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Prof. Neville A. Compton, Editor
Chemistry - A European Journal
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May 12, 2010

Prof. Compton:

We greatly appreciate the comments by the referees, and are gratified that they consider this manuscript to be important, as do we.

Below we address comments from the reviewers, which we denote in *italics*. Our changes are denoted in blue, and the previous phrasing in shown in red.

Cordially,

Bill Casey

William H. Casey
Professor of Geology
Professor of Chemistry

Comments by Referee 1

1) *This paper reports evidence for regioselective oxygen exchange rate acceleration on polyoxoniobate anions in the presence of an added anion (borate) and as such these are interesting findings and the work should be published.*

That said I am not sure that the authors have spotted the clear evidence for rate saturation with borate at some of the oxygen sites which gives strong clues as to how borate may be interacting with the polyoxoniobate structures. As a result the action of borate remains a mystery to the authors and the discussion lacks depth.

Close analysis of the rate of exchange versus borate concentration (figure S-2-3) reveals that depending upon the oxygen site (figure S-2-1) the rate is either independent of borate (site E); linear with borate (terminal sites G and F) or shows saturation with borate (sites C and D). Certainly the exchange at site D is strongly non-linear with borate and could be reflective of a strong associative interaction with borate at this site. The curvature is less apparent with C but it is clearly there. Sites C and D are bridging oxygens within a triangular face of the cluster unlike the other sites. Ignoring polynuclear borate species one could envisage an H-bonded association with B(OH)3 or B(OH)4- (both mononuclear species would be present at the chosen pH (8.9) close to the first pKa). Perhaps this association complex remains undetected in the MS. The differing degrees of rate saturation might be explainable by differing interaction of B(OH)3 and B(OH)4- with sites C and D. Tetrahedral B(OH)4- is set up better structurally to interact with both the C and D oxygens but is negatively charged which might weaken any H-bond interaction. However trigonal B(OH)3 is neutral so although it might form stronger H-bonds its structure means it might only bind strongly to one site (D) while interacting weakly with the C sites.

Response: We thank the referee. The richness of the results hadn't escaped us, but we were constrained by length restrictions. Figure 2 has been changed (see below) by adding the rates for μ_2-oxo site D as a function of borate concentration. Referee 1 is correct in saying that the rates of oxygen exchange observed for site D are saturated and this has been added to the figure. Rates were simply to fast to be estimated for site D above 50 mM borate concentrations. As for site C, the final data point at 75 mM borate could very well be beginning to show saturation of oxygen exchange but it is still fairly linear.

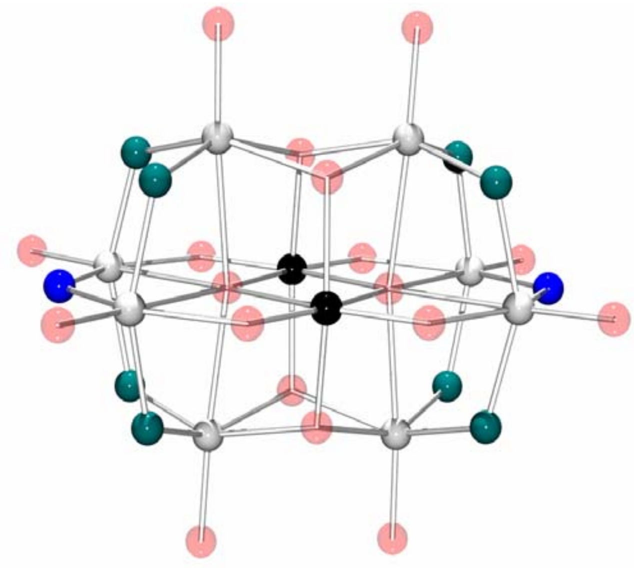
The figure caption first read:

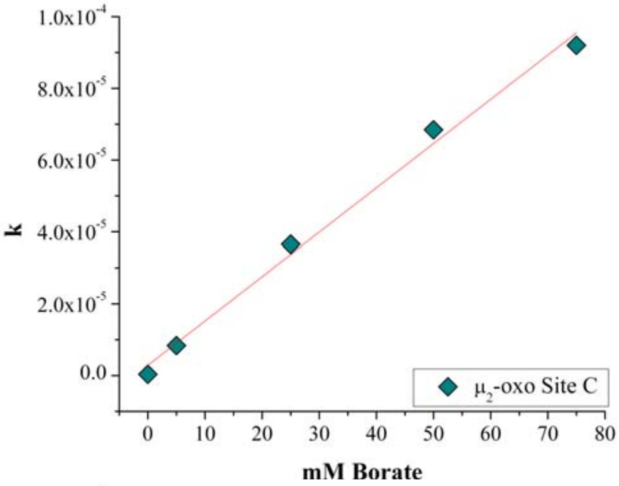
Figure 2: The rates of oxygen exchange of site C, shown in dark cyan, in the Ti_2Nb_8 ion (where titanium atoms are black, niobium atoms are gray, and all other oxygens are red and transparent). The rates linearly increase with the borate concentration. In all cases, the concentration of the Ti_2Nb_8 ion is constant at *ca* 2.8mM, save the experiment with 50 mM borate where the concentration of Ti_2Nb_8 was ~4.2 mM.

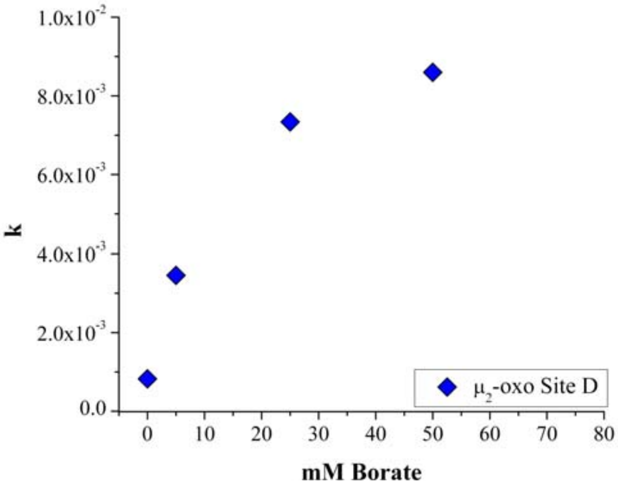
And has now been changed to:

Figure 2: The rates of oxygen exchange of sites C and D, shown in dark cyan and blue respectively, in the Ti_2Nb_8 ion (where titanium atoms are black, niobium atoms are gray, and all other oxygens are red and transparent). The rates linearly increase with the borate concentration for site C but apparently approach a maximum for site D; however, the final data point for site C at 75 mM borate could be approaching a maximum as well. In all cases, the concentration of the

Ti_2Nb_8 ion is constant at ca 2.8mM, save the experiment with 50 mM borate where the concentration of Ti_2Nb_8 was ~4.2 mM. Rates were too fast to be estimated above 50 mM borate for μ_2-oxo site D.







The paragraph at the bottom of page 2 used to read:

The rates of oxygen-isotope exchange increase for most, but not all, structural oxygens in the Ti_2Nb_8 ion as the amount of borate increases in solution. In Figure 2, the rates of oxygen-isotope exchange for site C (in dark cyan) in the Ti_2Nb_8 ion are shown with respect to total dissolved borate concentration. The rates linearly increase with the amount of borate in solution, a trend that is also seen for many of the other structural oxygens in the Ti_2Nb_8 ion (see Supporting Information for all rate data). The rates for some sites, such as the μ_3-oxygens, are unaffected by the presence of borate but these sites are inert to exchange for the Ti_2Nb_8 ion.[9] One set of slowly exchanging equatorial μ_2-oxygens, along the long side of the ion, are uninfluenced by borate in solution (Figure 3).

And has been changed to read:

The rates of oxygen-isotope exchange increase for most, but not all, structural oxygens in the Ti_2Nb_8 ion as the amount of borate increases in solution. In Figure 2, the rates of oxygen-isotope exchange for sites C (in dark cyan) and site D (in blue) in the Ti_2Nb_8 ion are shown with respect to total dissolved borate concentration. The rates for site C linearly increase with the amount of borate in solution, a trend that is also seen for the terminal oxygens in the Ti_2Nb_8 ion (see Supporting Information for all rate data). Although, the rate for site C at 75 mM borate may be exhibiting signs of rate saturation whereby the rates no longer linearly increase, as is seen for site D. This saturation of rates of oxygen exchange at sites C and D may help to indicate the preferred interaction sites on the ion. The rates of oxygen exchange for the terminal oxygens increase linearly and might indicate a different, weaker interaction with borate in solution. The rates for some sites, such as the μ_3-oxygens, are unaffected by the presence of borate but these sites are inert to exchange for the Ti_2Nb_8 ion.[9] One set of slowly exchanging equatorial μ_2-oxygens, along the long side of the ion, are uninfluenced by borate in solution (Figure 3).

2) *Certainly there is a noticeable drop in the rate of the C exchange with borate around pH 9 (figure S-2-2). Unfortunately there are no data below pH 9 for the D exchange with borate present. The authors should comment. Could the authors at least acknowledge the evidence of non-linearity in the C and D exchange with borate in offering a deeper discussion.*

Response: The authors do not see the noticeable drop in the rate of oxygen exchange for site C in the presence of borate around pH 9 in Figure S-2-2; however, the difference between the rates with and without borate are less dramatic as the pH decreases. The authors did not consider this small difference to be sufficiently profound to note. There are no data below pH 9 for site D at 50 mM borate concentrations because the rates were too fast to measure (0.1 M background salt, 50 mM pH buffer, and 35.5°C).

3) *The linear acceleration at the terminal site F close to C suggests an even weaker interaction but nonetheless an effect. Alternatively it could be due to a different mechanism of accelerated exchange to that at C and D. The authors need to comment. The same may be true for G although a 10x less acceleration is seen at 50mM borate. Site E shows no acceleration with borate so it is presumed here that borate does not interact strongly if at all on this side of the molecule. This is also very interesting.*

Response: The authors agree that because the terminal oxygens F and G increase linearly, there is most likely a different interaction with the borate in solution that there is with the μ_2-oxos sites C and D. As stated above: This saturation of rates of oxygen exchange at sites C and D may help to indicate the preferred interaction sites on the ion. The rates of oxygen exchange for the terminal oxygens F and G increase linearly and might indicate a different weaker interaction with borate.

Comments by Referee 2

1). *The paper by Casey and co-workers examines the influence of the buffer chosen to control pH on the rate of oxygen isotope exchange on polyoxoniobate anions. The authors have replaced the borate buffer with the ¿innocent¿ CAPS buffer and have found a significant decrease in the rate of oxygen exchange when this buffer is used. In contrast to anions like borate and carbonate, CAPS does not readily exchange its oxygen atoms or does so extremely slowly and, a consequence, cannot promote the rate of oxygen exchange through oxygen-transfer processes. The authors have further analysed the effect of borate concentration on isotope exchange and have found a linear relationship between the rate of oxygen exchange and borate concentration, providing further support for the view that these borate is not a spectator in these reactions. The work has been carried out with care and this communication represents a nice contribution to this field of research that is worthy of publication in Chem Eur J.*

Response: This comment is enormously gratifying.

We have been striving for over a decade to understand the controls on reactivity of simple oxides in water. These new interactions give us even more insight into how these ions react in solution with water and the ions around them.

Comments by Referee 3

1). *Villa et al report the role of borate in oxygen-isotope exchange reactions in three polyoxoniobate compounds. On a positive note, the manuscript is well written and the subject matter will be of interest to a wide variety of chemists. However, there is something about this manuscript that feels lacking. Part of the problem is that I don¿t like that the authors chose a Communication over an Article. The format choice, along with the large amount of info buried in the Supporting Information, make it feel that this was almost submitted prematurely. I like the authors¿ hypothesis about borate¿s ability to change in coordination number being responsible for the unique chemistry but if feels a bit speculative at this point. On page 2, the authors briefly mention work with polyoxotantalates, but it is not clear if the role of borate was examined with these systems. Overall, the positives do slightly outweigh the negatives so I am inclined to recommend publication at this time.*

Response: We thank the referee, but he/she is unaware of the enormous expense and work entailed in such an expansion. The experiments described in this *Communication* took two years. The cost of 17O is considerable ($1000/g), but also the NMR time is several tens of thousands of dollars because the peaks grow in so slowly. A complete study would also be enormous because the series must be expanded (with blanks) over pH, borate and temperature space. We felt that the *Communication* was the proper venue for the essential information.

We agree that our hypothesis is speculative, but it perfectly consistent with the experimental data and also just a minor part of the Communication. Our data for the preferred sites for interaction are more important and clear.

Also, we mention the polyoxotantalates only to reconcile the discordant trends in the literature between these two isostructural Lindqvist ions (hexaniobate and hexatantalate). No new experiments on hexatantalate were done in the presence of borate. We showed that the apparently inconsistency was due to borate enhancement.

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Borate Accelerates Rates of Steady Oxygen-Isotope Exchange for Polyoxoniobate Ions in Water

Eric M. Villa, C. André Ohlin, and William H. Casey*[a]

Understanding simple oxygen exchange reactions is important to a variety of communities concerned with the chemistry of oxides with water. Limitations in the methods available for studying reactions at these oxide-water interfaces, as well as difficulties in characterizing their structures, have led to the use of polyoxometalates (POMs) as model molecules. POMs are metal-oxide ions comprised of group 5 and 6 metals. These ions constitute discrete and often soluble clusters than can be spectroscopically probed with great confidence. In addition, POMs are interesting in their own right owing to their structural and chemical diversity, and are finding an increasing number of applications.[1-5] We have been investigating the oxygen-isotope-exchange kinetics in these ions and aqueous solution by ^{17}O-Nuclear Magnetic Resonance (NMR) to help better recognize what controls molecule-water interface processes on the level of individual oxygen sites.[6-10] These structures are chosen because the isotope-exchange reactions could be followed separately from dissociation or condensation of the structure.

Borate is widely used as a pH buffer owing to its low cost and conveniently located pK_a. In general, borate buffers are assumed to be inert. Most POMs are anions, as is borate, and it is reasonable to assume that the negative charges of the POM and the borate will minimise interactions in solution. Here we describe the interactions between borate and three different niobium-based POMs. These interactions are interesting in their own right, but also allow us to reconcile observed differences in the oxygen-exchange rates between the hexaniobate and hexatantalate ions.[6,7]

We observed a large increase in the rates of oxygen-isotope exchanges when a borate buffer was employed in experiments on the sodium salt of the dititanoniobate ion $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$.[9] This observation led us to further investigate this phenomenon in other systems. The rates of oxygen exchange for three separate POMs were discovered to be enhanced by having borate in solution: the potassium salt of the hexaniobate ion $[H_xNb_6O_{19}]^{(8-x)-}$, the tetramethylammonium salt of the decaniobate ion $[H_xNb_{10}O_{28}]^{(6-x)-}$, and sodium salt of the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion (represented by Nb_6, Nb_{10}, and Ti_2Nb_8 hereafter for clarity).

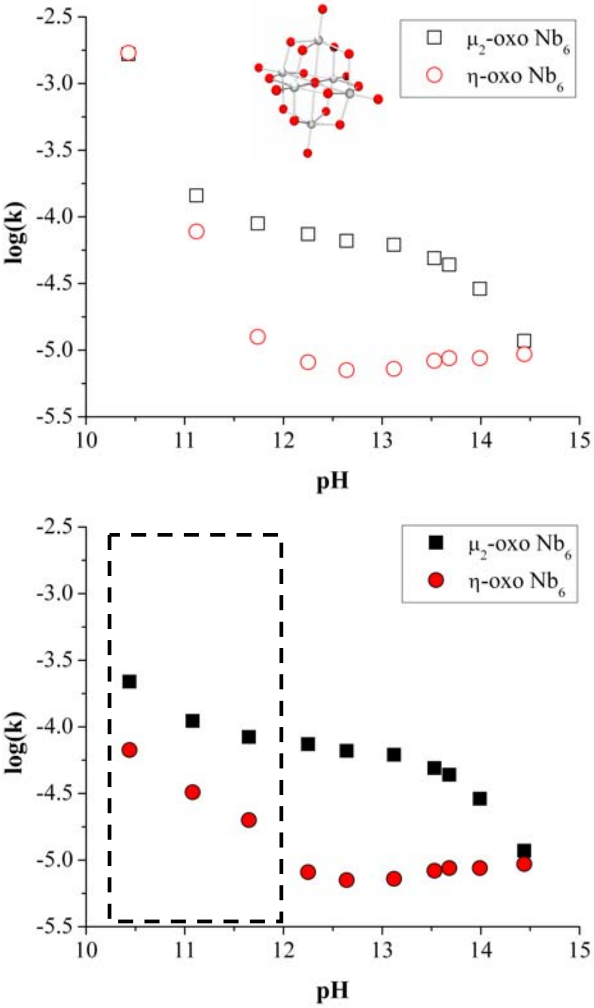

Figure 1: Re-examination of the pseudo-first-order rate coefficients for oxygen exchange for the $[H_xNb_6O_{19}]^{(8-x)-}$ ion. Top: original data published for the Nb_6 ion using borate and carbonate as pH buffers (pH 10.44 for borate; pH 11.65 and 11.08 for carbonate).[6] Bottom: boxed area indicating where new experiments were conducted, replacing borate and carbonate with CAPS (3-cyclohexylamino-1-propanesulfonic acid). The rates of oxygen exchange are heavily influenced by these small anions in solution.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

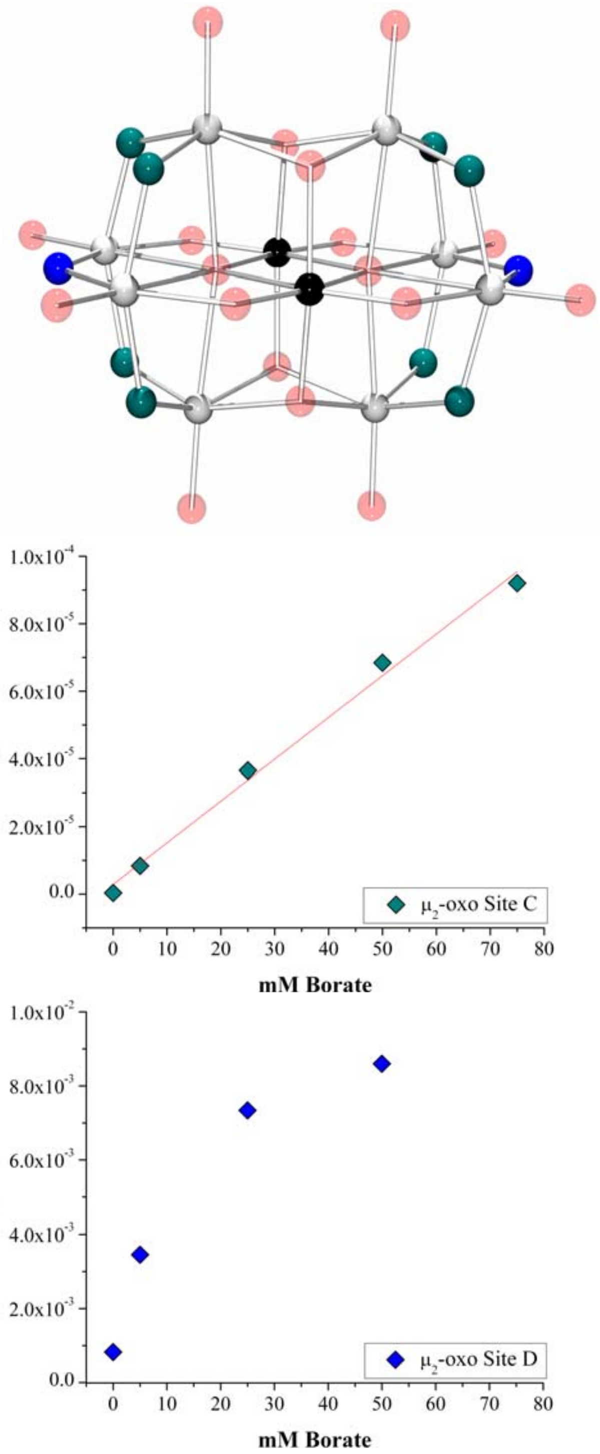

Figure 2: The pseudo-first-order rate coefficients for oxygen exchange of sites C and D, shown in dark cyan and blue respectively, in the Ti_2Nb_8 ion (where titanium atoms are black, niobium atoms are gray, and all other oxygens are red and transparent). The rates linearly increase with the borate concentration for site C but apparently approach a maximum for site D; however, the final datum for site C at 75 mM borate could be approaching a maximum as well. In all cases, the concentration of the Ti_2Nb_8 ion is constant at *ca* 2.8 mM, save the experiment with 50 mM borate where the concentration of Ti_2Nb_8 was ~4.2 mM. Rates were too fast to be estimated above 50 mM borate for μ_2-oxo site D.

After noticing this rate-enhancing effect, we repeated experiments on the Nb_6 ion. In the original work, we employed borate as a buffer at $10.1 \leq pH \leq 10.7$, which is a pH region where rates increase dramatically (Figure 1) and the bridging and terminal oxygens reach similar values for rates of oxygen-isotope exchange.[6] To check whether the increased rates resulted from pH buffer, we replicated the experiments with CAPS (3-cyclohexylamino-1-propanesulfonic acid) buffer. Rates for oxygen-isotope exchange for both reacting structural oxygens decreased dramatically, by at least a factor of 10 (Figure 1, Bottom, *i.e.* both the terminal oxygens and μ_2-oxo bridges). Borate buffer clearly had a significant effect on the rates of oxygen-isotope exchange. The effects of carbonate ion were also examined and a difference was apparent here too.

This enhancement of rates of oxygen-isotope exchange caused by the buffer clarifies our previous results for the hexatantalate ion $[H_xTa_6O_{19}]^{(8-x)-}$ (abbreviated Ta_6).[7] For the Ta_6 ion, we found a small increase in rates as the pH was lowered and the molecule became protonated. However, the increase was nowhere near as dramatic as was found for Nb_6 ion in borate buffer (Figure 1; Top). The experiments with CAPS show that the faster rates of oxygen exchange were due to dissolved borate in solution.

We then measured rates of isotope exchanges for the Nb_{10} and Ti_2Nb_8 ions in the presence of borate. The latter ion is stable between pH 7.5 and at least pH 13.[9] Isotope-exchange rates for sites in the Ti_2Nb_8 ion in sulfonate and amine buffers (see supporting information) were measured at $7 \leq pH \leq 10.5$,. This pH range was chosen to span across the first pK_a of borate (~9.14). At all pH conditions, borate accelerates the rates of oxygen-isotope exchange, with a somewhat larger increase close to pH~9.1 (see Supporting Information for rates and plots). We cannot state confidently that the rate-enhancement is due only to interactions of the polyoxoniobate ions with a monomeric borate complex because rates are enhanced across a broad range in pH. Polyborate species are also present at these concentrations and may influence the exchange rates. Such polyborate species are known to form in solutions where the borate concentration is above 50 mM.[11-14]

The rates of oxygen-isotope exchange increase for most, but not all, structural oxygens in the Ti_2Nb_8 ion as the amount of borate increases in solution. In Figure 2, the rates of oxygen-isotope exchange for sites C (in dark cyan) and site D (in blue) in the Ti_2Nb_8 ion are shown with respect to total dissolved borate concentration. The rates for site C linearly increase with the amount of borate in solution, a trend that is also seen for the terminal oxygens in the Ti_2Nb_8 ion (see Supporting Information for all rate data). Although, the rate for site C at 75 mM borate may be exhibiting signs of rate saturation whereby the rates are no longer linearly increasing, as is seen for site D. This saturation of rates of oxygen exchange at sites C and D may help to indicate the preferred interaction sites on the ion. The rates of oxygen exchange for the terminal oxygens increase linearly and might indicated a different, weaker interaction with borate in solution. The rates for some sites, such as the μ_3-oxygens, are unaffected by the presence of borate but these sites are inert to exchange for the Ti_2Nb_8 ion.[9] One set of slowly exchanging equatorial μ_2-oxygens, along the long side of the ion, are uninfluenced by borate in solution (Figure 3).

In Figure 3, structural oxygens are shown with the relative increases in rates of oxygen-isotope exchange in the presence, and absence, of borate buffer. The increases correspond to the ratio of the rates so that ~1x means that the rates are virtually unaffected. The oxygens that are most influenced correspond to the distal face on the short side of the ion, including two sets of μ_2-oxygens and two sets of terminal oxygens.

Richens and coworkers isolated a reduced niobate species where borate has coordinated to three μ_2-bridging oxygens.[15,16] This coordination looks similar to the most highly affected oxygens in the Ti_2Nb_8. However, no shifts or broadening of lines in the ^{17}O-NMR spectra were observed in the presence of borate. No borate coordination was indicated by electrospray-ionization mass spectrometry of the solutions either, suggesting that the interaction is weak or transient or both.

Finally, borate accelerated base-induced dissociation of the Nb_{10} ion to the Nb_6 products, which is even evident pH ~7 where it was previously unsuspected.[8] A separate side reaction, not dissociation, affects the Ti_2Nb_8 ion at pH ~7.1 (possibly a dimerization) and this reaction too was accelerated by borate buffer.[9]

Borate and carbonate both rapidly equilibrate with forms having a reduced coordination number. Boric acid is trigonal and rapidly adds an oxygen to form borate ion $H_3BO_3 \leftrightarrow B(OH)_4^-$,[11,17-20] trigonal carbonate ion equilibrates with hydrated CO_2, which is linear. We speculate that this interconversion and oxygen addition is key to the rate enhancement. The niobates are large anions and would repel borate or carbonate anions electrostatically. The facile interconversion of the anion to a neutral form, followed by oxygen addition and ejection, is a reasonable hypothesis to explore. Anions that are not able to lose an oxygen tend to be inert (*viz.* phosphate and sulfate) and are expected to have little to no effect on niobates.

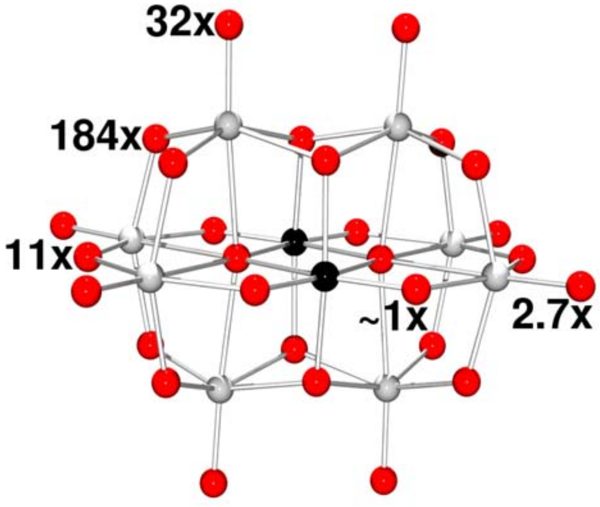

Figure 3: All reacting oxygens are shown with the increase in rates that is observed when the amount of total dissolved borate in solution is increased from 0 to 50 mM. These increases correspond to a ratio so that ~1x increase means that the rates are virtually unaffected by borate in solution (see Supporting Information for actual rates).

In conclusion, borate enhances rates of oxygen-isotope exchange of polyoxometalate oxygens. Borate also accelerates dissociation and perhaps dimerization side reactions. The exact nature of the interaction of the polyoxometalate ion with the buffer is unclear, but we suspect that borate, and perhaps other small anions that can rapidly add and lose oxygens, interact preferably with the distal face of the large polyoxometalate ions and stabilize intermediate forms of the structure. These interactions are well suited for simulation and may be general to other POMs, and perhaps even solid oxide surfaces.

Experimental Section

Synthesis and ^{17}O-enrichment of $K_8Nb_6O_{19}$, $[N(CH_3)_4]_6[Nb_{10}O_{28}]$, and $Na_8Ti_2Nb_8O_{28}$ were carried out according to published procedures.[6,8,9] $H_2{}^{17}O$ (40%) was purchased from Isotec Laboratories. The solution-state ^{17}O-NMR experiments were conducted on a 500 MHz Bruker Avance spectrometer located at the UCD NMR facility. A 0.3 M $TbCl_3$ solution was employed as an external intensity standard, which was included in the 10 mm NMR tube as a coaxial insert. More details on synthesis, ^{17}O-spectroscopy, ^{17}O-NMR stack plots, and rates of oxygen exchange provided as supporting information. The intensities for ^{17}O-NMR signals decrease exponentially with time according to a pseudo-first-order equation; k has units of s^{-1}.

Acknowledgements

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Keywords: Borate • Polyoxometalates • Oxygen Exchange • Kinetics • Niobates

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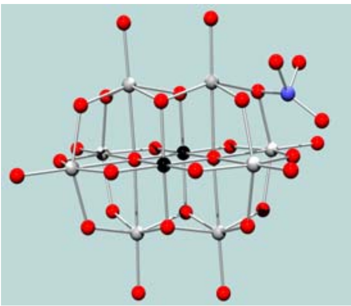
Borate: Guilty and Charged

*Eric M. Villa, C. André Ohlin, and William H. Casey** ………..…
Page – Page

Borate Accelerates Rates of Steady Oxygen-Isotope Exchange for Polyoxoniobate Ions in Water



Borate ion, and possibly carbonate, enhances rates of steady oxygen-isotope exchanges at some, but not all, structural sites in polyoxometalate ions. Here we show addition of an oxygen to an incoming neutral boric acid molecule (blue=boron) from a bridging oxygen on decametalate ion.

Supporting Information

Borate Accelerates Oxygen-Isotope Exchange for Polyoxoniobate Ions in Water

Eric M. Villa, C. André Ohlin, and William H. Casey

S-1: The Hexaniobate Ion

	pH	log(k, s^{-1}) for μ_2-bridging oxygens	log(k, s^{-1}) for η-terminal oxygens
14.0 mM Nb_6 in a 33 mM borate buffer	10.43	-2.78	-2.77
7.0 mM Nb_6 in a 50 mM CAPS buffer	10.44	-3.66 ± 0.11	-4.17 ± 0.05
20.5 mM Nb_6 in a 415 mM carbonate buffer	11.12	-3.84	-4.11
6.8mM Nb_6 in a 50mM CAPS buffer	11.08	-3.96 ± 0.04	-4.49 ± 0.03
10.2 mM Nb_6 in a 38mM carbonate buffer	11.74	-4.05	-4.90
6.9mM Nb_6 in a 50mM CAPS buffer	11.65	-4.08 ± 0.03	-4.70 ± 0.05

Table S-1-1: Comparing the log(k) values for the structural oxygens in the $[H_xNb_6O_{19}]^{(8-x)-}$ ion, which is abbreviated Nb_6. The buffer 3-cyclohexylamino-1-propanesulfonic acid (CAPS) was used to eliminate using buffers that can rapidly add or lose an oxygen. These data are shown visually in Figure 1 of the article. All solutions were run at 24.4°C and in ~3 M KCl background electrolyte. In all cases when a CAPS buffer was used, the pH was adjusted with potassium hydroxide to get to the desired pH.

S-2: The Dititanoniobate Ion:

pH	Buffer composition – Without Borate
7.15	50 mM PIPES: Piperazine-1,4-bis(2-ethanesulfonic acid)
8.03, 8.95	50 mM TRIS: 2-Amino-2-hydroxymethyl-1,3-propanediol
9.43	50 mM CHES: 2-(Cyclohexylamino)ethanesulfonic acid
10.45	50 mM CAPS: 3-(Cyclohexylamino)-1-propanesulfonic acid

Table S-2-1: Buffers used to control pH in the oxygen-isotope-exchange experiments in the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion. The final pH was reached by dropwise addition of $[N(CH_3)_4]OH$ and/or HCl. All buffers were prepared with a 0.1 M $[N(CH_3)_4]Cl$ background electrolyte.

pH	Buffer composition – With Borate
7.14	50 mM PIPES: Piperazine-1,4-bis(2-ethanesulfonic acid) with 50 mM Borate
8.01	50 mM TRIS: 2-Amino-2-hydroxymethyl-1,3-propanediol with 50 mM Borate
8.92, 9.47	50 mM Borate
10.48	50 mM CAPS: 3-(Cyclohexylamino)-1-propanesulfonic acid with 50 mM Borate

Table S-2-2: Buffers used to control pH in the oxygen-isotope-exchange experiments in the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion. The final pH was reached by dropwise addition of $[N(CH_3)_4]OH$ and/or HCl. All buffers were prepared with a 0.1 M $[N(CH_3)_4]Cl$ background electrolyte.

Temp °C	pH	Ti_2Nb_8 (mM)	log(k) s^{-1} μ_6-oxo (Site **A**)	log(k) s^{-1} μ_3-oxo (Site **B**)	log(k) s^{-1} μ_2-oxo (Site **C**)	log(k) s^{-1} μ_2-oxo (Site **D**)	log(k) s^{-1} μ_2-oxo (Site **E**)	log(k) s^{-1} η=O (Site **F**)	log(k) s^{-1} η=O (Site **G**)
35.5	7.15	4.22	-6.18±0.21	-6.13±0.19	-5.65±0.03	--	-6.23±0.10	-3.00±0.03	-3.50±0.03
35.5	7.14	2.93	-5.63±0.50	-5.55±0.25	-4.21±0.01	--	-5.87±0.15	--	-2.46±0.09
35.5	8.03	2.81	--	--	-6.13±0.10	-2.62±0.19	-6.59±0.10	-3.21±0.08	-3.34±0.02
35.5	8.01	2.98	--	--	-4.28±0.01	--	-6.25±0.04	--	-2.92±0.04
35.5	8.95	2.81	--	--	-6.42±0.07	-3.08±0.04	-6.87±0.09	-3.64±0.02	-3.73±0.01
35.5	8.93	4.26	--	--	-4.16±0.01	-2.07±0.05	-6.97±0.06	-2.14±0.05	-3.30±0.02
35.5	9.43	2.87	--	--	-6.58±0.13	-3.16±0.05	-7.14±0.08	-4.50±0.01	-4.70±0.01
35.5	9.47	3.01	--	--	-4.40±0.01	-2.41±0.13	-7.00±0.14	-2.78±0.05	-3.67±0.01
35.5	10.45	2.79	--	--	-6.81±0.38	-4.11±0.02	-7.89±0.11	-5.08±0.02	-5.32±0.02
35.5	10.48	2.95	--	--	-5.02±0.01	-2.99±0.06	-7.50±0.26	-3.81±0.02	-4.36±0.01

Table S-2-3: Comparing the log(k) values for the structural oxygens in the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion, which is abbreviated Ti_2Nb_8, with and without borate. Rates of oxygen-isotope exchange with borate are shown in gray. The buffers are shown in Tables S-2-1 and S-2-2. These data are shown visually in Figure S-2-1. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. The pH was adjusted with either tetramethylammonium hydroxide or hydrochloric acid to achieve the desired pH.

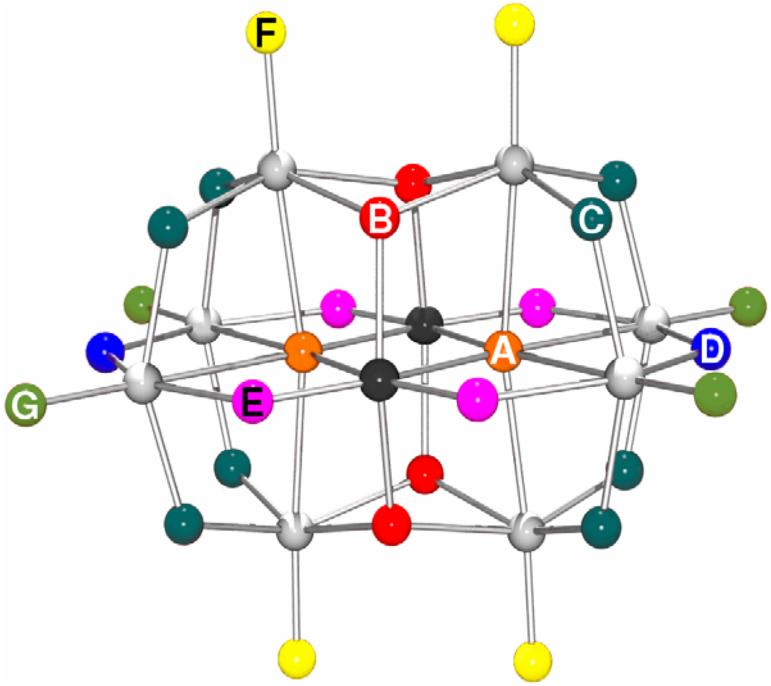


Figure S-2-1: The dititanoniobate Ti_2Nb_8 ion, where the titanium atoms are shown in black, the niobium atoms are shown in gray, and the oxygens are color coded and labeled. Rates are shown in both Table S-2-3 and visually in Figure S-2-2.

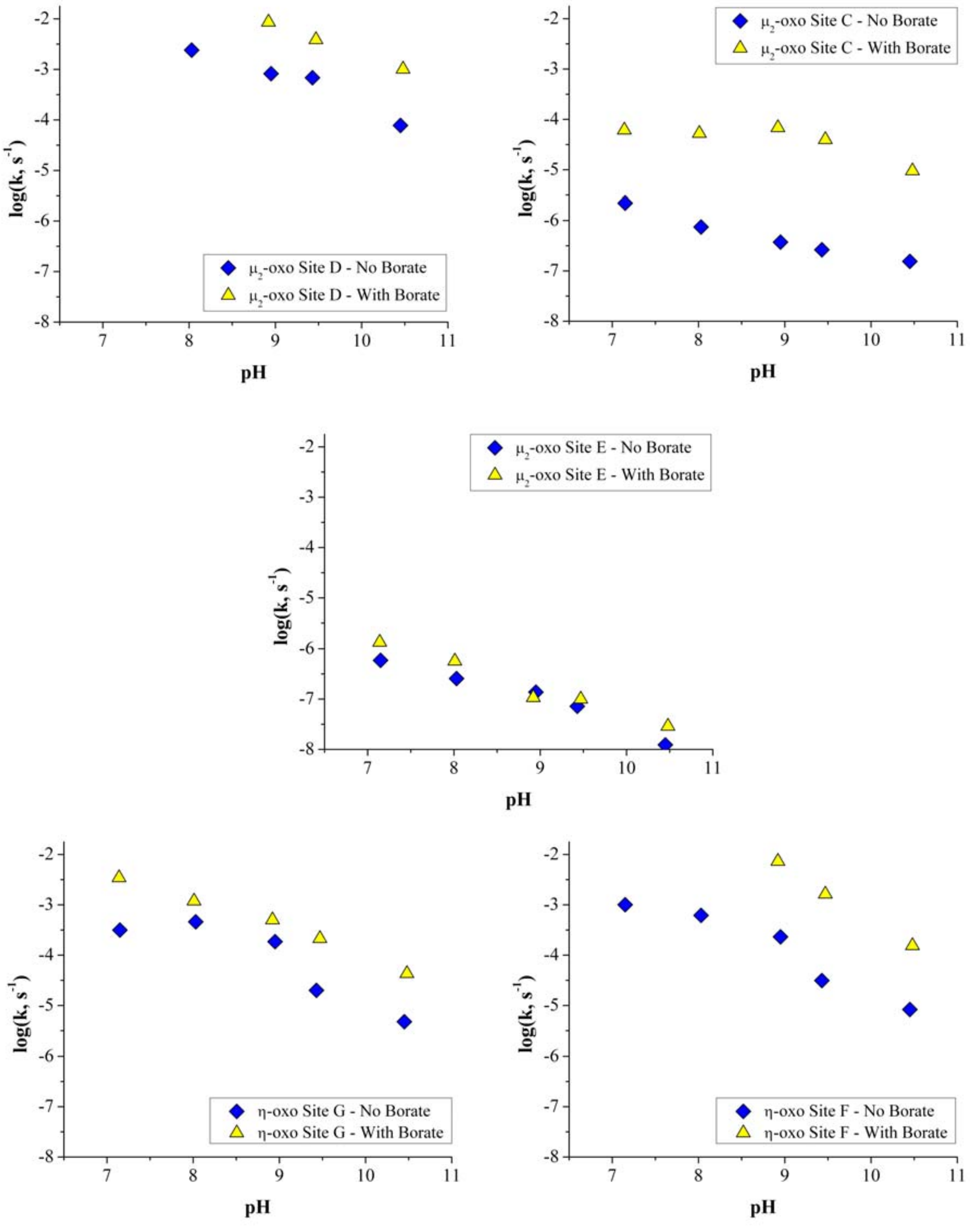


Figure S-2-2: Comparing the log(k) values for the structural oxygens in the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion, which is abbreviated Ti_2Nb_8. The blue diamonds are rates of oxygen-isotope exchange without borate in solution, whereas the yellow triangles are rates with borate. These actual rate data is shown in Table S-2-3. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. Sites A and B, μ_6-oxo and μ_3-oxo respectively, are not shown because they are only increase in rates of oxygen-isotope exchange at pH ~7.1.

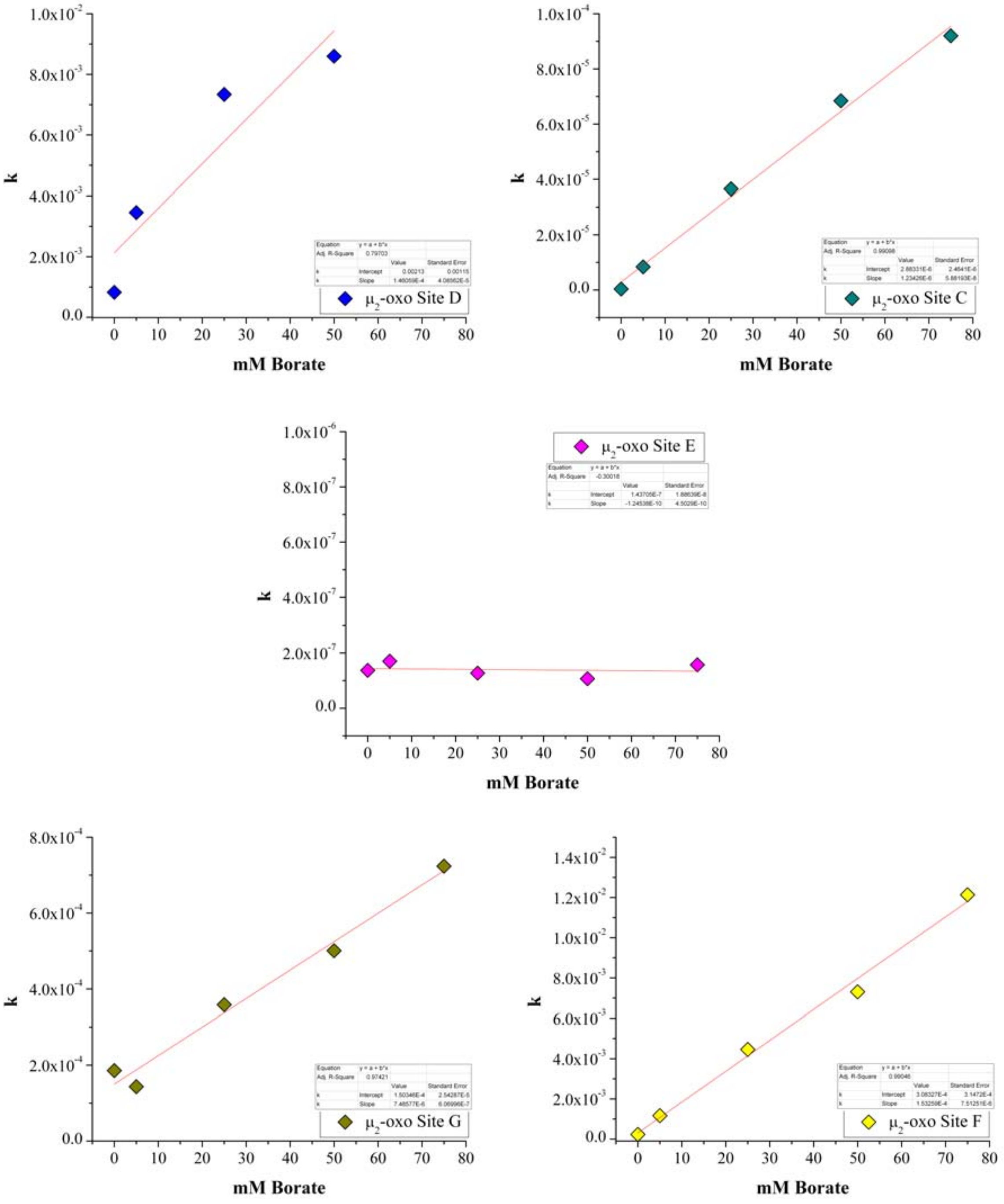


Figure S-2-3: Comparing the rate values for the structural oxygens in the Ti_2Nb_8 ion as a function of total dissolved borate in solution. These actual rate data is shown in Table S-2-4. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. Sites A and B, μ_6-oxo and μ_3-oxo respectively, are not shown as they are inert to isotope exchange.

	Borate (mM)	pH	log(k) s^{-1} μ_2-oxo (Site **C**)	log(k) s^{-1} μ_2-oxo (Site **D**)	log(k) s^{-1} μ_2-oxo (Site **E**)	log(k) s^{-1} η=O (Site **F**)	log(k) s^{-1} η=O (Site **G**)
2.81 mM Ti_2Nb_8 in a 50 mM TRIS buffer	0	8.95	3.73E-7 ± 3.16E-8	8.23E-4 ± 5.04E-5	1.37E-7 ± 1.81E-8	2.32E-4 ± 7.50E-6	1.86E-4 ± 4.12E-6
2.86 mM Ti_2Nb_8 in a 45 mM CHES buffer	5	8.97	8.37E-6 ± 2.80E-7	3.45E-3 ± 1.96E-4	1.70E-7 ± 1.81E-8	1.16E-3 ± 1.30E-4	1.43E-4 ± 6.78E-6
2.75 mM Ti_2Nb_8 in a 25 mM CHES buffer	25	8.98	3.65E-5 ± 5.44E-5	7.34E-3 ± 2.06E-4	1.28E-7 ± 1.06E-8	4.46E-3 ± 9.92E-4	3.58E-4 ± 1.61E-5
4.26 mM Ti_2Nb_8	50	8.93	6.84E-5 ± 1.27E-6	8.60E-3 ± 5.54E-4	1.07E-7 ± 1.39E-8	7.30E-3 ± 4.66E-4	5.01E-4 ± 2.02E-5
2.85 mM Ti_2Nb_8	75	8.99	9.20E-5 ± 1.24E-6	--	1.57E-7 ± 9.86E-9	1.21E-2 ± 3.44E-4	7.24E-4 ± 3.94E-5

Table S-2-4: Comparing the rate values for the structural oxygens in the Ti_2Nb_8 ion as a function of total dissolved borate in solution. These data are shown visually in Figure S-2-3. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. Sites A and B, μ_6-oxo and μ_3-oxo respectively, are not shown as they are inert to isotope exchange.

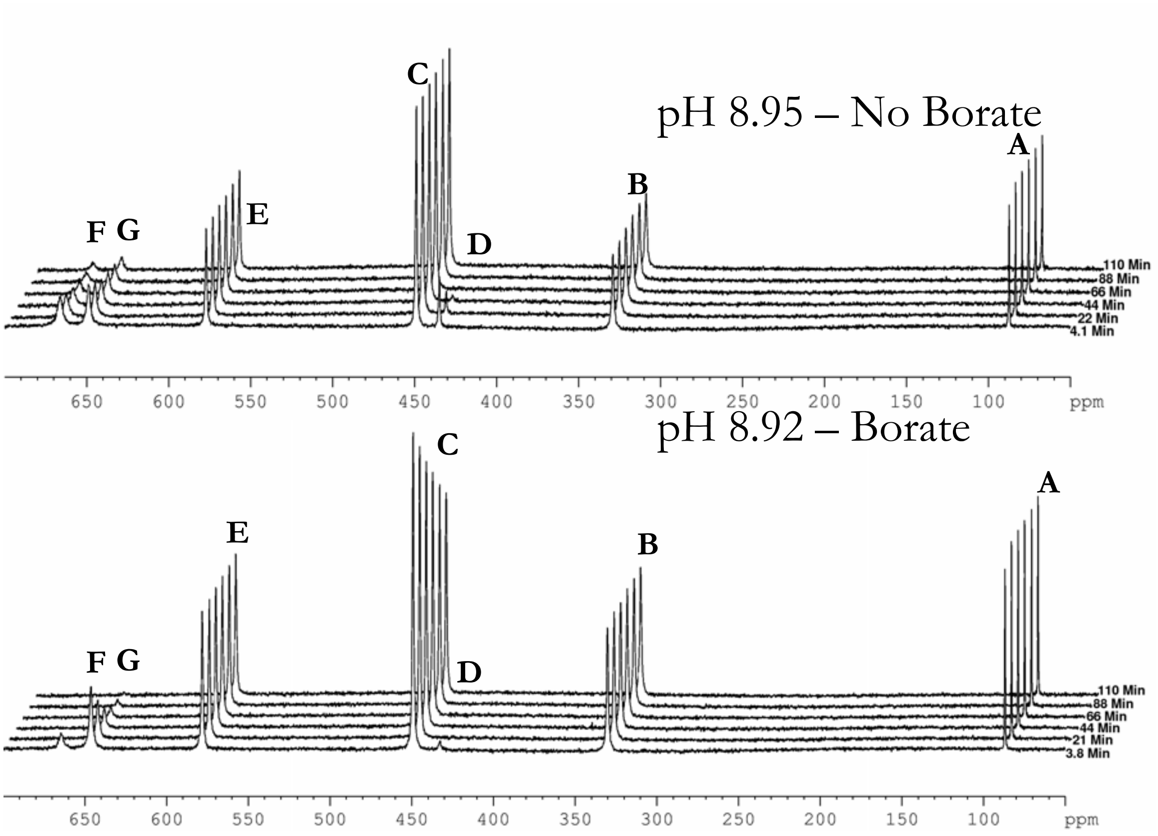
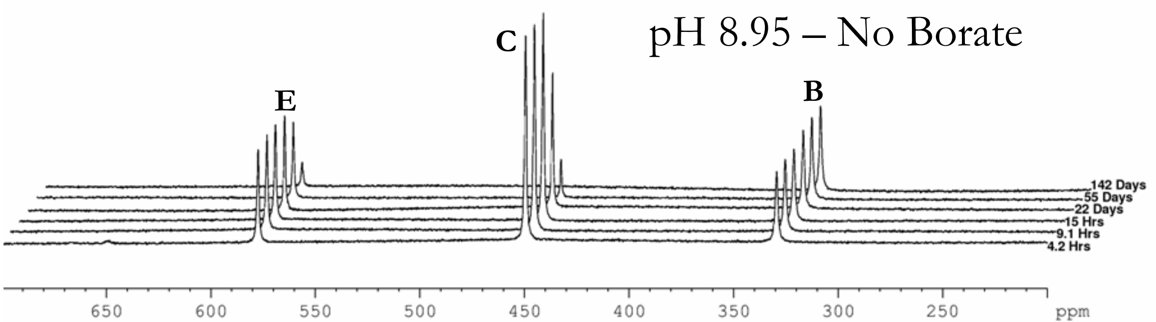


Figure S-2-4: ^{17}O-NMR stacked plots of the Ti_2Nb_8 ion without borate (top) and with borate (bottom). Times range from 4 minutes to 110 minutes. See Figure S-2-1 for the ion with labeled oxygens.



pH 8.92 – Borate

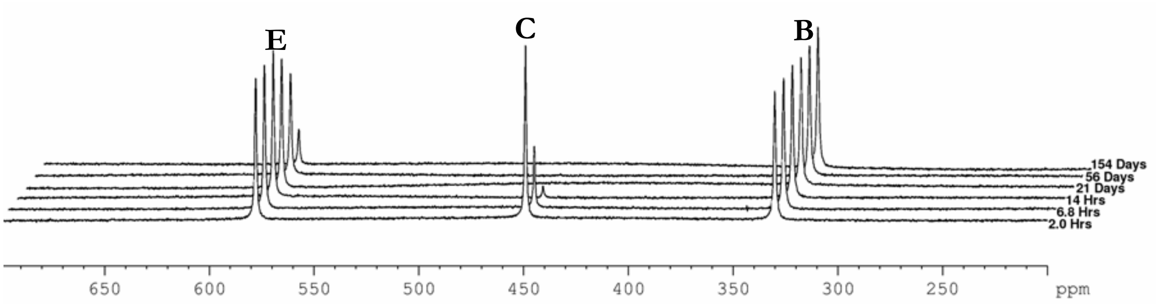


Figure S-2-5: ^{17}O-NMR stacked plots of the Ti_2Nb_8 ion without borate (top) and with borate (bottom). Times range from 2 hours to 154 days. See Figure S-2-1 for the ion with labeled oxygens.

S-3: The Decaniobate Ion

Temp °C	pH	Nb_{10} (mM)	log(k) s^{-1} μ_6-oxo (Site **A**)	log(k) s^{-1} μ_3-oxo (Site **B**)	log(k) s^{-1} μ_2-oxo (Site **C**)	log(k) s^{-1} μ_2-oxo (Site **D**)	log(k) s^{-1} μ_2-oxo (Site **E**)	log(k) s^{-1} η=O (Site **F**)	log(k) s^{-1} η=O (Site **G**)
35.5	7.10	5.57	--	-7.38±0.19	-5.74±0.06	-4.15±0.03	-6.74±0.06	-4.52±0.04	-4.25±0.04
35.5	7.05	5.32	-7.17±0.06	-6.98±0.03	-5.51±0.01	-3.93±0.02	-6.55±0.03	4.10±0.04	-3.82±0.02

Table S-3-1: Comparing the rate values for the structural oxygens in the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion, abbreviated Nb_{10}, with and without borate in solution. These data are shown visually in Figure S-3-1. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. The experiment in gray indicates the sample run without borate. The top experiment (in gray) was run in 10 mM PIPES buffer, whereas the bottom experiment (not in in gray) was also run with 50 mM borate present in solution. All rates accelerate in the presence of borate, and the dissociation of the Nb_{10} ion to the Nb_6 ion is enhanced with borate in solution.

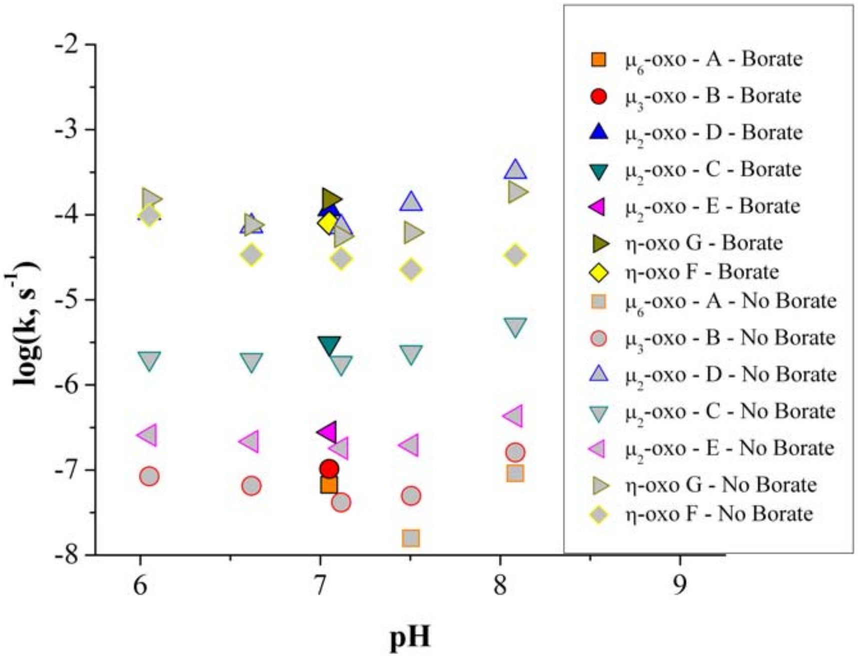


Figure S-3-1: Comparing the rate values for the structural oxygens in the Nb_{10} ion with and without borate in solution. All solutions were run at 35.5°C and in 0.1 M tetramethylammonium chloride background electrolyte. The data shown in gray indicate the samples run without borate. All rates accelerate in the presence of borate, including dissociation of the Nb_{10} ion to the Nb_6 ion.