can sometimes be used to determine the extent of association of the solute and surface. This behavior will be illustrated by results for alkali cations and Cl^- associated with clay mineral and hydroxide surfaces and with macromolecular natural organic matter in solution.