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Drs. Woodward:

Attached to this letter is the final report for the grant entitled: *'The Kinetics of Dissociation of Aluminum-Oxygen Bonds...'*. The DOE award number is DE-FG-0396ER14629 and the expiration date is April 30, 2002. This was loaded onto the OTIS web site electronically.

Cordially,

William H. Casey
Professor of Aqueous Geochemistry

cc: files
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GRANT: DE-FG-03-96ER14629

TITLE: The Kinetics of Dissociation of Aluminum-Oxygen Bonds in Aqueous Complexes

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Topical Keywords: Geochemical Transport, Isotope Geochemistry

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OBJECTIVES

In this project we determined rates and mechanisms of Al(III)-O bond rupture at mineral surfaces and in dissolved aluminum complexes. We then compared the experimental results to simulations in an attempt to predict rate coefficients.

PROJECT DESCRIPTION

Most of the low-temperature reactions that are geochemically important involve a bonded atom or molecule that is replaced with another. We probe these reactions at the most fundamental level in order to establish a model to predict rates for the wide range of reactions that cannot be experimentally studied.

RESULTS

The chemistry of small aluminum cluster (Figure) provides a window into the hydrolytic processes that control rates of mineral formation and the transformation of adsorbates into extended structures. The molecule shown below as an example exposes several types of oxygens to the bulk solution including seven structurally distinct sets of bridging hydroxyls. This molecule is a rich model for the aqueous interface of aluminum (hydr)oxide minerals, since it approaches colloidal dimensions in size, yet is a dissolved complex with +18 charge. We have conducted both ^{17}O - ^{27}Al - and ^{19}F -NMR experiments to identify the reactive sites and to determine the rates of isotopic exchange between these sites and the bulk solution. The research was enormously successful and led to a series of papers that are being used as touchstones for assessing the accuracy of computer models of bond ruptures in water.

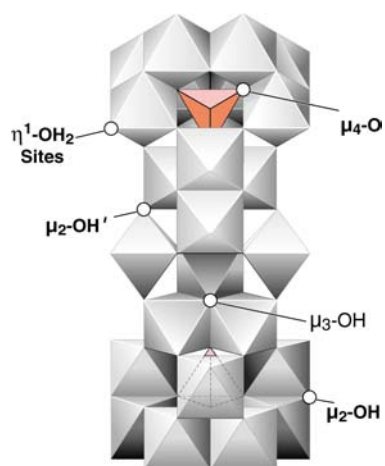


Figure 1: The Al_{30} molecule has the stoichiometry $\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}(\text{aq})$. It was crystallized by Taulelle et al., (2000) and Rowsell and Nazar (2001) and we are employing ^{17}O -NMR to determine the rates of oxygen-isotope exchange with the bulk solution. This molecule exhibits many of the properties of aluminum (hydr)oxide colloids.

We also showed that ^{19}F -NMR methods of tagging these large molecules can lead to rate coefficients describing bond ruptures at the elementary or near-elementary scale. These ^{19}F -NMR spectra are particularly useful because the nucleus has $\text{spin}=1/2$, so peaks in the spectra are relatively narrow, and because fluoride can substitute for some oxygens at defined rates. All fluorines are detectable by NMR, the chemical shift is very sensitive to small changes in structure and bonding, and an enormous range of molecules are available with ^{19}F in a nonbonding site. We can therefore tag different sites in the polyoxocations.

Finally, we conducted high-pressure experiments in a home-built titanium NMR probe that provide the first measurements of activation volumes for isotopic exchange in a bridging site. Some of the most recent articles that acknowledge support from grant are listed below. The entire list of articles is considerably longer.

References

- Allada, R., A. Navrotsky, H.T. Berbeco, and W.H. Casey. 2002. Thermochemistry and aqueous solubilities of hydrotalcite-like solids. *Science* **296**, 721-723.
- Allouche, L., Gérardin, C., Loiseau, T. Férey, G. and Taulelle, F. (2000) Al_{30} : A giant aluminum polycation. *Angew Chem Int Ed*, 39: 511-514.
- Casey, W. H. and Swaddle, T. W. (2003) Why small? The use of small inorganic clusters to understand mineral surface and dissolution reactions in geochemistry. *Reviews Geophysics* **41**, 1-20.
- Casey, W. H., Phillips, B. L., and Furrer, G. (2001) Aqueous aluminum polynuclear complexes and nanoclusters: a review. ch 5 in: *Nanoparticles in the Environment* (J. F. Banfield and A. Navrotsky, eds). *Reviews in Mineralogy and Geochemistry* **44**, pp. 167-216.
- Casey, W.H. and B.L. Phillips. 2001. Kinetics of oxygen exchange between sites in the $\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$ molecule and aqueous solution. *Geochim. Cosmochim. Acta* **65**, 705-714.
- Casey, W.H., B.L. Phillips, M. Karlsson, S. Nordin, J.P. Nordin, D.J. Sullivan, S. Neugebauer-Crawford. 2000. Rates and mechanisms of oxygen exchanges between sites in the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$ complex and water: Implications for mineral surface chemistry. *Geochim. Cosmochim. Acta* **64**, 2951-2964.
- Furrer, G., B.L. Phillips, K.-U. Ulrich, R. Pöthig, and W.H. Casey. 2002. The origin of aluminum flocs in polluted streams. *Science* **297**:2245-2247
- Lee, A.P., B.L. Phillips, and W.H. Casey. 2002. The kinetics of oxygen exchange between the $\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_8^{8+}(\text{aq})$ molecule and aqueous solutions. *Geochim. Cosmochim. Acta*, **66**, 577-587.
- Lee, A.P., B.L. Phillips, M.M. Olmstead, and W.H. Casey. 2001. Synthesis and characterization of the $\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_8^{8+}$ polyoxocation. *Inorg. Chem.* **40**, 4485-4487.
- Loring, J. S., Yu, P., Phillips, B. L. and W.H. Casey (2003) Activation volumes for oxygen exchange between the $\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$ (GaAl_{12}) polyoxocation and aqueous solution from variable pressure ^{17}O NMR spectroscopy. *Geochim. Cosmochim. Acta* submitted.

- Phillips, B. L., Lee, A.P., and W.H. Casey (2003) Rates of oxygen exchange between the $\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}(\text{aq})$ (Al_{30}) molecule and aqueous solution, *Geochim. Cosmochim. Acta* **67**, 2725-2733
- Rowse, J. and L. F. Nazar (2000); Speciation and thermal transformation in alumina sols: structures of the polyhydroxyoxoaluminum cluster $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$ and its δ -Keggin moiety. *J Amer Chem Soc* **122**: 3777-3778.
- Yu, P., A.P. Lee, B.L. Phillips, and W.H. Casey (2003) Potentiometric and ^{19}F -NMR spectroscopic study of fluoride substitution in the GaAl_{12} polyoxocation: implications for aluminum (hydr)oxide mineral surfaces. *Geochim. Cosmochim. Acta*. **67**, 1065-1080.
- Yu, P., B.L. Phillips, and W.H. Casey. 2001. Water exchange in fluoroaluminate complexes in aqueous solution: A variable temperature multinuclear NMR study. *Inorg. Chem.* **40**, 4750-4754.
- Yu, P., B.L. Phillips, M.M. Olmstead, and W.H. Casey. 2002. Rates of solvent exchange in aqueous