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Oxygen–Isotope Exchange and Metastable Dissociation in Oxides

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Abstract

To understand the corrosion of bulk oxide materials at the molecular scale, oxygen–isotope exchanges were examined in two classes of nanometer-sized ions, one cation and one anion, and subsets that differ by targeted single-atom substitutions. In niobate anions, the different oxygen sites within each molecule differ by $\sim 10^3$ – 10^4 in overall rates of isotopic exchange, yet all structural oxygens exhibit similar pH dependencies that relate to the dissociation pathways. In aluminate cations of the ϵ -Keggin structure, single-atom substitutions cause a 10^7 – 10^{10} variation of rates of oxygen–isotopic exchange into two sets of μ_2 -OH. Molecular-dynamic simulations indicate that metastable forms of these structures exist as loose, long-lived intermediates. A series of common steps is observed to access the intermediate structures, and these are best resolved in the symmetric ϵ -Keggin aluminate ions. In the first step, solvation forces, or a nucleophile, cause a near-surface metal to partly detach from a deeper over-bonded oxygen via concerted motions of many atoms. Isotopically distinct oxygens then add to the newly undercoordinated metal in the partly detached metastable state. Protons transfer to more basic oxygens and oxygens shuffle. Finally, the metastable structure collapses and dehydrates. The number of such metastable states depends on the symmetry and composition of the starting structure and access to the metastable state controls the overall rates. Surprisingly, polyoxometalate ions with only 40–100 atoms already seem to capture much of the macroscopic chemistry observed for dissolving minerals and glasses.

ABBREVIATIONS

ox oxalate
ssal sulfosalicylate
sal salicylate
mMal methylmalonate

1. INTRODUCTION

My research group undertook close study of polyoxometalate ions in order to understand how bulk oxide materials and minerals react in water at the molecular scale. The features that control the surface chemistry of minerals and glasses in water are nanometers in scale. These are conspicuous features in atomic-force microscopy images. They include the kink sites and unit-cell-high steps, where mass is added or removed from the interfaces as the material grows or dissolves in solution. Spanning beyond this microscopic scale to understand molecular controls on the reactions, however, is difficult. It is impossible to intuit the rate-controlling steps in such complicated reactions without knowledge of the elementary steps (1), and there must be hundreds or thousands of such steps in the reaction networks. To span the enormous range in scales, the field came to rely heavily on simulations and electronic-structure calculations to infer the molecular steps that they could not observe.

Any molecular-scale interpretations were often based upon an imagined fragment of the mineral (or glass) structure and electronic-structure calculations. Thus, for example, two decades were spent running experiments on bulk materials in water, like silica (SiO_2), and then interpreting the results using electronic-structure calculations on a few atoms (2). In such models, the local acid-base chemistry of the dissociating oxygen is often considered paramount and uninfluenced by the rest of the structure. The flaw of these simulations is the mismatch in scales—it was never demonstrated that these imagined molecular fragments capture the essential chemistry of the nanometer-sized structure. Acceptance was largely a matter of faith.

Polyoxometalate ions, however, provide the experimental models that could answer exactly this question and advance an understanding of aqueous reactions at the molecular scale. Unlike minerals or glasses, the structure of these ions in solution, which are also nanometer in size, can be known unequivocally. Furthermore, the mechanisms of reactions at these ions are approachable by both experiment and simulation. While there are

certainly features of extended oxides that cannot be reproduced in an oxide polyoxometalate ion, a theory for molecular-scale reactions at interfaces could be tested fairly. The simulations and the experiments are both at the same scale, and these polyoxometalate ions even exist in nature (3), so it is hard to dismiss the conclusions as environmentally irrelevant.

In this paper I discuss pathways for oxygen–isotope exchanges and dissociations of two large ions—both an anion and a cation (Fig. 1), that have a few dozen to a 100 atoms. Of course a wealth of information exists from ^{17}O NMR about oxygen–isotope exchange in polyoxometalate ions (4), but unlike in those previous studies, I review results for sets of isostructural molecules that differ only by targeted single-atom substitutions. As I show, these substitutions have profound, systematic, and understandable effects on the

Fig. 1 The two experimental molecules. (A) The polyoxometalate anions: $[\text{Nb}_{10}\text{O}_{28}]^{6-}$, $[\text{Nb}_9\text{TiO}_{28}]^{7-}$, and $[\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{8-}$ with the site of Ti(IV) substitution colored *purple*. Other metals are *black* and oxygens are *dark gray*. (B) The $[\text{MAIO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7/8+}$ cation, where $\text{M} = \text{Al(III)}, \text{Ga(III)},$ or Ge(IV) . The site of metal substitution in the inert center of the molecule is shown in *red*, and the two sets of hydroxyl bridges for which oxygen–isotope-exchange rates were measured are identified with *green* and *purple* colors. Oxygens are *dark gray*, protons are *white*, and nonhighlighted Al(III) metals are *black*.

rates of isotopic exchange. They are sufficiently simple that pathways can be postulated, and, in some cases, the rate-controlling steps can be identified.

2. BROAD REACTIVITY TRENDS FOR DISSOLVING MATERIALS AND GLASSES

Some trends are apparent if one looks at the dissolution kinetics of minerals on the bulk scale. First, for minerals without a polymeric fabric, such as the simple rocksalt-oxide structures with the stoichiometry: MO , or an orthosilicate mineral with the stoichiometry M_2SiO_4 (orthosilicates have $[\text{SiO}_4]^{4-}$ tetrahedra isolated from one another), the rates recapture the familiar trends found for ligand exchange around octahedral aqua ions (Fig. 2).

These trends are observed because the overall coordination number of the metal is retained in both cases. The Ni(II) is hexacoordinated to oxygens in the mineral bunsenite, NiO(s) , and in the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ ion that is released by dissolving bunsenite. The time scales for these two processes, water exchange around an ion and dissolution of a mineral, are vastly different. Rates of water exchange around $[\text{Ni}(\text{OH}_2)_6]^{2+}$ are milliseconds or less, whereas the rates of elimination of a monolayer on NiO(s) take many, many hours or days. In both cases, however, Ni(II) undergoes a set of ligand-exchange reactions that preserve the octahedral coordination of the metal to oxygens. Similarly, at the surface of a step on a mineral interface, stepwise ligand-exchange reactions replace bridging oxygens with solvation waters.

The reactivity trends are both familiar and odd. For example, the trend for minerals of pure composition is shown in Fig. 2A. Minerals with only octahedrally coordinated d^8 Ni(II) (e.g., NiO(s)) dissolve slower than, say, an identical mineral made up of d^5 Mn(II) (MnO(s)) because of ligand-field stabilization of the octahedral geometry. Similarly, reactivity to ligand exchange among alkaline-earth metals reflects ion size: $\text{Be(II)} < \text{Mg(II)} < \text{Ca(II)}$ as does the dissolution rates of the corresponding simple minerals. The orthosilicate minerals trend is: $\text{Be}_2\text{SiO}_4 < \text{Mg}_2\text{SiO}_4 < \text{Ca}_2\text{SiO}_4$. Of course, this reactivity trend says nothing about the rate-controlling elementary steps.

There are also key differences. The mineral larnite, $\text{Ca}_2(\text{SiO}_4)$, dissolves much faster than the mineral forsterite, $\text{Mg}_2(\text{SiO}_4)$, as one expects, even though the two phases are isostructural. However, if an isostructural mineral is made with by combining the two metals in equal proportions,

Fig. 2 Dissolution rates at pH 2 of simple oxide (A) and orthosilicate (B and C) minerals containing divalent metals. In A and B the abscissa is the rate of exchange of water from the corresponding metal ion (e.g., Mg²⁺(aq)), and the ordinate is the dissolution rate of the mineral (e.g., Mg₂SiO₄, forsterite) normalized to area. The oxide minerals have the rocksalt structure. The orthosilicate minerals (5) have the stoichiometry: M₂SiO₄(s) and isolated SiO₄⁴⁻ tetrahedra. The end-member compositions of orthosilicates are shown in *red squares* in (B), whereas the mixed-metal compositions are shown as *blue dots*. For the mixed-metal compositions, dissolution rates are plotted against the weighted sum of the logarithm of rates of water exchange for the component ions. Note that the dissolution rates for mixed-metal compositions (*blue dots* in (B)) fall intermediate between the end-member compositions. The rates of ligand exchange of the aquated ions (●) and the dissolution rates of the orthosilicate minerals (●) at pH 2 are plotted as a function of the number of *d* electrons in (C), illustrating the role of ligand-field stabilization in the rates. *Panels (B) and (C) are adapted from Ref. Casey, W.H.; Swaddle, T.W. Reviews of Geophysics 2003, 41 (2), 4/1–4/20.*

as in the mineral monticellite, $\text{MgCa}(\text{SiO}_4)$, a dissolution rate that is an *average* of the two end-member rates is observed (Fig. 2). These ionic minerals react as though both heterometals contribute to the reactivity. This is interesting.

Materials with a polymeric structure, such as a silicate fabric, dissolve in complicated fashions because the polymer resists hydrolysis more than other components. Thus, not surprisingly, polymerizing the isolated silicate tetrahedra into covalent chains, sheets, or frameworks has a profound effect on dissolution reactivities and stoichiometries. In Fig. 3, the flux of materials is shown from two minerals that differ only in the organization of the silicate tetrahedra. In one case, the silicate groups are organized into isolated three-membered rings. These are highly energetic, and the material dissolves very quickly with equal fluxes of calcium and silicon. If the silicate groups are organized into polymeric chains, however, the rates of dissolution are much slower and the fluxes of calcium and silicon diverge because silica builds up on the dissolving surface. The key point is that small changes in the polymer structure have large effects on the dissolution rates of the solid and the fluxes of elements. In minerals, the changes in polymer structures are discrete. The polymer, for example, is either a ring or a chain or a double chain or a framework, but the changes in polymeric structure in glasses can be continuous. Unlike minerals, glass polymers require statistical descriptions of the polymer network.

Dissolution rates of oxide minerals also exhibit a broad amphoteric variation with pH that resembles other oxide reactions in water, such as ester hydrolysis, oxygen–isotope exchange in sugars (7), and pesticide hydrolysis (8). An example is shown in Fig. 4 where the dissolution rates of the tectoaluminosilicate mineral, orthoclase (KAlSi_3O_8 ; from Ref. (9)) are compared with rates of oxygen–isotope exchanges into anomeric oxygens in three sugars. In this broad amphoteric chemistry, the minimum in rates can be moved to more acidic or basic conditions with the overall proton affinity of the molecule (or the surface). For interfaces, the Brønsted acid–base chemistry of surface oxygens manifests as measurable positive or negative net surface charge (10). Dissolution rates correlate with these charge concentrations and can be proton-promoted, hydroxyl-promoted, or unpromoted. Practically, these terms mean that rates go up as pH drops (proton-promoted), as pH increases (hydroxyl-promoted) and the unpromoted region is where rates are independent of pH; here, water molecules are the most effective nucleophile. All three such regions can be seen in Fig. 4.

Fig. 3 The dissolution of two forms of CaSiO₃ in acidic (initially pH 2) solutions reflects the linkages of the silicate polymer. In the curves, moles of dissolved silicon (○) and calcium (●) are divided by the area of the solid so that the slope of the curves gives the dissolution fluxes directly. (*top, incongruent* dissolution) Wollastonite (α -CaSiO₃) has silicate groups linked in chains and the flux of silicon and calcium differs remarkably from the stoichiometry as saturation with amorphous silica, a solid reaction product, is approached. (*bottom*) Pseudowollastonite (β -CaSiO₃) has silicate groups in highly energetic three-membered rings. Fluxes of dissolved calcium and silicon are virtually identical and dissolution is more rapid, so much so that the solution composition far exceeds the saturation point with amorphous silica. The *horizontal line* identifies the point at which the solution was supersaturated with amorphous silica (6).

Exceptions are easily found. In strongly acidic solutions, more polymerized minerals sometimes dissolve incongruently, meaning that one metal is released by acid hydrolysis to leave a porous structure behind. The most familiar such case is the dealumination of zeolite minerals in acids. These

Fig. 4 Amphoteric variation in rates. (A) Rates of dissolution of the common mineral orthoclase (KAlSi_3O_8) as a function of pH at 25°C (9) and (B) rates of isotopic exchange of oxygen into three sugars at 25°C (7b) as a function of pH; (D-ribose, square symbol; D-2-deoxyribose, open circle; and glucose, line).

materials are tectoaluminosilicate minerals, meaning that the polymeric metals have bridging bonds only. Acid or hydrothermal treatment replaces Al(III) with protons within the framework structure, leaving behind catalytic Brønsted acid sites.

3. ACID–BASE CHEMISTRY AND REACTIVITY IN NIOBATES

The role of acid–base chemistry in the kinetics of isotope exchange and dissociation of polyoxometalates has been studied before (4a,b,g,11), but much more detailed information is available if one studies versions of polyoxometalate anions that differ by single-atom substitutions. Substitutions of Ti(IV) in the decaniobate structure, for example, change the net molecular charge without changing the structure. The first set of such

substituted molecules are: $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$, $[\text{H}_x\text{Nb}_9\text{TiO}_{28}]^{(7-x)-}$, and $[\text{H}_x\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{(8-x)-}$ ions. These decametalate ions are synthesized in solvent that was enriched to $\sim 40\%$ in ^{17}O (12). The salts are crystallized, separated, and, to begin an experiment, dissolved back into isotopically normal solutions.

The ^{17}O -NMR signals for the various oxygen sites, which are given alphabetic labels, are spectrally well resolved (Fig. 5). The molecules are very stable in aqueous solution. For the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ molecule, for example, there are three metal positions, all containing Nb(V), and seven oxygen sites, all of which are evident in an NMR spectrum. There are two sets of $\eta = \text{oxo}$ (Sites F, G), three $\mu_2\text{-oxo}$ (Sites C, D, and E), one set of four $\mu_3\text{-oxo}$ (Site B), and two central $\mu_6\text{-oxo}$ (Site A). The two central $\mu_6\text{-oxo}$ are inert to isotopic exchange unless the molecule completely dissociates and then reforms from isotopically normal bulk solution. Thus, the constant ^{17}O signal for the $\mu_6\text{-oxo}$, labeled “A” in Fig. 5, means that the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ molecule remains intact even as the ^{17}O -NMR signals for some oxo sites

Fig. 5 An ^{17}O -NMR spectrum of the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ molecule with the various oxygen sites labeled. In this case, the molecule was isotopically enriched to $\sim 40\%$ in ^{17}O , crystallized as a tetramethylammonium salt and redissolved into an isotopically normal background electrolyte (4e, 12a, 13). The oxygens are identified by letter and color coded to match later figures in this paper. Note that some of the signals disappear with time due to steady isotopic exchange with the solution.

diminish as they undergo steady isotopic exchange with the solution. The rates of isotopic equilibration are fit to a simple exponential rate law: $I(t) = I_0 e^{-kt}$, where I = intensity; $k = 1/\tau$ and has units of s^{-1} ; τ is a characteristic time for disappearance of the signal and has units of s .

Two features become apparent when one compiles the thus-calculated oxygen–isotope-exchange rates for the various oxygens in all three molecules. First, within a given molecule, such as the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion (Fig. 6), all of the exchangeable oxygens exhibit nearly the same pH dependence for their rates of isotopic exchange. The total range for all oxygens in that molecule differ by a range of $\sim 10^3 \sim 10^4$, as shown in Fig. 6 for the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion and Fig. 7 for the $[H_xNb_8Ti_2O_{28}]^{(8-x)-}$ ion. In the case of the $[H_xNb_8Ti_2O_{28}]^{(8-x)-}$, for example, all rates increase as pH decreases.

Fig. 6 Rates of oxygen–isotope exchange for seven sites in the $[H_xNb_{10}O_{28}]^{(6-x)-}$ molecule as a function of solution pH. The letter designation and coordination chemistry of the various oxygens are shown in the legend. The ion structure is color coded to correspond to the rate data so that individual oxygens can be identified and the number in parenthesis indicates how many of those particular oxygens exist in a molecule. The rate of loss of signal from the A site, the central μ_6 -oxo, indicates dissociation of the molecule. Note that all oxygen sites have roughly the same pH dependence to dissociation and that this variation is also observed for dissociation of the molecule. The units are s^{-1} and are determined by fitting an exponential rate law to the loss of ^{17}O -NMR signal as a function of time (12,14a) (see also Ref. (4e,13)).

Fig. 7 Rates of oxygen–isotope exchange for seven sites in the $[\text{H}_x\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{(8-x)-}$ molecule as a function of solution pH. The letter designation and coordination chemistry of the various oxygens are shown in the legend, as in Fig. 6, and the ion structure is color coded to correspond to the rate data. The number in parenthesis indicates how many of those particular oxygens exist in a molecule. The rate of loss of signal from the A site, the central μ_6 -oxo, indicates dissociation of the molecule. Note that all oxygen sites have roughly the same pH dependence to dissociation and isotopic exchange (12,14a).

Second, dissociation of the molecule, as indicated by diminution of the ^{17}O -NMR signals from the central μ_6 -oxo, has the same pH dependence as the rates of isotope exchange (Figs. 6 and 7). Thus, whatever molecular motions activate the structure to dissociate also seem to be involved in the pathways for isotopic exchange. For the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ ion, dissociation is apparent when pH is raised and is slower than the isotope exchanges at other sites. For the $[\text{H}_x\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{(8-x)-}$, dissociation is evident in acidic solutions, where the loss of signal for Site A is at about the same rate as isotopic exchange of other relatively unreactive bridging oxygens.

The fact that all oxygens exhibit the same pH dependence to isotopic exchange and dissociation suggests that these reactions involve concerted motions of all atoms. The reactivity of any particular oxygen to isotopic exchange can be modified somewhat by choice of a different background electrolyte (12b). The effect is regiospecific in the decaniobate ion, with some oxygens remaining unaffected by choice of the background electrolyte while others varying by $\sim 10^2$. The observation indicates that charge separations are important to the isotopic-exchange pathways, which can be facilitated by counterions. Such a conclusion is consistent with many studies indicating that polyoxometalate ions are coordinated, and perhaps are stabilized by, electrostatic interactions with counterions (15).

The pH dependencies reflect the total unprotonated charge of the molecules, -6 for $[\text{Nb}_{10}\text{O}_{28}]^{6-}$, -7 for $[\text{Nb}_9\text{TiO}_{28}]^{7-}$, and -8 for $[\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{8-}$, which is a measure of their relative affinity for protons and overall basicity. Correspondingly, the $[\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{8-}$ ion is the strongest base in the series, and it exhibits proton-enhanced rates of isotopic exchange of all structural oxygens, over a $\sim 10^3$ range (Fig. 7). In contrast, the $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ ion is the weakest base and the pH dependence of oxygen–isotopic-exchange rates is enhanced by $[\text{OH}^-]$, although there is some evidence for proton-enhanced pathways at low pH (Fig. 6). Data for the $[\text{H}_x\text{Nb}_9\text{TiO}_{28}]^{(7-x)-}$ molecule are not shown, but the oxygen sites in this molecule exhibit an amphoteric variation in rates that falls intermediate between the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ and $[\text{H}_x\text{Nb}_8\text{Ti}_2\text{O}_{28}]^{(8-x)-}$ ions. In this molecule, rates increase with $[\text{OH}^-]$ concentration at high pH, with $[\text{H}_3\text{O}^+]$ at lower pH and exhibit a conspicuous minimum in rates at near-neutral pH conditions. This minimum is shifted to higher pH values than the one observed for the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ ion, as one expects since the $[\text{H}_x\text{Nb}_9\text{TiO}_{28}]^{(7-x)-}$ molecule is a stronger base. All of these observations are consistent with an amphoteric chemistry dominated by the *average* proton affinities of each molecule, and not the affinity of a particular exchanging oxygen bridge. Stated differently, the proton affinities of the oxygens involved in the isotope-exchange reaction are similar to one another.

4. THE TRANSITION TO A PARTLY DETACHED STRUCTURE IN MAI_{12} CATIONS

The idea that reactions at the nanometer size are controlled by meta-stable equilibria is best illustrated by detailed studies of Group 13 cations that all have the structure of the ϵ -isomer of the Baker–Figgis–Keggin structure. These have the stoichiometry: $[\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7/8+}$. The “M” site can be Al(III), Ga(III), or Ge(IV), and in this chapter, the abbreviations: $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+} = \text{AlAl}_{12}$, $[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+} = \text{GaAl}_{12}$, and $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{8+} = \text{GeAl}_{12}$ are used.

There are two sets of 12 μ_2 -OH in each structure that differ slightly from one another—one set of 12 μ_2 -OH lies *within* one of the four trimeric groups that comprise the ϵ -Keggin structure, shown in green in Fig. 1. Another set of 12 μ_2 -OH links each trimeric fragment (Fig. 1 bottom), which is shown in purple. Beyond this difference, the oxygens have identical coordination

environments; the $\langle \text{Al–O} \rangle$ bond lengths, for example, are virtually identical. The single central “M” metal is tetrahedrally coordinated to four μ_4 -oxo, and these oxygens are inert to steady isotopic exchange. The rates of isotopic exchange for all other oxygen sites in these molecules have been measured via ^{17}O -NMR (4i,k–m,16). The rates of isotopic exchange of the 12 bound waters with bulk solution all lie in the millisecond time range, which is the range that is expected for Al(III) complexes of similar charge densities (17) (Table 1). Rates of water exchanges with bulk solution for the 12 sites on each of the AlAl_{12} , GaAl_{12} , and GeAl_{12} all lie within a factor of ~ 5 of one another, which contrasts sharply with the wide range observed for isotope exchanges into the hydroxide bridges.

The central metal in the MAl_{12} molecule exerts an enormous effect on the rates of exchange of both sets of μ_2 -OH. The rates of exchange of μ_2 -OH across the entire set of molecules differ by factors of at least $\sim 10^7$ (Fig. 8) depending

Table 1 A Compilation of Rate Coefficients and Activation Parameters for Exchange of Water Molecules From the Inner-Coordination Sphere of Al(III) Complexes to the Bulk Solution, as Determined From ^{17}O -NMR

Species	k_{ex}^{298} (s^{-1}) ($\pm 1\sigma$)	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$)	Source
Monomeric complexes				
$\text{Al}(\text{H}_2\text{O})_6^{+3}$	1.29(± 0.03)	85 (± 3)	42 (± 9)	(18)
$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$	31,000(± 7750)	36 (± 5)	−36 (± 15)	(19)
$\text{AlF}(\text{H}_2\text{O})_5^{2+}$	240(± 34)	79 (± 3)	17 (± 10)	(20)
$\text{AlF}_2(\text{H}_2\text{O})_4^{+}$	16,500(± 980)	65 (± 2)	53 (± 6)	(20)
$\text{Al}(\text{ssal})^{+}$	3000(± 240)	37 (± 3)	−54 (± 9)	(21)
$\text{Al}(\text{sal})^{+}$	4900(± 340)	35 (± 3)	−57 (± 11)	(21)
$\text{Al}(\text{mMal})^{+}$	660(± 120)	66 (± 1)	31 (± 2)	(22)
$\text{Al}(\text{mMal})_2^{-}$	6900(± 140)	55 (± 3)	13 (± 11)	(22)
$\text{Al}(\text{ox})^{+}$	109(± 14)	69 (± 2)	25 (± 7)	(23)
Multimeric complexes				
AlAl_{12}	1100(± 100)	53 (± 12)	−7 (± 25)	(4k, 16a)
GaAl_{12}	227(± 43)	63 (± 7)	29 (± 21)	(4l)
GeAl_{12}	190(± 43)	56 (± 7)	20 (± 21)	(4m)

From Lee, A.P.; Phillips, B.L.; Casey, W.H. *Geochim. Cosmochim. Acta* **2002**, 66 (4), 577–587.

Fig. 8 The oxygen-exchange rates (k , s^{-1} ; left-hand-side) and average lifetimes (τ_i ; $i = 1, 2$; right-hand-side) for the two μ_2 -OH sites in each of the $AlAl_{12}$, $GaAl_{12}$, and $GeAl_{12}$ molecules, as measured in ^{17}O -NMR experiments (4*k–m*). The open and closed symbols correspond to fast- and slow-reacting μ_2 -OH sites in the same molecule and are color coded: $AlAl_{12}$ = (●, ○), $GaAl_{12}$ = (▲, △), and $GeAl_{12}$ = (■). Arrows link the values of τ_1 and τ_2 within to each molecule. There is no value of τ_2 for the $GeAl_{12}$ since the rates are too fast to measure. Note that the rates span at least a factor of 10^7 in rates depending upon the metal in the inert “M” site of the $[MO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7/8+}$ molecules and could be as high as 10^{10} if the typical $\sim 10^3$ difference in τ_1 and τ_2 values is also observed for the $GeAl_{12}$ molecule.

upon the metal in the inert “M” site of the $[MO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7/8+}$ molecules. The two sets of μ_2 -OH colored green and purple in Fig. 1 yield time constants for exchange (τ_1 , τ_2) (Fig. 8) and these differ by $\sim 10^3$ within a single molecule. The range could be as high as $\sim 10^{10}$ if the typical $\sim 10^3$ difference in τ_1 and τ_2 values is found for the $AlAl_{12}$ and $GaAl_{12}$ molecules is also observed for the $GeAl_{12}$ molecule. The rates are compiled in Fig. 8 for both sets of μ_2 -OH bridges in all three molecules: $AlAl_{12}$, $GaAl_{12}$, and $GeAl_{12}$.

No pH variation was detected in exchange rates of oxygens into μ_2 -OH bridges for the $GaAl_{12}$ and $AlAl_{12}$ molecules (4*k–m*), although experiments could only be conducted over a narrow range ($4.2 < \text{pH} < 6.5$). The isotope-exchange rates for the less-labile μ_2 -OH bridge in the $GeAl_{12}$ cluster exhibited a near-first-order dependence on proton concentration (4*m*), and, of course, the more labile μ_2 -OH bridge reacted too quickly for NMR measurement by injection.

5. METASTABLE INTERMEDIATES

The ions described earlier were chosen because they were at an appropriate scale for dynamic simulation. Correspondingly, Rustad *et al.* (14b) built a force field for Al(III) hydrolysis in water and from his simulations posulated a mechanism that explains the enormous sensitivity of the rates of exchange of hydroxyl bridges in the MAI_{12} cations. He later extended the model to treat the niobate ions in water (14), which will be discussed later. Although the two experimental sets of molecules differ considerably in charge and structure, a similar set of reaction steps to produce a metastable form of the structure could be identified. The central idea is that loose metastable structures form that are essential to the rates of isotopic exchange of bridging oxygens. Forming the metastable structure involves concerted motions of all atoms. They cannot be intuited by examining the static, stable form of the molecule nor can a separated fragment of the structure be assumed to capture the entire chemistry.

The MAI_{12} set of molecules were particularly well suited for unraveling the mechanism because they had such high symmetry that the number of potential metastable intermediates was limited. The reaction pathway identified in the molecular–dynamic simulations is illustrated in Fig. 9 for the MAI_{12} series of molecules.

The metastable forms are established via a predictable series of steps:

- Step 1.** A loose, metastable form of the structure forms by partial detachment of a surface metal from the deeper and often overbonded oxygens. Solvation forces, and nucleophiles such as OH^- and H_2O , induce the detachment. The overbonded oxygen is the central $\mu_4\text{-O}$ for the MAI_{12} series of molecules and the central $\mu_6\text{-O}$ for the series of niobate ions. The energy required to establish this partly detached structure depends upon concerted motions of all atoms in the molecule and, of course, several sets can exist that are accessible via different transformations. Because charge separations are involved in forming the metastable structure, counterions can influence the rates, as discussed earlier.
- Step 2.** Oxygens add to the newly undercoordinated metals in the loose, metastable structure. In the case of the AlAl_{12} molecule (Fig. 9) the result is a dimer-like intermediate at the top of the ϵ -Keggin structure. This loose structure forms by the lifting

Step 1: Stepwise partial detachment

Step 2: Addition of water; hydrolysis

Step 3: μ_2 -O₂H₃ bridge formation

Fig. 9 A series of reaction steps postulated by Rustad *et al.* (24) that account for the ^{17}O -NMR data for the MAI_{12} series of the reactions. First is stepwise detachment of surface metals from deeper overbonded oxygens, here the μ_2 -oxo that bond to the “M” site. Detachment is induced by solvation forces in this case. In the second step, isotopically normal oxygens add to the now-undercoordinated metals; in this example, it is as a water molecule. The third and fourth steps are bond rupture and proton transfers, which in the MAI_{12} molecules forms a μ_2 -O₂H₃⁺ bridge. The bridge dehydrates and reestablishes to release the isotopic tag and in the last step, the metastable structure collapses. In the MAI_{12} series of molecules, the energy to form the loose metastable structure in Step 1 depends very sensitively on the strength of M- μ_2 -oxo bonding (see Fig. 10).

Step 4: Proton transfers

Step 5: Reestablishment of the bridge

Step 6: Collapse of the metastable state

Fig. 9—Cont'd

of two hexacoordinated Al(III) away from the μ_4 -O. This lifting is of course undoubtedly actually stepwise but is illustrated as a simultaneous reaction in Fig. 9 to save space. In the case of the niobates, which have lower symmetry than the MAl_{12} molecules, many sets of intermediates could form (14b), but all require partial detachment of a metal from the overbonded μ_6 -O (see later).

Step 3. Protons transfer among oxygens in the metastable structure. For the ϵ -Keggin structures, one of the μ_2 -OH bridges in the dimer-like intermediate protonates to form a μ_2 -O₂H₃⁺. In the niobates, the protons transfer to structural oxo bridges and to solvent.

Step 4. Bridging and nonbridging oxygens swap. In the case of the ϵ -Keggin structure, the swapping is via a water molecule in the μ_2 -O₂H₃⁺ bridge, which returns to form a μ_2 -OH and release an ¹⁷O-enriched water to solution.

Step 5. The metastable structure collapses (Fig. 9) and dehydrates to release the isotopic tag to solution.

For the MAI₁₂ molecules, “M” metals influence the reaction by constraining access to the metastable state that is essential to isotopic exchange. The two types of μ_2 -OH in the ϵ -Al₁₃ structures differ subtly in the structure, lying either *cis* or *trans* to the μ_4 -O, but do not differ much in the structure of the intermediates formed. One set of μ_2 -OH has more energetic latitude to form the intermediate structure and the energies of forming the intermediate scale GaAl₁₂ > AlAl₁₂ > GeAl₁₂, just as is expected from the experimental observations (24) (Fig. 10). Key to the reaction is the strength of the bond between the M site and the μ_4 -O, which affects the facility with which the metastable structure can be accessed. The energies of forming this dimer-like cap for the GaAl₁₂, AlAl₁₂, and GeAl₁₂ molecules, are shown along with Rustad’s force-field result, as Fig. 10.

A similar set of low-energy transitions to metastable structures can be identified for the niobate series of molecules, but the unique tie to experimental data is unclear because of the lack of symmetry in the molecules. But what was found in the isostructural niobate series of [H_xNb₁₀O₂₈]^{(6-x)-}, [H_xNb₉TiO₂₈]^{(7-x)-}, and [H_xNb₈Ti₂O₂₈]^{(8-x)-}, is that a single-atom substitution, well away from the sites of isotopic exchange, has an enormous effect on the kinetics of oxygen–isotope exchange and dissociation.

Rustad *et al.* also built a force field for molecular-dynamic simulations of these niobate anions in a dissociating water solvent (14b). As with the MAI₁₂ Keggin ions, he found that the molecules were constantly sampling their energy landscape and forming metastable forms of their structures via a similar set of steps as those outlined earlier. The steps were similar, although the number and character of the metastable structures were very sensitive to the symmetry and composition of the starting structures.

As with the aluminate ions, the first step is detachment of one of the three metals from the deep overbonded μ_6 -oxo via solvation forces. This detachment forms an intermediate structure (Fig. 11) with loosely bonded set of

Fig. 10 Calculated energies at the DFT/ccpVDZ/B3LYP level of theory to form the dimer-like intermediate structure at the cap of the MAl_{12} ion as a function of the various metals (Ge(IV), Al(III), or Ga(III)) in the central “ $\text{M}(\text{O})_4$ ” position (24). The energy to form the dimer-like intermediate structure depends sensitively upon the strength of the bond between the central metal and the inert μ_4 -oxo. A highly charged metal like Ge(IV) polarizes that bond and makes the adjacent bond to an $\text{Al}(\text{O})_6$ correspondingly weaker so that the intermediate forms easily. The reverse is true as well—placement of a large metal with relatively low charge in the central position, like Ga(III), weakens bonds to the μ_4 -oxo and, correspondingly, the bond to the adjacent $\text{Al}(\text{O})_6$ site is stronger and forming the intermediate is less favored. The rates of exchange of the outer μ_2 -OH trend: $\text{GeAl}_{12} > \text{AlAl}_{12} > \text{GaAl}_{12}$. Also shown is the potential-energy trend for the molecular-dynamics model that was used to identify the reaction coordinate (24).

metals. The second step is addition of an isotopically normal oxygen, which can be either a H_2O , OH^- , or H_3O^+ . The added oxygen can be in any form because the protons reshuffle immediately to more basic oxygens in the niobate structures or to the solvent. Thus, he termed the reactions “*oxygen-stuffing reactions*” because of the similar character regardless of the incoming nucleophile and because of the proton ambiguity. Access to this metastable state involves concerted motions by all oxygens in the nanometer-sized structure, which is a second reason why single-atom substitutions affect the kinetics of the reaction, as is observed. Protons do not activate individual bridging oxygens to isotopic exchange, they activate the entire molecule.

Several points are important in this model: (i) all atoms are involved in forming the intermediate; thus changes in composition have an averaging

Fig. 11 A reaction that yields one possible metastable form of the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ molecule. The steps are broadly similar to those illustrated in Fig. 9 for the MAI₁₂ series of molecules, although these are structurally very dissimilar. The first step is partial detachment of a surface metal from a deeper overbonded oxygen, which in this molecule is the central μ_6 -oxo (Site A). An oxygen adds to the now-undercoordinated metal, which can be as a hydroxide ion, a hydronium, or a water molecule. Protons transfer to more basic oxygens and the metastable form exists for an appreciable lifetime. At some point the oxygens shuffle to a bridging position and the metastable structure collapses.

Fig. 11—Cont'd

effect on reactivity. (ii) The number of accessible metastable forms reflects the energy landscape, which in turn reflects the molecule's symmetry and composition. The MA_{12} molecules have T_d symmetry, but the $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ ion has D_{2d} symmetry and thus a more complicated energy landscape to explore. This landscape is further complicated by the Ti(IV) substitutions. (iii) The energy barrier to forming the intermediate structures can be dramatically affected by single-atom substitutions. (iv) These intermediate structures seem to be implied in both dissociation pathways and in oxygen–isotope–exchange rates, and it is not difficult to see that a

molecule with little energy could experience exchange of some oxygens at varying rates but that a molecule with much energy dissociates via the same metastable intermediate.

Thus, for example, the μ_3 -oxo in the center of the $[\text{H}_x\text{Nb}_{10}\text{O}_{28}]^{(6-x)-}$ anion only begin to exchange oxygen isotopes when there is also evidence for isotopic exchange of the normally inert μ_6 -oxo, which indicates that the molecule is dissociating. The μ_3 -oxo exchange at rates that are 2–3 times faster than the rates of dissociation, as indicated by isotopic equilibration of the μ_6 -oxo (Fig. 6).

6. CONCLUSIONS

What results on two limited polyoxometalate systems means for scientists studying interfacial reactions is actually profound. For both of these cluster ions, the pathways for isotopic exchange and dissociation would *never* have been identified without considering the entire structure and how it interacted dynamically with solution. A truncated model, for example, attempting to treat SiO_2 dissolution via a silicate dimer ($2k-n$) is worse than useless because it is misleading. To emphasize this point even further, niobate molecules have been synthesized with siloxane and silanol groups (4j). In these Si-substituted niobates, the siloxane (Si-O-Si) and silanol ($>\text{Si-OH}$) groups exhibit the same pH dependencies, and overall reactivities, to oxygen–isotopic substitution as all other oxygens in the molecule.

Thus, the setting is everything—even such simple reactions as isotope exchanges are controlled by access to metastable structures that are unique to the entire structure have their own acid–base chemistry and exist for long lifetimes. Access to the metastable states reflects the entire nanometer-sized structure and its interactions with solution.

A second point concerns that the daunting amount of structural information needed to constrain a reaction pathway at these nanometer-sized features in aqueous solutions at molecular scales. The amount of information needed to detail the reaction pathway in the MAI_{12} ions, for example, was considerable. The reaction pathways would also never have been identified without close coupling of experiment to simulation, and without accurate information about the structures in solution. There is no equivalent structural detail available for any interfacial reaction on any mineral, which is why the community relied so much on simulation of

inferred key fragments to understand the molecular transformations and transition states. Stated succinctly, any model for molecular-scale reactions on the nanometer-sized features on a mineral or glass surface must be structurally faithful to the actual site of reaction or it will miss the essential chemistry.

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