

***Adding Reactivity to Structure--***

***Reaction Dynamics in a Nanometer-size Oxide Ion in Water***

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## Abstract

We examine oxygen-isotope exchanges in a nanometer-size oxide molecule in water and, separately, both its rates of dissociation and molecular products. This molecule, the decaniobate ion ( $[H_xNb_{10}O_{28}]^{(6-x)-}$ ), is at the same size scale as geochemically interesting features on minerals, such as surface polymers and kink sites on growth steps, although it is structurally quite dissimilar. Unlike mineral surface structures, however, we have complete confidence in the aqueous structure of this molecule and it yields a clear spectroscopic signature as it reacts. We thus can follow proton-enhanced isotope exchanges and base-induced dissociation in unprecedented detail and clarity.

These structures are, of course, not minerals but the results are surprising and require new thinking about geochemical reactions at the molecular scale. For example, base-induced dissociation of the molecule, which is unprotonated, causes rates of oxygen-isotope exchanges of all structural oxygens to accelerate dramatically. Similarly, protonation of the molecule causes sets of oxygens to react, although protonation is limited. In general, all reactions are via concerted motions of many atoms and the reactivities vary as though the entire structure was responding to changes in solution composition. The site reactivities could not be inferred from the stable structure of the decaniobate molecule because so much of the structure is involved in each exchange event. Thus, computational models must be structurally faithful to an extraordinary degree, and inherently dynamic, or they will miss the essential chemistry.

## Introduction

Why do Earth scientists need to understand molecules? Most geochemists estimate large fluxes of matter in the Earth or estimate the stability of materials via thermodynamic calculations. These are questions of bulk chemistry and don't require any information about molecular structures.

Geochemists need to work with molecules to the extent that they need to relate bonding to reaction pathways, or to sample individual atoms for environmental information, as in isotopic analysis. They also need to work with molecules in order to fully exploit advances in computational chemistry. These advances now allow Earth scientists to estimate isotopic fractionations (Black and others, 2007, Hill and Schable, 2008, Klochko and others, 2006, Liu and Tossell, 2005, Rustad and Bylaska, 2007, Rustad and others, 2008, Schable, Ghosh, and Eiler, 2006, Tossell, 2005), predict phase transitions (Mao and others, 2005, Stixrude and others, 2007, Stixrude and Peacor, 2002), to follow biochemical reactions (Allen, Andersen, and Roux, 2004, Kerisit and Rosso, 2007) and speculate about dissolution and growth (Casey, Lasaga, and Gibbs, 1990, Criscenti, Kubicki, and Brantley, 2006, Liu, Olsen, and Rimstidt, 2006, Pelmenschikov and others, 2000). Most importantly, computation promises a means of estimating properties for reactions in the Earth that are impossible to sample experimentally.

Because so many natural reactions at the Earth surface are aqueous, hydrolytic reactions are particularly important. These, of course, lead to mineral dissolution, growth and alteration and to the elimination of pollutants by hydrolysis into metal-hydroxide surface complexes and polymers. Unfortunately, well-accepted ideas about how pH affects bond ruptures, and how these might trend with bond strengths, have little

experimental support. Geochemists need molecular experiments to tell us if computational predictions are accurate. This level of resolution is well beyond more familiar approaches of interpreting supramolecular results, such as fluxes, surface geometries or step-flow rates, in terms of bond ruptures. These interpretations may be reasonable but they are poorly constrained. With molecules such as the one discussed here, we can tell if the interpretation about reaction pathways are wrong.

We here examine how a nanometer-size oxide molecule reacts with water. Although much of this information derives from our recent paper in the chemical literature (Villa and others, 2008), the work has particular relevance to Earth science. The decaniobate molecule is not itself geochemically relevant, but has such a simple acid-base chemistry and reacts sufficiently slowly that the rates of oxygen-isotopic exchanges can be followed in unprecedented detail. It has a structure that is sufficiently complicated to capture some of the complexity of a mineral surface. We show that simple reactions in this molecule are extraordinarily counterintuitive.

### **The Experimental Model**

The decaniobate ion  $[(\text{H}_x\text{Nb}_{10}\text{O}_{28})^{(6-x)}]$ ; Figure 1] has seven types of structural oxygens and three structurally distinct metal sites. These oxygens are well resolved by  $^{17}\text{O}$ -NMR spectroscopy. The bond lengths and angles determined from X-ray structural analysis of a crystal are shown in Figure 2. The decaniobate ion protonates very weakly in water and is stable in near-neutral solution. If the molecule is enriched in  $^{17}\text{O}$ , one can follow rates of steady oxygen-isotope exchanges as a function of solution pH using  $^{17}\text{O}$ -NMR spectroscopy. In addition, the clusters do not dissociate into monomers under

electrospray-ionization mass spectrometry (ESI-MS) conditions so that the reaction products can be identified from mass spectra of the solutions.

Among the seven structural oxygens, there are two central six-coordinated oxygens ( $\mu_6$ -oxo; Site A), two sets of four  $\eta=$ O sites, (labeled G and F), three sets of  $\mu_2$ -oxo sites (Site D is a set of two, Sites E is a set of four and C is a set of eight  $\mu_2$ -oxygens), and one set of four  $\mu_3$ -oxo (Site B). [We here employ the standard formalism that  $\eta^i$  sites are nonbridging sites with ' $i$ ' atoms from the ligand bonding to the metal, and  $\mu_i$  sites are ligands that bridge ' $i$ ' metals, in this case all Nb(V).]

We synthesized crystals of  $[\text{N}(\text{CH}_3)_4]_6[\text{Nb}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$  (Graeber and Morosin, 1977, Marek, 2001, Villa and others, 2008) using  $^{17}\text{O}$ -enriched water (40%, Isotec). A small amount ( $\sim 20$  mg) of these isotopically enriched crystals were dissolved into 2 ml of isotopically normal background electrolyte containing an anionic pH buffer and 0.1 M  $[\text{N}(\text{CH}_3)_4]\text{Cl}$ . This dissolution step releases the isotopically-enriched molecule to the aqueous solution, in a similar fashion as other aqueous clusters (Balogh and others, 2007a, Black, Nyman, and Casey, 2006, Casey and Phillips, 2001, Casey and others, 2000, Lee, Phillips, and Casey, 2002, Loring and others, 2004, Phillips, Casey, and Karlsson, 2000, Phillips, Lee, and Casey, 2003). The counterions, which in this case is oxygen-free tetramethylammonium ion, bond ionically to the intact oxide molecule, which is an anion. The array of peaks in the  $^{17}\text{O}$ -NMR spectrum [Figure 1] have intensities that correspond to the stoichiometry of the molecule, indicating that it is stable in solution, that extensive isotope-exchange did not occur in the solid state, and that there are no other unwanted  $^{17}\text{O}$ -NMR signals from impurities or breakdown products.

The decline in intensity of the  $^{17}\text{O}$ -NMR signals for each site as a function of time yields rates of isotopic exchange for all seven structural oxygen types with bulk solution [Figure 1]. Electrospray-ionization mass spectrometry also confirmed that the molecules are stable in neutral aqueous solutions. Charge assignments were confirmed by study of isotopically substituted molecules, created by equilibrating  $[\text{N}(\text{CH}_3)_4]_6 [\text{Nb}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$  or  $[\text{N}(\text{CH}_3)_4]_8 [\text{Nb}_6\text{O}_{19}] \cdot \sim 16\text{H}_2\text{O}$  salts with  $\text{H}_2^{18}\text{O}$ . These data also give us great confidence that the molecule structure remains intact in solution.

The peak intensities decrease exponentially with time as the  $^{17}\text{O}$  exchanges from structural sites with isotopically normal solution. To estimate rates,  $^{17}\text{O}$ -NMR peak intensities, relative to a standard, were fit to:  $I(t) = I_0 \cdot \exp(-k \cdot t)$  where  $I_t$ , and  $I_0$  are the peak intensities at times  $t$  and zero, respectively, as expected from the McKay equations (McKay, 1938). Assignment of the  $^{17}\text{O}$ -NMR signals in solution was guided by previous work on decaniobate and decavanadate ions (Comba and Helm, 1988, Day, Klemperer, and Maltbie, 1987, Marek, 2001) with the exception of the 722 ppm  $\eta=\text{O}$  peak, which was assigned to Site F based on *ab initio* calculations of  $^{17}\text{O}$ -NMR chemical shifts.

## Results

### *Rates of Steady Oxygen-Isotope Exchanges at Different Structural Oxygens*

The seven structurally distinct oxygens in this molecule all equilibrate at different rates with the aqueous solution and these rates vary with solution pH. Only the central  $\mu_6\text{-O}$  sites do not isotopically equilibrate with the bulk solution at most pH conditions, as is also observed for the smaller but related  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-} \cdot \text{(aq)}$  Lindqvist polyoxoanion (Black, Nyman, and Casey, 2006, Black, Nyman, and Casey, 2007). These central oxygens are inert to exchange. At  $\text{pH} > 7.5$ , we can detect a slow loss in intensity of the

$^{17}\text{O}$ -NMR signal from this  $\mu_6\text{-O}$ , indicating that the molecule is dissociating [Figure 3].

This decline in intensity is slower than the rates of isotopic equilibration of other structural sites in the molecule.

This molecule protonates very weakly, yet the pH-variation in the isotopic exchange is complicated and spans the entire pH range of the experiments. Approximate equilibrium constants can be assigned from the studies of the isostructural and isovalent  $[\text{H}_x\text{V}_{10}\text{O}_{28}]^{(6-x)-}$  molecule (Howarth and Jarrold, 1978, Pettersson and others, 1983) with  $\text{pK}_x$  values of:  $\text{pK}_1 = 6.0$ ;  $\text{pK}_2 = 3.74$  and  $\text{pK}_3 = 1.6$  ( $\text{I}=0.6 \text{ M}$ ). Using these equilibrium constants, one can show that the  $[\text{Nb}_{10}\text{O}_{28}]^{6-}$  species dominates at most pH conditions of this study [Figure 4] with the monoprotonated form  $[\text{HNb}_{10}\text{O}_{28}]^{5-}$  becoming important at  $\text{pH} < 6.5$ . The fact that the  $^{17}\text{O}$  signals do not change positions with pH is consistent with very weak protonation of this molecule. Site F, which is one set of four terminal  $\eta=\text{O}$ , is the most basic oxygen and is the most energetically favorable site of protonation (Villa and others, 2008).

The reactivity trend at near-neutral pH is:  $\text{D}(\mu_2\text{-oxo}) > \text{G}(\eta=\text{oxo}) > \text{F}(\eta=\text{oxo}) > \text{C}(\mu_2\text{-oxo}) >> \text{E}(\mu_2\text{-oxo}) >> \text{B}(\mu_3\text{-oxo}) >> \text{A}(\mu_6\text{-oxo})$  and all oxygens except Site A, and possibly Site B, increase rates of isotopic substitution at  $\text{pH} \leq 7.0$ . Notably, the relative rates of isotopic exchange in the three  $\mu_2\text{-O}$  (Sites C, D and E) differ by  $\sim 10^4$ . One  $\mu_2\text{-O}$  site, (Site D) even exchanges more rapidly than either terminal oxygen (Sites F and G) at  $\text{pH} \geq 6.6$ . Furthermore another  $\mu_2\text{-O}$  site, Site E, is extraordinarily slow to exchange at these conditions [Figures 3 and 4].

Entire *sets* of oxygen sites become labile to isotopic exchange as the molecule is protonated, probably at Site F. This terminal oxo is the most basic oxygen and probably the site of protonation, which probably explains why the dimer  $[\text{Nb}_{20}\text{O}_{54}]^{8-}$  is formed via protonation and dehydration of two adjacent F-Sites (Maekawa, Ozawa, and Yagasaki, 2006). (Site B is also basic but protonation here destabilizes the structure in *ab initio* calculations.) Proton exchange among the various oxygens is on the millisecond time scale (see (Houston, Phillips, and Casey, 2006)) weighted by their energies of protonation. Our *ab initio* calculations of proton affinities also indicate that Sites F (and B) are the most favored for protonation by 20-40 kJ/mol. In the crystal, Site F also has a strong hydrogen bond to structural waters.

However, Site F is neither the most rapid to exchange nor the only structural oxygen affected by changes in pH. At  $\text{pH} > 7$ , the rates of isotopic exchange of Sites F, G and D differ by a factor of  $\sim 10^2$ . At  $\text{pH} < 7$ , however, the rates for Sites F, G and D are nearly equal. Even the relatively inert equatorial  $\mu_2$ -oxygens (Site E), with strongly asymmetric bonding to Nb(V), exhibit a pH dependence for isotopic exchange that is similar to most of the other structural oxygens.

#### *Dissociation Rate, Pathways and Products*

We could follow dissociation of the oxide molecule into products from the slow decline in the  $^{17}\text{O}$ -NMR signal for the  $\mu_6$ -oxo and from changes in the ESI-MS spectrum. Dissociation is clearly detectable at  $\text{pH} \geq 7.5$  and the rate increases with pH [Figure 4]. At  $\text{pH} < 9.3$ , dissociation of the decaniobate molecule is still significantly slower than the rates of isotopic exchange for most oxygen sites [Figure 4]. At much higher pH (pH=12.5), however, dissociation is much faster than isotope exchanges at some, or most,

oxygen sites in the decaniobate ion. This is clear because the  $[H_xNb_6O_{19}]^{(8-x)-}$  product retains  $^{17}O$  enrichments originally in the  $[Nb_{10}O_{28}]^{6-}$  ion.

At pH=9.3 we observe that the  $\mu_6$ -oxo from the  $[H_xNb_{10}O_{28}]^{(6-x)-}$  ion transforms intact into the  $\mu_6$ -oxo of the smaller  $[H_xNb_6O_{19}]^{(8-x)-}$  ion during dissociation [Figure 5]. Furthermore, there is some evidence that the reaction is reversible. The simplest explanation for disappearance of the  $^{17}O$ -NMR signal for Site A in the hexaniobate reaction product is that the  $[Nb_{10}O_{28}]^{6-}$  ion and the  $[H_xNb_6O_{19}]^{(8-x)-}$  ion interconvert. This interconversion diminishes the  $^{17}O$ -NMR signal from both ions with time as isotopically normal oxygen is repeatedly incorporated.

Thus, a major pathway for base-enhanced dissociation transfers a  $\mu_6$ -oxo intact from the dissociating  $[Nb_{10}O_{28}]^{6-}$  ion to a  $\mu_6$ -oxo site in the newly formed  $[H_xNb_6O_{19}]^{(8-x)-}$  ion [Figure 6]. This pathway is consistent with one suggested for the isostructural decavanadate ion (Comba and Helm, 1988), which was then inferred from experiments over a much narrower range of rates and conditions. The tetraniobate fragment remaining after dissociation of the  $[H_xNb_{10}O_{28}]^{(6-x)-}$  ion subsequently forms higher oligomers, one of which is detectable both by  $^{17}O$ -NMR and ESI-MS. We do not know all of the fragments into which the tetraniobate dissociates, but a transient species was identified as heptaniobate,  $[Nb_7O_{22}]^{9-}$ , based on the spectroscopic data. The heptaniobate has been isolated in two separate labs with copper ethylenediamine as charge-balancing and decorating cations (Bontchev and Nyman, 2006, Niu and others, 2007).

## Geochemical Implications

Geochemists now employ various levels of approximation to understand hydrolytic reactions involving minerals. These vary from wholly empirical relations

(Casey and Westrich, 1992, Lasaga, 1998, Ludwig, Casey, and Rock, 1995), to step-flow models that relate growth and dissolution features to saturation states and adsorbate densities (Dove, Han, and De Yoreo, 2005, Lasaga and Luttge, 2001) to quantum-mechanical simulations (Criscenti, Kubicki, and Brantley, 2006, Felipe, Xiao, and Kubicki, 2001, Xiao and Lasaga, 1996) and molecular dynamic methods (Rustad, Rosso, and Felmy, 2004). Of these, only the molecular dynamic and quantum methods have the chance to identify actual pathways because these work at the level of individual bonds. The step-flow and step-pinning models have, at their core, a combination of the Law of Detailed Balance, the Gibbs-Thompson effect, adsorption isotherms and the Arrhenius relation (Burton, Cabrera, and Frank, 1949, De Yoreo and Vekilov, 2003, Thomas and others, 2004). The key variables (energies, saturation states, adsorbate densities) are supramolecular in scale so that molecular interpretations that derive from the surface morphologies may be reasonable, but they are also usually untested.

Such definitive test could come from large molecules in which we have complete confidence in the aqueous structure. These molecules, of course, are not minerals but they are at the appropriate scale to observe bond ruptures and compare the reaction kinetics with computation. In previous work with aluminum-oxide clusters, for example, this approach led to estimation of water-substitution rates for surface sites (Wang, Rustad, and Casey, 2007) see also (Balogh and others, 2007b). Additionally, interpretation of isotope-exchange rates in aluminum polyoxocations led to greater appreciation of distal bonding and overbonded oxygens in controlling the rates and pathways (Rustad, Loring, and Casey, 2004). In these clusters, reduction of the formal

charge at key highly bonded oxygens by substitution of a less-charged metal in the inert core enhanced the rates of isotopic exchange substantially.

These conceptual advances derived from study of the  $[H_xNb_{10}O_{28}]^{(6-x)-}$  ion:

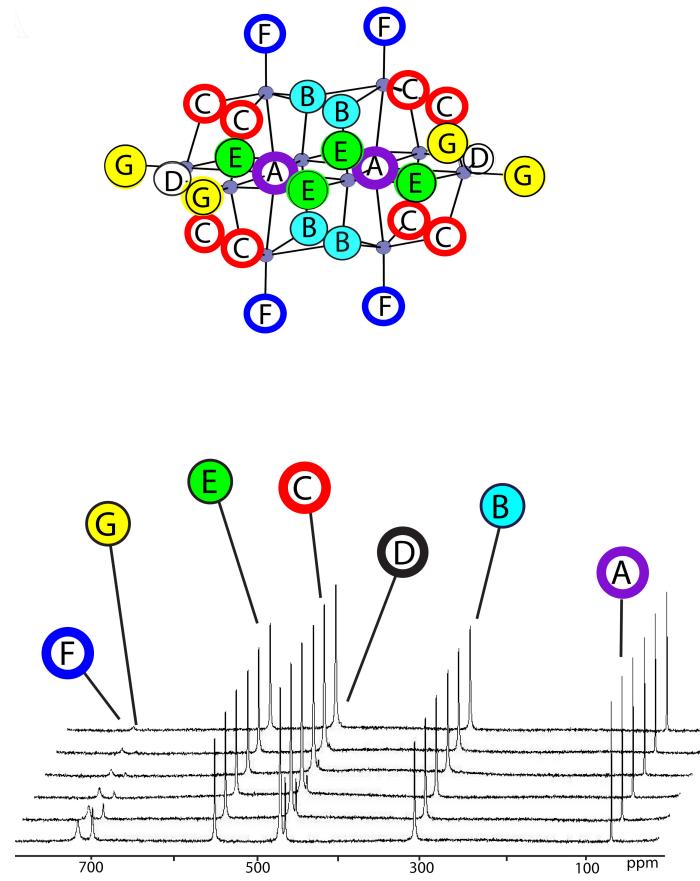
- (1) At the nanometer-size scale, reactivities are not identifiable from the ground-state structures. Oxygen-isotope exchange rates do not suggest themselves from bond lengths, partial charges or from easily calculated parameters such as Pauling bond strengths. The rates span a range of  $\sim 10^4$  and aren't predictable from the simple structural features of the stable molecule shown in Figure 2.
- (2) Oxygens in the structure react in concert. At low pH, the single protonation, probably at Site F, causes Sites F, D, C and E to increase rates of isotopic substitution.
- (3) As pH rises and the molecule begins to slowly dissociate, the entire cluster responds to increased  $[OH^-]$  concentrations. Most of these isotope-exchange rates are much more rapid than rates of base-induced dissociation. Even Site B, the  $\mu_3$ -oxo site that is the nexus of dissociation, isotopically exchanges 2-3 times faster than the molecule dissociates so clearly, the entire molecule is affected by changes in solution composition.
- (4) Reaction via these concerted motions probably becomes muted as molecular size increases. The  $\mu_2$ -OH on the basal plane of gibbsite, for example, are inert to isotopic exchange yet rates of isotopic substitution into bridges in the  $Al_{13}$  Keggin cation are fast (Rosenqvist and Casey, 2004).
- (5) Large dynamic simulations are needed on molecules that themselves are not geochemically relevant, but that allow us to improve our understanding of solution dynamics. Static models, such as *ab initio* calculation of a reaction barrier, are not

accurate (Evans, Rustad, and Casey, 2008). Also inaccurate are models that employ an imagined fragment of an extended structure as shorthand, such as use of a silicate dimer as shorthand for the surface of quartz. The data here indicate that any computation model must be structurally faithful to a considerable extent or will miss the essential chemistry.

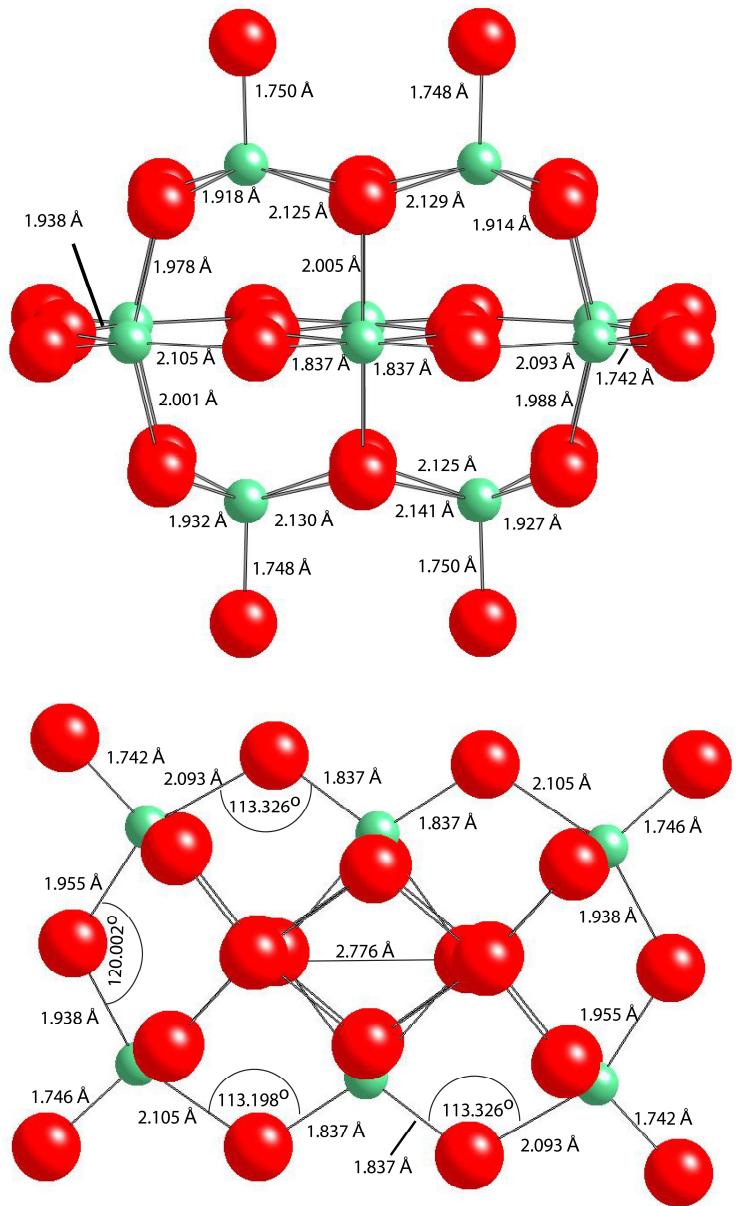
We recognize that it is tempting to dismiss these results because they involve a structure that is not represented in minerals. Certainly the pathways for these reactions are unique to this decaniobate structure. However, one need remember that the important features during mineral growth and dissolution are also often nanometer-size in scale and we yet have limited ability to follow these reactions *in situ*. Furthermore, the decaniobate ion is one of many polyoxometalate ions, usually of  $d^0$  transition metals, that are stable in water and have well-defined structures (Pope, 2003, Pope, 2004). These molecules are generally anionic, but the most familiar class to geochemists contains the  $Al_{13}$  Keggin cation molecules, which are important aluminum-hydroxide species and as precursors to some pollutant floc (Furrer and others, 2002). The Keggin class of polyoxometalates is one of the most common, albeit most are not cations. Molecules such as these could be enormously useful to geochemists because they provide a clear path forward in understanding reaction pathways in Earth materials at the molecular scale.

### **Acknowledgements**

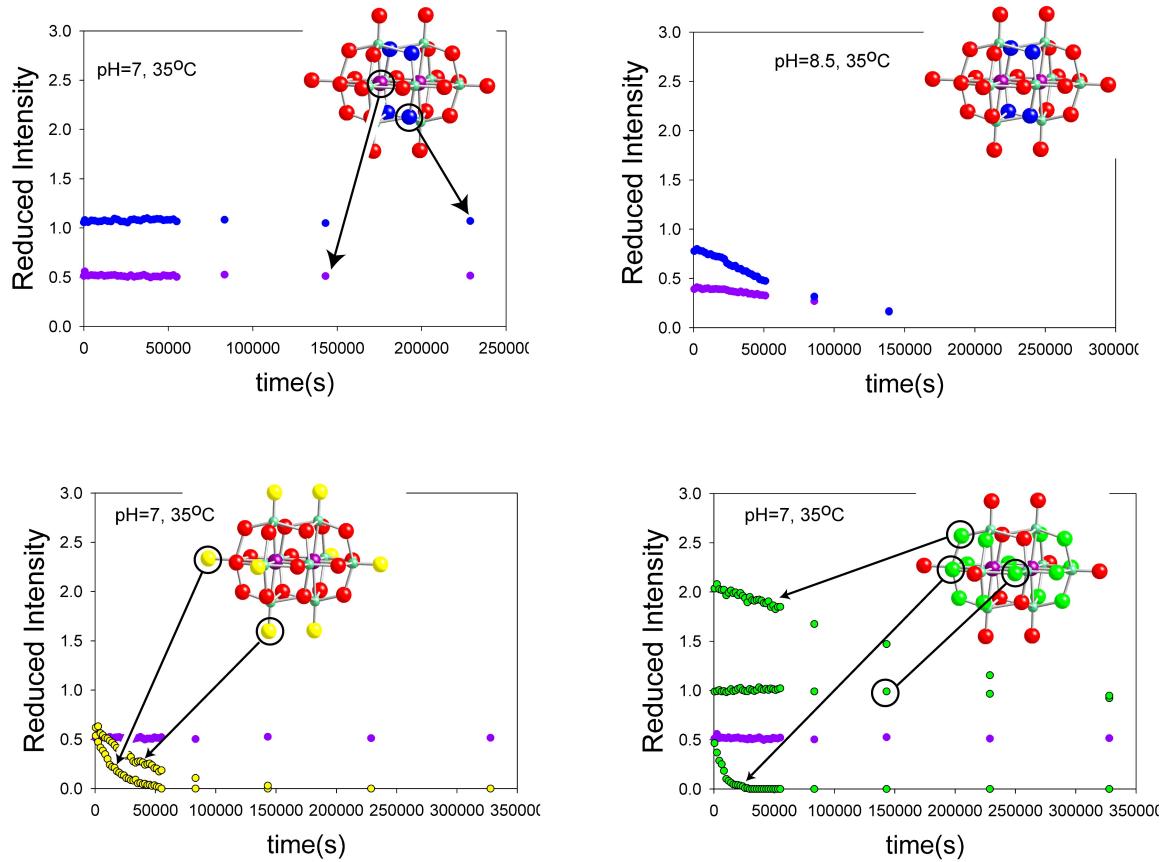
This work is dedicated to the memory of Prof. Bernard Spinner, who was a pioneer in the solution chemistry of isopolyoxoniobate molecules (e.g., (Spinner, 1968)). Support for this research was from the U.S. National Science Foundation via EAR-0515600 and the U.S. Department of Energy, Office of Basic Energy Research via DE-FG02-05ER15693.



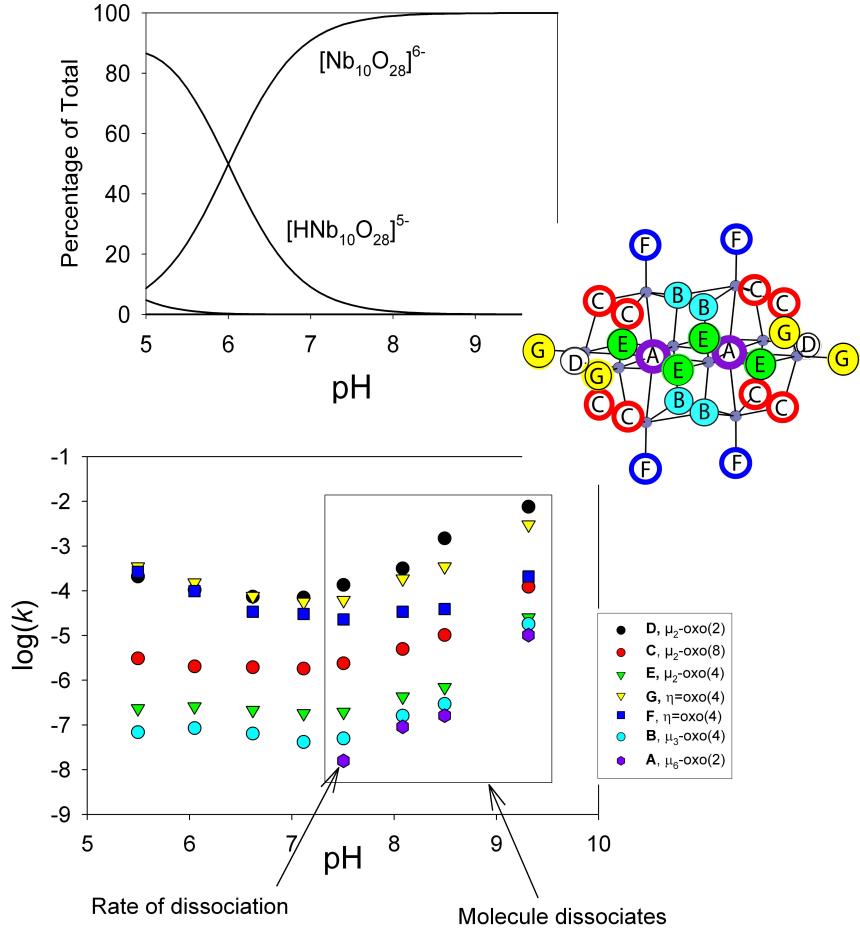
**Figure 1:** The decaniobate ion has seven structurally distinct oxygens, all of which can be detected in a typical  $^{17}\text{O}$ -NMR spectrum. The ion has the stoichiometry:  $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$  in solution, with two sets of terminal oxos (Sites G and F), three sets of oxygens shared by two metals (Sites D, E and C), one set of oxygens bonded to three metals (Site B) and a set of two oxygens (Site A) bonded to six oxygens. The  $^{17}\text{O}$ -NMR spectra are at  $\text{pH}=6.6$  and  $308.5\text{ K}$  and times range from 25 minutes to 15.5 hours. This figure is modified from Villa et al. (2008).



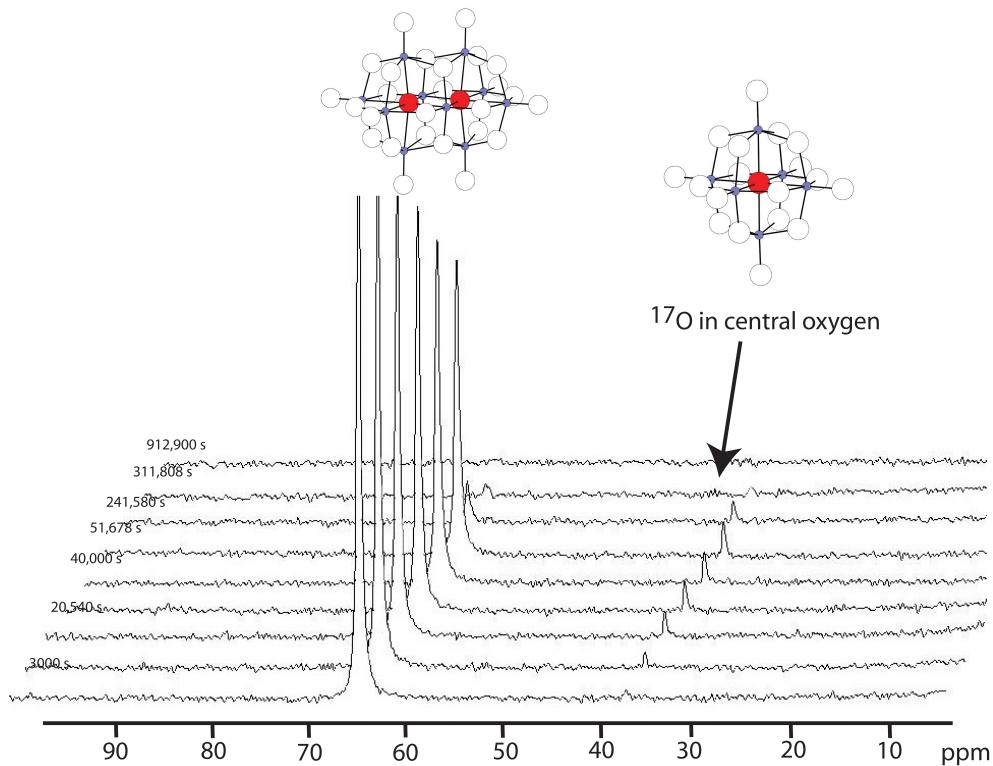
**Figure 2:** Structural parameters for the decaniobate ion in the solid state, as a  $[Nb_{10}O_{28}]^{6-}$ - tetramethylammonium salt. Bond lengths are in Ångström. This figure is was originally published in the Supplemental Information of Villa and others, (2008).



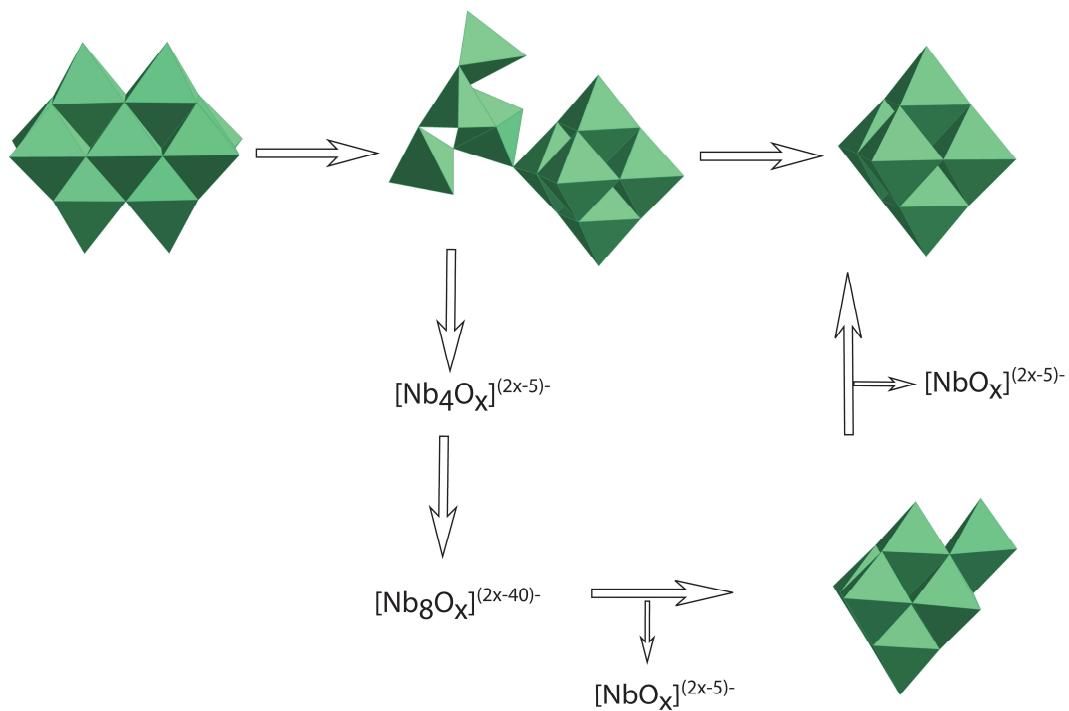
**Figure 3:** Rates of steady oxygen-isotope exchange can be followed in the decaniobate ion at a level of resolution that is impossible for a mineral. At pH=7, the constant <sup>17</sup>O-NMR signal from the central  $\mu_6$ -O site (here shown in purple) indicates that the molecule is not dissociating. At most pH conditions, the <sup>17</sup>O-NMR signals decline from other structural oxygens as they isotopically equilibrate with the aqueous solution. At pH $\geq$ 8.5, slow loss of <sup>17</sup>O-NMR signal from the  $\mu_6$ -O can be detected (upper right) along with a loss of signal for the four  $\mu_3$ -O (Sites B). These equilibration rates are generally much faster than the molecule dissociates.



**Figure 4:** The variation in rates of steady oxygen-isotope exchanges in the decaniobate ion as a function of solution pH. The topmost figure is an estimate of the acid-base speciation of the molecule by analogy with the isostructural and isovalent  $[\text{H}_x\text{V}_{10}\text{O}_{28}]^{(6-x)}$ -molecule. The unprotonated  $[\text{Nb}_{10}\text{O}_{28}]^{6-}$  species dominates at most pH conditions of this study, with the monoprotonated form  $[\text{HNb}_{10}\text{O}_{28}]^{5-}$  becoming important at  $\text{pH} < 6.5$ , consistent with the pH variation of isotope-exchange rates (bottom). Rates of steady oxygen isotopic correspond to 308.5 K, with  $k=1/\tau$ , the characteristic time derived from the McKay equations. The rates of exchange of Site A, the  $\mu_6$ -oxo, is proportional to the rate of dissociation of the molecule. The rate data were originally published in Villa et al., (2008).



**Figure 5:** Stacked  $^{17}\text{O}$ -NMR spectra at pH=9.3 showing the disappearance of the  $\mu_6$ -oxo (red) for the decaniobate ion and the simultaneous appearance, then subsequent disappearance, of the signal for the  $\mu_6$ -oxo in the hexaniobate ion, which is a product of dissociation of the decaniobate ion. The first spectrum was collected at 50 minutes and the last at 10.5 days. This figure was modified from Figure 2 in Villa et al. (2008).



**Figure 6:** A model for the dissociation of the decaniobate ion into a hexaniobate product

that retains some of the  $^{17}\text{O}$ -isotopic tag in the  $\mu_6\text{-oxo}$ . This hexaniobate product then repeatedly interconverts to the decaniobate ion, which reduces the  $^{17}\text{O}$ -NMR signal for both molecules with time. The heptameric product is detectable using ESI-MS.

## References

Allen, T. W., Andersen, O. S., and Roux, B., 2004, Energetics of ion conduction through the gramicidin channel: *Proceedings of the National Academy of Sciences of the United States of America*, v. 101, p. 117-122.

Balogh, E., Anderson, T. A., Rustad, J. R., Nyman, M. D., and Casey, W. H., 2007a, Rates of oxygen-isotope exchange between sites in the  $[H_xTa_6O_{19}]^{(8-x)-}(aq)$  Lindqvist ion and aqueous solutions-comparisons to  $[H_xNb_6O_{19}]^{(8-x)-}(aq)$ : *Inorganic Chemistry*, v. 46, p. 7032-7039.

Balogh, E., Todea, A. M., Muller, A., and Casey, W. H., 2007b, Rates of ligand exchange between  $>Fe^{III}-OH_2$  functional groups on a nanometer-size aqueous cluster and bulk solution: *Inorganic Chemistry*, v. 46, p. 7087-7092.

Black, J. R., Nyman, M., and Casey, W. H., 2006, Rates of oxygen exchange between the  $[H_xNb_6O_{19}]^{(8-x)-}(aq)$  Lindquist ion and aqueous solutions: *Journal of the American Chemical Society*, v. 128, p. 14712-14720.

-, 2007, Rates of oxygen exchange between the  $[H_xNb_6O_{19}]^{(8-x)-}(aq)$  Lindqvist ion and aqueous solutions [ Erratum for [J. Am. Chem. Soc. 2006, 128, 14712-14720]. ]: *Journal of the American Chemical Society*, v. 129, p. 5298.

Black, J. R., Yin, Q.-Z., Rustad, J. R., and Casey, W. H., 2007, Magnesium isotopic equilibrium in chlorophylls: *Journal of the American Chemical Society*, v. 129, p. 8690-8691.

Bontchev, R. P., and Nyman, M., 2006, Evolution of polyoxoniobate cluster anions: *Angewandte Chemie, International Edition*, v. 45, p. 6670-6672.

Burton, W. K., Cabrera, N., and Frank, F. C., 1949, Dislocations in crystal growth: *Nature (London, United Kingdom)*, v. 163, p. 398-9.

Casey, W. H., Lasaga, A. C., and Gibbs, G. V., 1990, Mechanisms of silica dissolution as inferred from the kinetic isotope effect: *Geochimica et Cosmochimica Acta*, v. 54, p. 3369-78.

Casey, W. H., and Phillips, B. L., 2001, Kinetics of oxygen exchange between sites in the  $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}(aq)$  molecule and aqueous solution: *Geochimica et Cosmochimica Acta*, v. 65, p. 705-714.

Casey, W. H., Phillips, B. L., Karlsson, M., Nordin, S., Nordin, J. P., Sullivan, D. J., and Neugebauer-Crawford, S., 2000, Rates and mechanisms of oxygen exchanges between sites in the  $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}(aq)$  complex and water: Implications for mineral surface chemistry: *Geochimica et Cosmochimica Acta*, v. 64, p. 2951-2964.

Casey, W. H., and Westrich, H. R., 1992, Control of dissolution rates of orthosilicate minerals by divalent metal-oxygen bonds: *Nature (London, United Kingdom)*, v. 355, p. 157-9.

Comba, P., and Helm, L., 1988, The solution structure and reactivity of decavanadate: *Helvetica Chimica Acta*, v. 71, p. 1406-20.

Criscenti, L. J., Kubicki, J. D., and Brantley, S. L., 2006, Silicate glass and mineral dissolution: Calculated reaction paths and activation energies for hydrolysis of a Q3 Si by  $H_3O^+$  using ab initio methods: *Journal of Physical Chemistry A*, v. 110, p. 198-206.

Day, V. W., Klemperer, W. G., and Maltbie, D. J., 1987, Where are the protons in  $\text{H}_3\text{V}_{10}\text{O}_{28}$ : *J. Am. Chem. Soc.*, v. 109, p. 2991-3002.

De Yoreo, J. J., and Vekilov, P. G., 2003, Principles of crystal nucleation and growth: *Reviews in Mineralogy & Geochemistry*, v. 54, p. 57-93.

Dove, P. M., Han, N., and De Yoreo, J. J., 2005, Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behavior: *Proceedings of the National Academy of Sciences of the United States of America*, v. 102, p. 15357-15362.

Evans, R. J., Rustad, J. R., and Casey, W. H., 2008, Calculating geochemical reaction pathways - Exploration of the inner-sphere water exchange mechanism in  $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + n\text{H}_2\text{O}$  with ab initio calculations and molecular dynamics: *J. Phys. Chem. A*, v. 112, p. 4125-4140.

Felipe, M. A., Xiao, Y., and Kubicki, J. D., 2001, Molecular orbital modeling and transition state theory in geochemistry: *Reviews in Mineralogy & Geochemistry*, v. 42, p. 485-531.

Furrer, G., Phillips, B. L., Ulrich, K. U., Pothig, R., and Casey, W. H., 2002, The origin of aluminum flocs in polluted streams: *Science*, v. 297, p. 2245-2247.

Graeber, E. J., and Morosin, B., 1977, Molecular configuration of the decaniobate ion  $\text{Nb}_{10}\text{O}_{28}^{6-}$ : *Acta Crystallographica B*, v. 33, p. 2137-2143.

Hill, P. S., and Schauble, E. A., 2008, Modeling the effects of bond environment on equilibrium iron isotope fractionation in ferric aquo-chloro complexes: *Geochimica et Cosmochimica Acta*, v. 72, p. 1939-1958.

Houston, J. R., Phillips, B. L., and Casey, W. H., 2006, Residence times for protons bound to three oxygen sites in the  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  polyoxocation: *Geochimica et Cosmochimica Acta*, v. 70, p. 1636-1643.

Howarth, O. W., and Jarrold, M., 1978, Protonation of the decavanadate(6-) ion: a vanadium-51 nuclear magnetic resonance study: *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999)*, p. 503-6.

Kerisit, S., and Rosso, K. M., 2007, Kinetic Monte Carlo model of charge transport in hematite (a- $\text{Fe}_2\text{O}_3$ ): *Journal of Chemical Physics*, v. 127, p. 124706/1-124706/10.

Klochko, K., Kaufman, A. J., Yao, W., Byrne, R. H., and Tossell, J. A., 2006, Experimental measurement of boron isotope fractionation in seawater: *Earth and Planetary Science Letters*, v. 248, p. 276-285.

Lasaga, A. C., 1998, *Kinetic Theory in the Earth Sciences*, Princeton University Press, 728 p.

Lasaga, A. C., and Luttge, A., 2001, Variation of crystal dissolution rate based on a dissolution stepwave model: *Science*, v. 291, p. 2400-2405.

Lee, A. P., Phillips, B. L., and Casey, W. H., 2002, The kinetics of oxygen exchange between the  $\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}^{8+}(\text{aq})$  molecule and aqueous solutions: *Geochimica et Cosmochimica Acta*, v. 66, p. 577-587.

Liu, Y., Olsen, A. A., and Rimstidt, J. D., 2006, Mechanism for the dissolution of olivine series minerals in acidic solutions: *American Mineralogist*, v. 91, p. 455-458.

Liu, Y., and Tossell, J. A., 2005, Ab initio molecular orbital calculations for boron isotope fractionations on boric acids and borates: *Geochimica et Cosmochimica Acta*, v. 69, p. 3995-4006.

Loring, J., Yu, P., Phillips, B. L., and Casey, W. H., 2004, Activation volumes for oxygen exchange between the  $\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$  ( $\text{GaAl}_{12}$ ) polyoxocation and aqueous solution from variable pressure  $^{17}\text{O}$  NMR spectroscopy: *Geochimica et Cosmochimica Acta*, v. 68, p. 2791-2798.

Ludwig, C., Casey, W. H., and Rock, P. A., 1995, Prediction of ligand-promoted dissolution rates from the reactivities of aqueous complexes: *Nature (London)*, v. 375, p. 44-7.

Maekawa, M., Ozawa, Y., and Yagasaki, A., 2006, Icosaniobate: A new member of the isoniobate family: *Inorganic Chemistry*, v. 45, p. 9608-9609

Mao, W. L., Meng, Y., Shen, G., Prakapenka, V. B., Campbell, A. J., Heinz, D. L., Shu, J., Caracas, R. E., C. R., Fei, Y., J., H. R., and Mao, H.-K., 2005, Iron-rich silicates in the Earth's D" layer: *Proc Natl Acad Sci*, v. 102, p. 9751-3.

Marek, K. A., 2001, Polyoxoniobates: how solution chemistry helps to understand the solid state, Department of Chemistry: Champaign-Urbana, University of Illinois, p. 145 p.

McKay, H. A. C., 1938, Kinetics of exchange reactions: *Nature* v. 142, p. 997-8.

Niu, J., Ma, P., Niu, H., Li, J., Zhao, J., Song, Y., and Wang, J., 2007, Giant polyniobate clusters based on  $[\text{Nb}_7\text{O}_{22}]^{9-}$  units derived from a  $\text{Nb}_6\text{O}_{19}$  precursor: *Chemistry--A European Journal*, v. 13, p. 8739-8748.

Pel'menschikov, A., Strandh, H., Pettersson, L. G. M., and Leszczynski, J., 2000, Lattice resistance to hydrolysis of Si-O-Si bonds of silicate minerals: ab initio calculations of a single water attack onto the (001) and (111) cristobalite surfaces: *Journal of Physical Chemistry B*, v. 104, p. 5779-5783.

Pettersson, L., Hedman, B., Andersson, I., and Ingri, N., 1983, Multicomponent polyanions. 34. A potentiometric and vanadium-51 NMR study of equilibria in the  $\text{H}^+-\text{HVO}_4^{2-}$  system in 0.6 M sodium chloride medium covering the range  $1 < \text{lg}[\text{H}^+] < 10$ : *Chemica Scripta*, v. 22, p. 254-64.

Phillips, B. L., Casey, W. H., and Karlsson, M., 2000, Bonding and reactivity at oxide mineral surfaces from model aqueous complexes: *Nature*, v. 404, p. 379-382.

Phillips, B. L., Lee, A., and Casey, W. H., 2003, Rates of oxygen exchange between the  $\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}(\text{aq})$  ( $\text{Al}_{30}$ ) molecule and aqueous solution: *Geochimica et Cosmochimica Acta*, v. 67, p. 2725-2733.

Pope, M. T., 2003, Introduction to polyoxometalate chemistry: *NATO Science Series, II: Mathematics, Physics and Chemistry*, v. 98, p. 3-31.

-, 2004, Polyoxo anions: synthesis and structure: *Comprehensive Coordination Chemistry II*, v. 4, p. 635-678, 5 Plates.

Rosenqvist, J., and Casey, W. H., 2004, The flux of oxygen from the basal surface of gibbsite ( $\text{a}-\text{Al}(\text{OH})_3$ ) at equilibrium: *Geochimica et Cosmochimica Acta*, v. 68, p. 3547-3555.

Rustad, J. R., and Bylaska, E. J., 2007, Ab initio calculation of isotopic fractionation in  $\text{B}(\text{OH})_3(\text{aq})$  and  $\text{BOH}_4^-(\text{aq})$ : *Journal of the American Chemical Society*, v. 129, p. 2222-2223.

Rustad, J. R., Loring, J. S., and Casey, W. H., 2004, Oxygen-exchange pathways in aluminum polyoxocations: *Geochimica et Cosmochimica Acta*, v. 68, p. 3011-3017.

Rustad, J. R., Nelmes, S. L., Jackson, V. E., and Dixon, D. A., 2008, Quantum-chemical calculations of carbon-isotope fractionation in  $\text{CO}_2(\text{g})$ , aqueous carbonate species, and carbonate Minerals: *Journal of Physical Chemistry A*, v. 112, p. 542-555.

Rustad, J. R., Rosso, K. M., and Felmy, A. R., 2004, Molecular dynamics investigation of ferrous-ferric electron transfer in a hydrolyzing aqueous solution: Calculation of the pH dependence of the diabatic transfer barrier and the potential of mean force: *Journal of Chemical Physics*, v. 120, p. 7607-7615.

Schauble, E. A., Ghosh, P., and Eiler, J. M., 2006, Preferential formation of  $^{13}\text{C}-^{18}\text{O}$  bonds in carbonate minerals, estimated using first-principles lattice dynamics: *Geochimica et Cosmochimica Acta*, v. 70, p. 2510-2529.

Spinner, B., 1968, Etude quantitative de l'hydrolyse des niobates de potassium: *Rev. Chim. Miner.*, v. 5, p. 839-868.

Stixrude, L., Lithgow-Bertelloni, C., Kiefer, B., and Fumagalli, P., 2007, Phase stability and shear softening in  $\text{CaSiO}_3$  perovskite at high pressure: *Physical Review B: Condensed Matter and Materials Physics*, v. 75, p. 024108/1-024108/10.

Stixrude, L., and Peacor, D. R., 2002, First-principles study of illite-smectite and implications for clay mineral systems: *Nature*, v. 420, p. 165-168.

Thomas, T. N., Land, T. A., Casey, W. H., and DeYoreo, J. J., 2004, Emergence of supersteps on  $\text{KH}_2\text{PO}_4$  crystal surfaces: *Phys Rev Lett*, v. 92, p. 216103.

Tossell, J. A., 2005, Boric acid, carbonic acid, and N-containing oxyacids in aqueous solution: ab initio studies of structure, pKa, NMR shifts, and isotopic fractionations: *Geochimica et Cosmochimica Acta*, v. 69, p. 5647-5658.

Villa, E. M., Ohlin, C. A., Balogh, E., Anderson, T. M., Nyman, M. D., and Casey, W. H., 2008, Reaction dynamics of the decaniobate  $([\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-})$  ion in water: *Angew Chem Int Ed*, v. 47, p. 1-4.

Wang, J., Rustad, J. R., and Casey, W. H., 2007, Calculation of water-exchange rates on aqueous polynuclear clusters and at oxide-water interfaces: *Inorganic Chemistry*, v. 46, p. 2962 - 2964.

Xiao, Y., and Lasaga, A. C., 1996, Ab initio quantum mechanical studies of the kinetics and mechanisms of quartz dissolution: OH- catalysis: *Geochimica et Cosmochimica Acta*, v. 60, p. 2283-2295.