^{99}Tc- and ^{11}B-MAS-NMR spectra of oxide material to sequester TcO_4^-

WILLIAM H. CASEY[1]*, BRIAN L. PHILLIPS[2], PING YU[3], SHUAO WANG[4], THOMAS ALBRECHT-SCHMITT[4], EVGENY V. ALEKSEEV[5], JUAN DIWA[4] AND WULF DEPMEIER[5]

[1]Dept. Chemistry, Dept. Geology, U. C., Davis, CA, 95616 (*correspondence: whcasey@ucdavis.edu)
[2]Dept. of Geological Sciences, SUNY Stony Brook (brian.phillips@sunysb.edu)
[3]NMR Facility, U. C., Davis, CA, 95616 (pyu@ucdavis.edu)
[4]Dept. Dept. Chem. and Biochem., University of Notre Dame, 46556 (talbrec1@nd.edu)
[5]Dept. Crystallography, University of Kiel, 24118, Kiel, Germany (ea@min.uni-kiel.de)

Geochemists need a way to eliminate soluble oxyanions from radioactive waste streams and polluted waters. Pertechnetate is particularly troublesome because it is radioactive and relatively unreactive. Our collaborative group has been working on a cationic framework material [1] that has channels with the potential to story TcO_4^-. Here we discuss the ^{11}B-MAS-NMR and ^{99}Tc-MAS-NMR spectra that indicate its efficacy. To our knowledge, these are the first ^{99}Tc-MAS-NMR spectra reported.

The structure of the Notre Dame Thorium Borate (NDTB-1) material is a porous supertetrahedral framework with twelve-coordinated Th (IV) surrounded by BO_3 and BO_4^- anions. A key feature of the NDTB-1 material are channels that parallel [110] and have the potential to store oxyanions.

Solid-state ^{11}B-MAS-NMR spectra show distinct signals from well-ordered BO_3 and BO_4 groups, as expected from the X-ray data. However, the ^{11}B-MQ-MAS NMR data also indicate a second BO_3 environment that experiences a range of local structures, as reflected in the NMR parameters. This second type of BO_3 environment is characterized by a correlated distribution of isotropic chemical shift (from 17.0 to 14.5 ppm), C_q from 2.55 to 2.35 MHz and decreasing intensity. This feature is in accord with the presence of a disordered BO_3 group, such as would be consistent with extraframework borate anions.

The potential of this material to take up TcO_4^- was confirmed in ion-exchange and ^{99}Tc-MAS-NMR experiments. The preliminary ^{99}Tc-MAS-NMR data suggest the presence of TcO_4^- ion in two sites, which we suspect correspond to nearly intact pertechnetate ions in the channels.

[1] Wang, S. *et al*. (2010) *Angewandte Chem*. **49**, 1057–60.

How do oxides react? A look at isotope-exchange dynamics in nanometer-size structures in water

WILLIAM H. CASEY*, ERIC M. VILLA AND C. ANDRÉ OHLIN

Department of Chemistry and Department of Geology, University of California, Davis, CA (whcasey@ucdavis.edu)

Geochemists are trying to organize reactivity trends for complicated structures in water. Much can be learned, however, by looking at reactions in smaller fragments where one can follow isotope exchanges and dissociations at individual sites with confidence. The structures in solution of nanometer-size ions are often well known and powerful spectroscopies can be used. Dissociation can be followed through loss of a characteristic isotope tag and/or via mass spectrometry with unprecedented clarity to detail the role of pH, counterions, structural substitutions, etc. Furthermore, the results couple well to simulation.

We here discuss oxygen-isotope-exchange rates and dissociation pathways for three isostructural nanometer-size ions that contain 38-41 atoms. These ions differ only by targeted metal substitutions and in their Brønsted acid-base properties. We find that rates for all oxygen sites within a particular molecule differ by at least ~10^4, but throughout the series the relative reactivities rank in nearly the same relative order. Within a single ion, rates of isotopic exchange for most structural oxygens vary together with pH, indicating that each structure responds as a whole to changes in solution composition; isotope-exchange pathways are via concerted motions of much of the structure and relate to pathways for dissociation. We also find catalysis affects some oxygen sites within a structure.

The most striking result is that reactivities seem to reflect global properties of the molecules. Across the series, the pH dependencies for isotope exchanges and dissociation differ distinctly and reflect different contributions from proton- or base-enhanced pathways. The trends are understandable in terms of the molecular charge of each unprotonated ion. In addition, the local effect on oxygen reactivities of single-atom substitution could be assessed by comparing rates for structurally similar oxygens on each side of one ion with a single atom substitution. These local effects are surprisingly small. Thus these nanometer-size ion manifest the same general and averaged amphoteric chemistry that is familiar for other reactions affecting extended oxides in water, like proton- and base-enhanced dissolution.