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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.

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 (Liu and Tossell, 2005; Tossell, 2005; Schauble and others, 2006; Klochko and others, 2006; Rustad and Bylaska, 2007; Black and others, 2007a; Hill and Schauble, 2008; Rustad and others, 2008), predict phase transitions (Stixrude and Peacor, 2002; Mao and others, 2005; Stixrude and others, 2007), to follow biochemical reactions (Allen and others, 2004; Kerisit and Rosso, 2007) and speculate about dissolution and growth (Casey and others, 1990; Pelmenschikov and others, 2000; Criscenti and others, 2006; Liu and others, 2006). 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-

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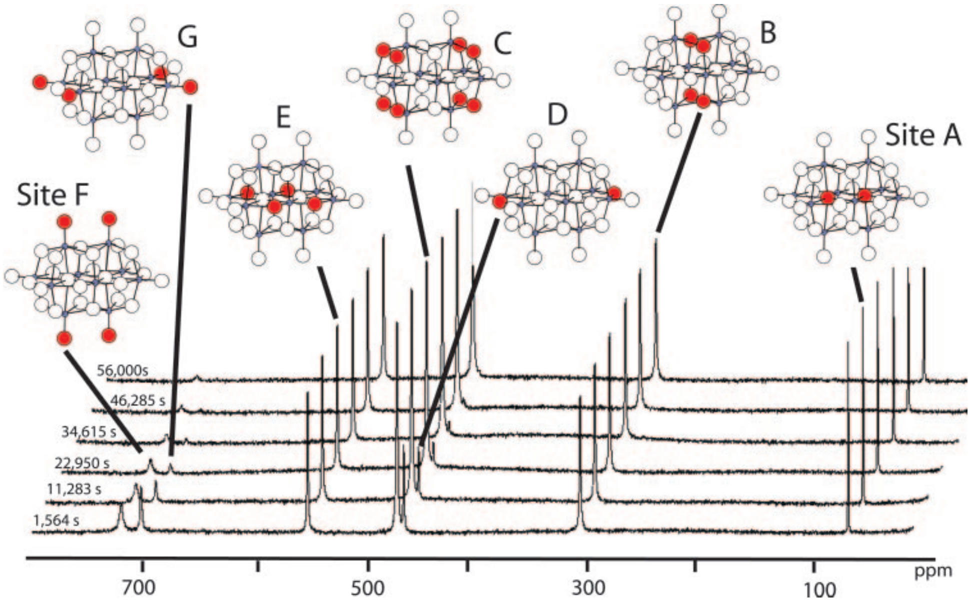

Fig. 1. The decaniobate ion has seven structurally distinct oxygens, all of which can be detected in a typical ^{17}O-NMR spectrum. The ion has the stoichiometry: $[H_xNb_{10}O_{28}]^{(6-x)-}$ in solution, with two sets of terminal oxos ($\eta = O$; Sites G and F), three sets of oxygens shared by two metals (μ_2-O; Sites D, E and C), one set of oxygens bonded to three metals (μ_3-O; Site B) and a set of two oxygens (μ_6-O; Site A) bonded to six oxygens. The ^{17}O-NMR spectra are at pH = 6.6 and 308.5 K. This figure is modified from Villa and others (2008).

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. Computational methods have become increasingly important in identifying molecular-level geochemical processes, however, geochemists need molecular experiments to tell us if computational predictions are accurate and to indicate whether the computational methods are likely to be able to identify reaction mechanisms in the absence of molecular-level information on reaction rates. This level of resolution is well beyond more familiar approaches of interpreting larger-scale 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 little assurance about the uniqueness of the inferred mechanisms. With molecules such as the one discussed here, we can tell quantitatively 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 [$([H_xNb_{10}O_{28}]^{(6-x)-}$); fig. 1] has seven types of structural oxygens and three structurally distinct metal sites. These oxygens are well resolved by

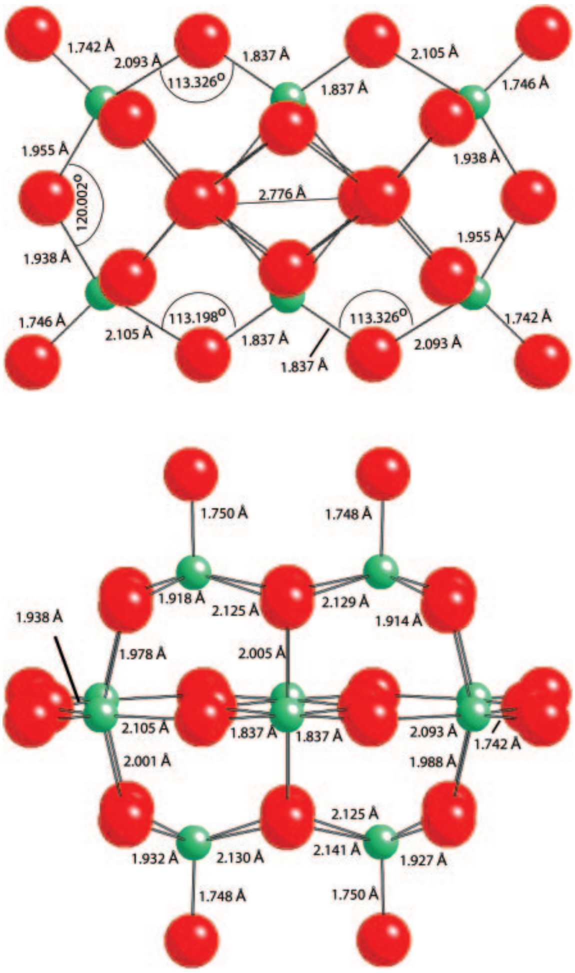

Fig. 2. Structural parameters for the decaniobate ion in the solid state, as a $[Nb_{10}O_{28}]^{6-}$- tetramethylammonium salt. Bond lengths are in Ångström. This figure was originally published in the Supplemental Information of Villa and others (2008) in modified form.

^{17}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}O, one can follow rates of steady oxygen-isotope exchanges as a function of solution pH using ^{17}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 (μ_6-oxo; Site A), two sets of four $\eta = O$ sites, (labeled G and F), three sets of μ_2-oxo sites (Site D is a set of two, Sites E is a set of four and C is a set of eight μ_2-oxygens), and one set of four μ_3-oxo (Site B). [We here employ the standard formalism that η^i sites are nonbridging sites with '*i*' atoms from the ligand bonding to the metal, and μ_i sites are ligands that bridge '*i*' metals, in this case all Nb(V).]

We synthesized crystals of $[N(CH_3)_4]_6[Nb_{10}O_{28}] \cdot 6H_2O$ (Graeber and Morosin, 1977; Marek, ms, 2001; Villa and others, 2008) using ^{17}O-enriched water (40%, Isotec).

A small amount (~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 $[N(CH_3)_4]Cl$. This dissolution step releases the isotopically-enriched molecule to the aqueous solution, in a similar fashion as other aqueous clusters (Casey and others, 2000; Phillips and others, 2000; Casey and Phillips, 2001; Lee and others, 2002; Phillips and others, 2003; Loring and others, 2004; Black and others, 2006; Balogh and others, 2007a). 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}O-NMR spectrum (fig. 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}O-NMR signals from impurities or breakdown products.

The decline in intensity of the ^{17}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 (fig. 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 $[N(CH_3)_4]_6\ [Nb_{10}O_{28}] \cdot 6H_2O$ or $[N(CH_3)_4]_8[Nb_6O_{19}] \cdot \sim 16H_2O$ salts with $H_2{}^{18}O$. 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}O exchanges from structural sites with isotopically normal solution. To estimate rates, ^{17}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}O-NMR signals in solution was guided by previous work on decaniobate and decavanadate ions (Day and others, 1987; Comba and Helm, 1988; Marek, ms, 2001) with the exception of the 722 ppm η=O peak, which was assigned to Site F based on *ab initio* calculations of ^{17}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 μ_6-O sites do not isotopically equilibrate with the bulk solution at most pH conditions, as is also observed for the smaller but related $[H_xNb_6O_{19}]^{(8-x)-}{}_{(aq)}$ Lindqvist polyoxoanion (Black and others, 2006, 2007b). These central oxygens are inert to exchange. At pH>7.5, we can detect a slow loss in intensity of the ^{17}O-NMR signal from this μ_6-O, indicating that the molecule is dissociating (fig. 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 $[H_xV_{10}O_{28}]^{(6-x)-}$ molecule (Howarth and Jarrold, 1978; Pettersson and others, 1983) with pK_x values of: $pK_1 = 6.0$; $pK_2 = 3.74$ and $pK_3 = 1.6$ ($I = 0.6$ M). Using these equilibrium constants, one can show that the $[Nb_{10}O_{28}]^{6-}$ species dominates at most pH conditions of this study (fig. 4) with the monoprotonated form $[HNb_{10}O_{28}]^{5-}$ becoming important at pH < 6.5. The fact that the ^{17}O signals do not change positions with pH is consistent with very weak protonation of this molecule.

The reactivity trend at near-neutral pH is: D(μ_2-oxo)>G(η = oxo)> F(η = oxo)>C(μ_2-oxo)>>E(μ_2-oxo)>>B(μ_3-oxo)>>A(μ_6-oxo) and all oxygens except Site A, and possibly Site B, increase rates of isotopic substitution at pH ≤ 7.0. Notably, the relative rates of isotopic exchange in the three μ_2-O (Sites C, D and E) differ by $\sim 10^4$.

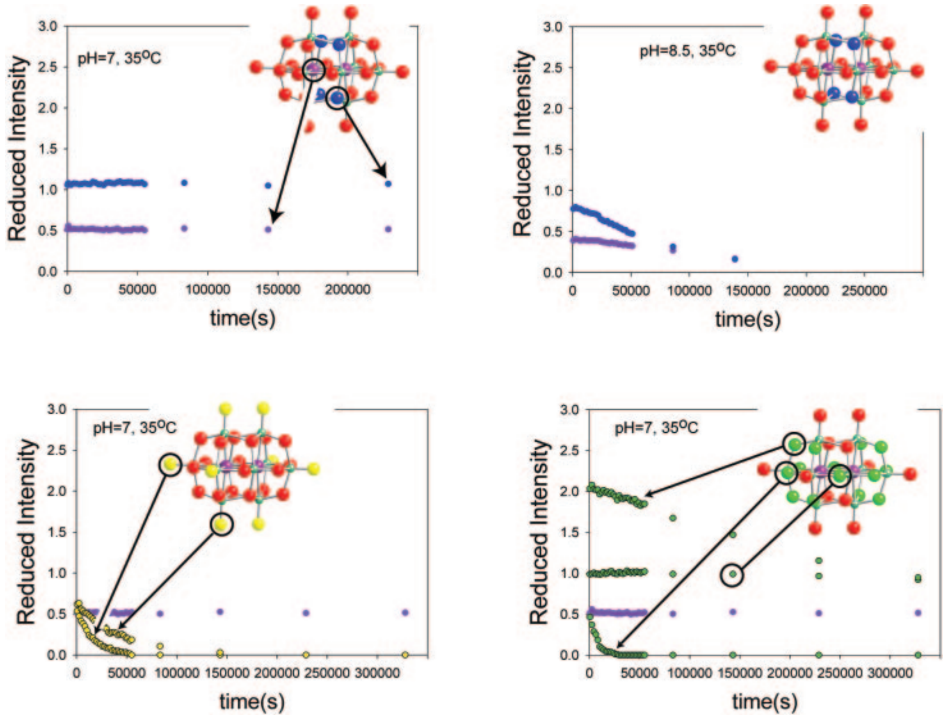

Fig. 3. Rates of steady oxygen-isotope exchange at different structural oxygens in the nanometer-size decaniobate ion. The rates can be followed in the decaniobate ion at a level of resolution that is impossible for a mineral. At pH=7, the constant ^{17}O-NMR signal from the central μ_6-O site (here shown in purple) indicates that the molecule is not dissociating. At most pH conditions, the ^{17}O-NMR signals decline from other structural oxygens as they isotopically equilibrate with the aqueous solution. At pH≥8.5, slow loss of ^{17}O-NMR signal from the μ_6-O can be detected (upper right) along with a loss of signal for the four μ_3-O (Sites B). These equilibration rates are generally much faster than the molecule dissociates.

One μ_2-O site, (Site D) even exchanges more rapidly than either terminal oxygen (Sites F and G) at pH $\geq$ 6.6. Furthermore another μ_2-O site, Site E, is extraordinarily slow to exchange at these conditions (figs. 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 $[Nb_{20}O_{54}]^{8-}$ is formed via protonation and dehydration of two adjacent F-Sites (Maekawa and others, 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 and others, 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 to 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 pH > 7, the rates of isotopic exchange of Sites F, G and D differ by a factor of ~10^2. At pH < 7, however, the rates for Sites F, G and D are nearly equal. Even the relatively inert equatorial μ_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.

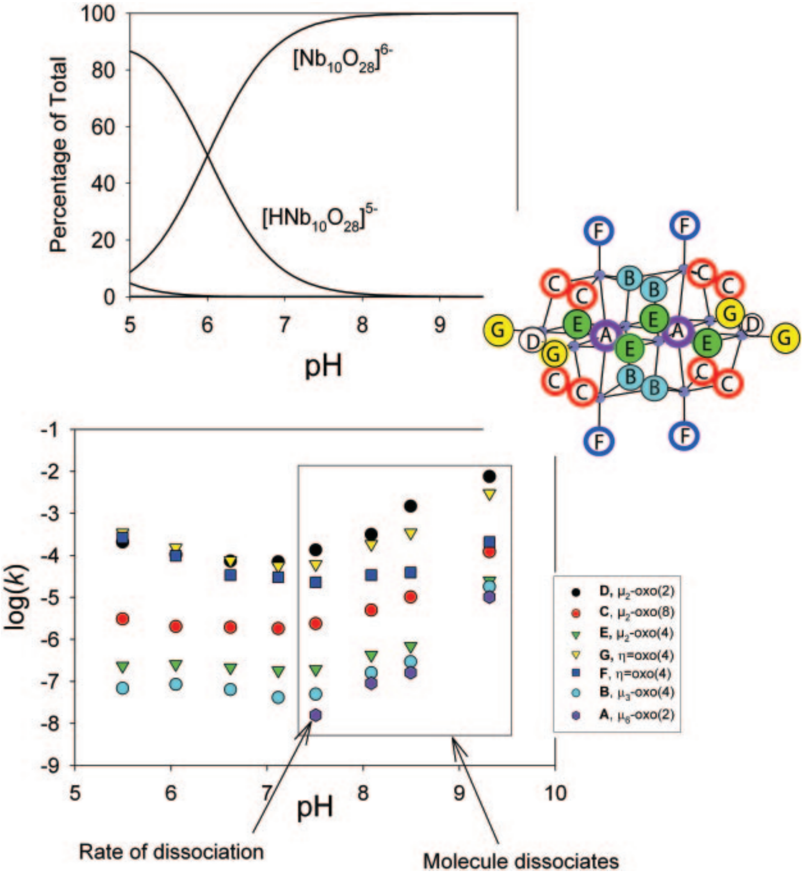

Fig. 4. The variation in rates of steady oxygen-isotope exchanges in the decaniobate ion as a function of solution pH. The topmost figure is an estimate of the acid-base speciation of the molecule by analogy with the isostructural and isovalent $[H_xV_{10}O_{28}]^{(6-x)-}$ molecule. The unprotonated $[Nb_{10}O_{28}]^{6-}$ species dominates at most pH conditions of this study, with the monoprotonated form $[HNb_{10}O_{28}]^{5-}$ becoming important at 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/τ, the characteristic time derived from the McKay equations. The rates of exchange of Site A, the μ_6-oxo, is proportional to the rate of dissociation of the molecule. The rate data were originally published in Villa and others (2008).

Dissociation Rate, Pathways and Products

We could follow dissociation of the oxide molecule into products from the slow decline in the ^{17}O-NMR signal for the μ_6-oxo and from changes in the ESI-MS spectrum. Dissociation is clearly detectable at pH ≥ 7.5 and the rate increases with pH (fig. 4). At pH < 9.3, dissociation of the decaniobate molecule is still significantly slower than the rates of isotopic exchange for most oxygen sites (fig. 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 μ_6-oxo from the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion transforms intact into the μ_6-oxo of the smaller $[H_xNb_6O_{19}]^{(8-x)-}$ ion during dissociation (fig. 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

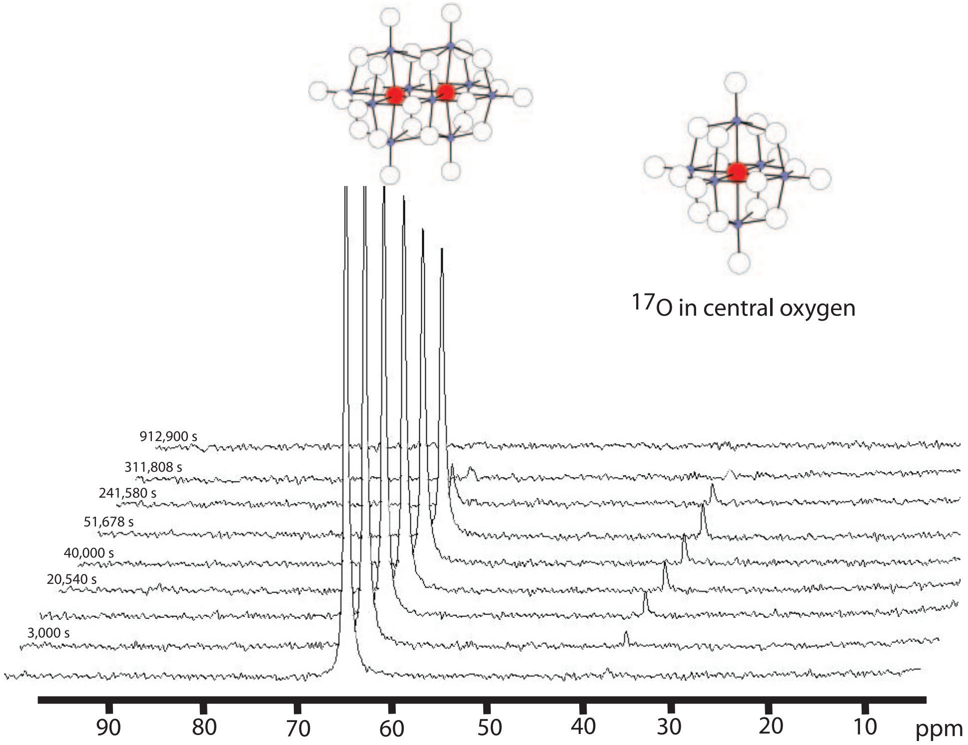

Fig. 5. Stacked ^{17}O-NMR spectra at pH = 9.3 showing the disappearance of the μ_6-oxo (red) for the decaniobate ion and the simultaneous appearance, then subsequent disappearance, of the signal for the μ_6-oxo in the hexaniobate ion, which is a product of dissociation of the decaniobate ion. The first spectrum was collected at 50 minutes and the last at 10.5 days. This figure was modified from Villa and others (2008).

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 μ_6-oxo intact from the dissociating $[Nb_{10}O_{28}]^{6-}$ ion to a μ_6-oxo site in the newly formed $[H_xNb_6O_{19}]^{(8-x)-}$ ion (fig. 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; Ludwig and others, 1995; Lasaga, 1998), to step-flow models that relate growth and dissolution features to saturation states and adsorbate densities

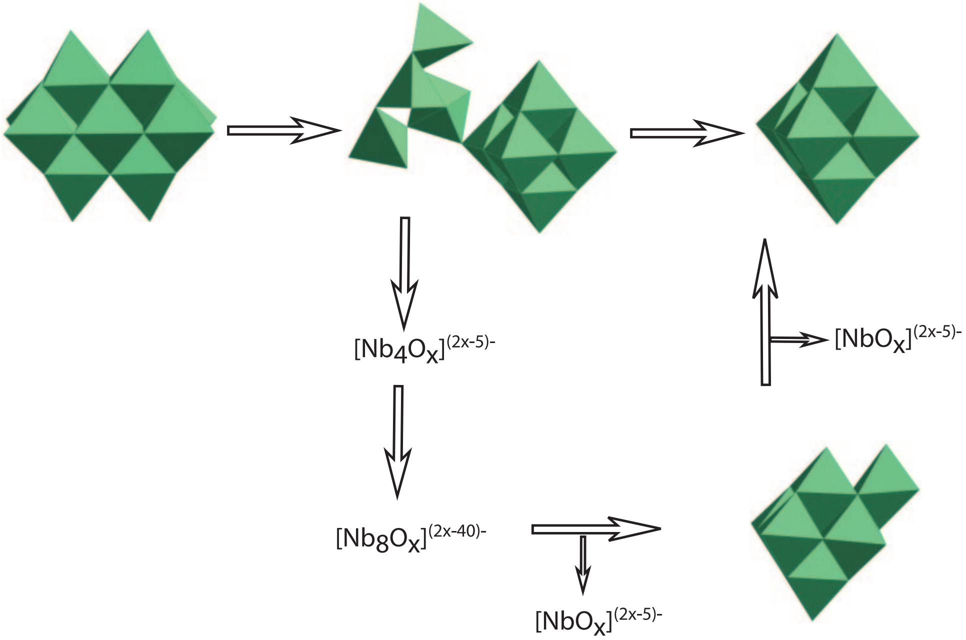

Fig. 6. A model for the dissociation of the decaniobate ion into a hexaniobate product that retains some of the ^{17}O-isotopic tag in the μ_6-oxo. This hexaniobate product then repeatedly interconverts to the decaniobate ion, which reduces the ^{17}O-NMR signal for both molecules with time. The heptameric product is detectable using ESI-MS.

(Lasaga and Luttge, 2001; Dove and others, 2005) to quantum-mechanical simulations (Xiao and Lasaga, 1996; Felipe and others, 2001; Criscenti and others, 2006) and molecular dynamic methods (Rustad and others, 2004a). 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 and others, 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 are not unique or verified.

Such a definitive test could come from large, structurally interesting molecules in which we have complete confidence in the aqueous structure. These molecules, of course, are not minerals (see, however, Atencio and others, 2008) 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 mineral surface sites (Wang and others, 2007) see also (Balogh and others, 2007b). Additionally, interpretation of isotope-exchange rates in aluminum polyoxocations led to greater appreciation of the role of distal bonding and overbonded oxygens in controlling the rates and pathways (Rustad and others, 2004b). 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. It is possible to make a clean substitution of Ti(IV) for Nb(V) near Site B in the decaniobate ion structure (Nyman and others, 2003), allowing geochemists to see if a similar suppression of rates is observed.

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 unprotonated anion 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 μ_3-oxo site that is the nexus of dissociation, isotopically exchanges 2 to 3 times faster than the molecule dissociates. 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 μ_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). This could be just a function of the (001) structure that dominated the reaction; edges are anticipated to be much more reactive. Oxygens on the (012) surface of hematite appears to be highly dynamic in ultra-high vacuum experiments (Henderson and others, 1998), which are the only other data available.

(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 and others, 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 the significance of these results for geochemistry 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, 2004). These molecules are generally anionic, but the most familar 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.

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