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## NIOBIUM IS HIGHLY MOBILE AS A POLYOXOMETALATE ION DURING NATURAL WEATHERING

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### ABSTRACT

Niobium is usually considered to be one of the least mobile elements during alteration of rocks in geological processes and is thought to only be mobile at elevated temperatures and/or pressures. Since niobium is assumed to be unaffected by weathering it can be used in geochemical-evolution calculations to estimate the loss of material from the weathering of rocks. There are roughly a hundred niobium-bearing minerals, including those in the pyrochlore group, which comprises the main ores for Nb and Ta. Furthermore, pyrochlores are identified as potential hosts for nuclear waste because of their resistance to weathering. Here we show that niobium can be highly mobile even at near-surface geochemical conditions as a soluble and unreactive polyoxometalate ion. Discovery of the first natural hexaniobate minerals, all formed at near-surface conditions, provides evidence that niobium is being actively leached out of nearby primary minerals and easily transported as polyoxometalate ions. In addition, we show how Nb and Ta can be fractionated during low-temperature processes.

*Keywords:* polyoxometalates, hexaniobates, Nb-Ta mobility, Nb-Ta fractionation, molecular geology.

### INTRODUCTION

For a geologist, the immobility of niobium is a key property that can be used to decipher past processes encoded in Earth's rock record (*e.g.*, Cann 1970, Kurtz *et al.* 2000, Hastie *et al.* 2011). Despite this general belief that Nb is not mobile, there are vast Nb deposits in the world, which is indicative that a renewed understanding of Nb mobility is required. Many of these large Nb deposits are associated with evolved rock types such as nepheline syenites and carbonatites. Furthermore, minerals containing Group V elements (mostly Nb and Ta) have two qualities that make them interesting for current technologies. First, these minerals, especially pyrochlore, are the major Nb ores that are mined in amounts of thousands of metric tons per year (United States Geological Survey 2015) to make alloys and electronic devices; the EU classifies Nb as one of 20 Critical Raw Materials (European

Union 2014). Second, pyrochlore resists dissolution and weathering (see Table 1 for formulae), making it a proposed host for nuclear waste (Ewing *et al.* 2004). Most studies demonstrating the resistance of pyrochlores to weathering, however, are conducted in near-neutral or acidic solutions where the solid niobic acid is insoluble (Lumpkin & Ewing 1995, Geisler *et al.* 2004). Niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) is a term applied to the X-ray amorphous product formed when fully protonated and uncharged complexes of niobate condense out of solution. Experimental solubility studies of Nb and Ta in geology have typically focused on high temperature acidic conditions and often with fluorine as a complexing agent (*e.g.* Mitchell & Kjarsgaard 2004, Kjarsgaard & Mitchell 2008, Zraisky *et al.* 2010, Timofeev *et al.* 2015, 2017). The most familiar aqueous complex of Nb(V) is the polyoxometalate Lindqvist ion having a stoichiometry of  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$ , and this ion dominates in

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TABLE 1. FORMULAE OF SELECTED MINERALS MENTIONED IN THE TEXT

Mineral	Formula
Chiavennite	$\text{CaMnBe}_2\text{Si}_5\text{O}_{13}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
Columbite-group	$(\text{Fe}, \text{Mn})\text{Nb}_2\text{O}_6$
Fersmite	$\text{CaNb}_2\text{O}_6$
Hansemarkite	$\text{Ca}_2\text{Mn}_2[\text{Nb}_6\text{O}_{19}] \cdot 20\text{H}_2\text{O}$
Hydroxylgugiaite	$(\text{Ca}_3\Box)_{\Sigma 4}(\text{Si}_{3.5}\text{Be}_{2.5})_{\Sigma 6}\text{O}_{11}(\text{OH})_3$
Lueshite	$\text{NaNbO}_3$
Melcherite	$\text{Ba}_2\text{Na}_2\text{Mg}[\text{Nb}_6\text{O}_{19}] \cdot 6\text{H}_2\text{O}$
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
Pascoite	$\text{Ca}_3[\text{V}_{10}\text{O}_{28}] \cdot 17\text{H}_2\text{O}$
Peterandresenite	$\text{Mn}_4[\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}$
Pyrochlore <i>sensu lato</i>	$(\text{Ca}, \text{Na})_2\text{Nb}_2\text{O}_6(\text{O}, \text{OH})$
Studtite	$[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$
Tuperssuatsiaite	$\text{Na}_2\text{Fe}_3\text{Si}_8\text{O}_{20}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
Wöhlerite	$\text{Na}_2\text{Ca}_4\text{ZrNb}(\text{Si}_2\text{O}_7)_2(\text{O}, \text{F})_4$

solutions with  $\text{pH} > 8$  when it has an anionic charge (Fig. 1) (Lindqvist 1953, Etxebarria *et al.* 1994, Deblonde *et al.* 2015). A detailed review of the aqueous geochemistry of certain high-field strength elements suggested that hexaniobates could be important for geological processes (Wood 2005). The polyoxometalates are a large group of anionic metal-oxo clusters typically centered by small and highly charged cations such as group V and VI metals (V, Nb, Ta, Mo, and W) and structured as oxides. The importance of polyoxometalate ions in nature has

been suspected by polyoxometalate chemists for a long time (Müller *et al.* 1991). What has not been appreciated is the effect of the presence of these large ions in mineral structures on the assumption that highly charged metals like Nb(V) are immobile in geochemical processes. This paper will provide insight into a mechanism whereby Nb and Ta can be remobilized at low temperature and pressure without the aid of fluorine and how the two elements can be fractionated.

#### METHODOLOGY

A Hitachi S-3600 scanning electron microscope (SEM) equipped with a Bruker XFlash 5030 EDS detector, housed at the Natural History Museum in Oslo, was used for imaging and to obtain standardless semi-quantitative analyses. The SEM was operated in low-vacuum mode (typically 10 Pa) and both images and chemical data were acquired directly from the specimens without prior coating.

#### RESULTS

The formation of secondary Nb-minerals is known from all alkaline complexes and here we will illustrate the typical parageneses for such minerals, from two complexes. It is beyond the scope of this paper to give detailed descriptions of the parageneses or the mineralogy of the two complexes, hence only short descriptions are provided.

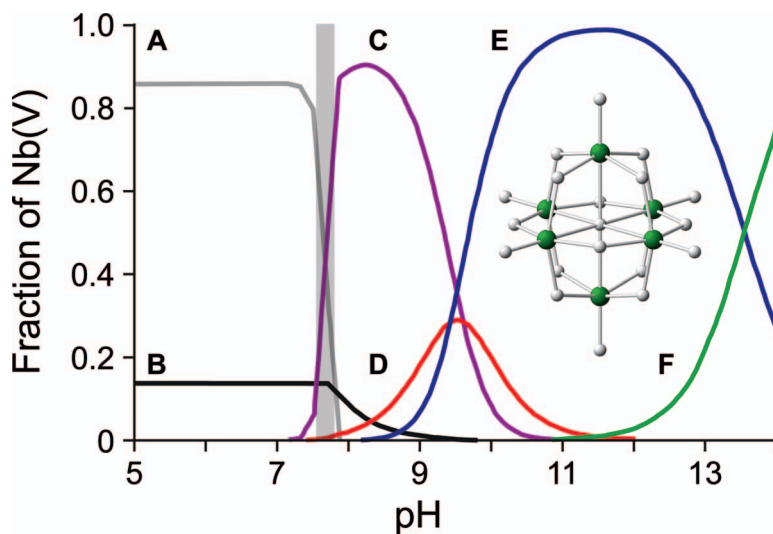


FIG. 1. Nb(V) speciation in solution as a function of pH. (A)  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (s); (B)  $\text{Nb}(\text{OH})_5$  (aq); (C)  $[\text{H}_3\text{Nb}_6\text{O}_{19}]^{5-}$  (aq); (D)  $[\text{H}_2\text{Nb}_6\text{O}_{19}]^{6-}$  (aq); (E)  $[\text{HNb}_6\text{O}_{19}]^{7-}$  (aq); (F)  $[\text{Nb}_6\text{O}_{19}]^{8-}$  (aq). The ball and stick structure is the Lindqvist ion of (F) where the green spheres are Nb and the light grey are O. The grey area represents the lower stability field of the Lindqvist ion. Modified after Etxebarria *et al.* (1994).

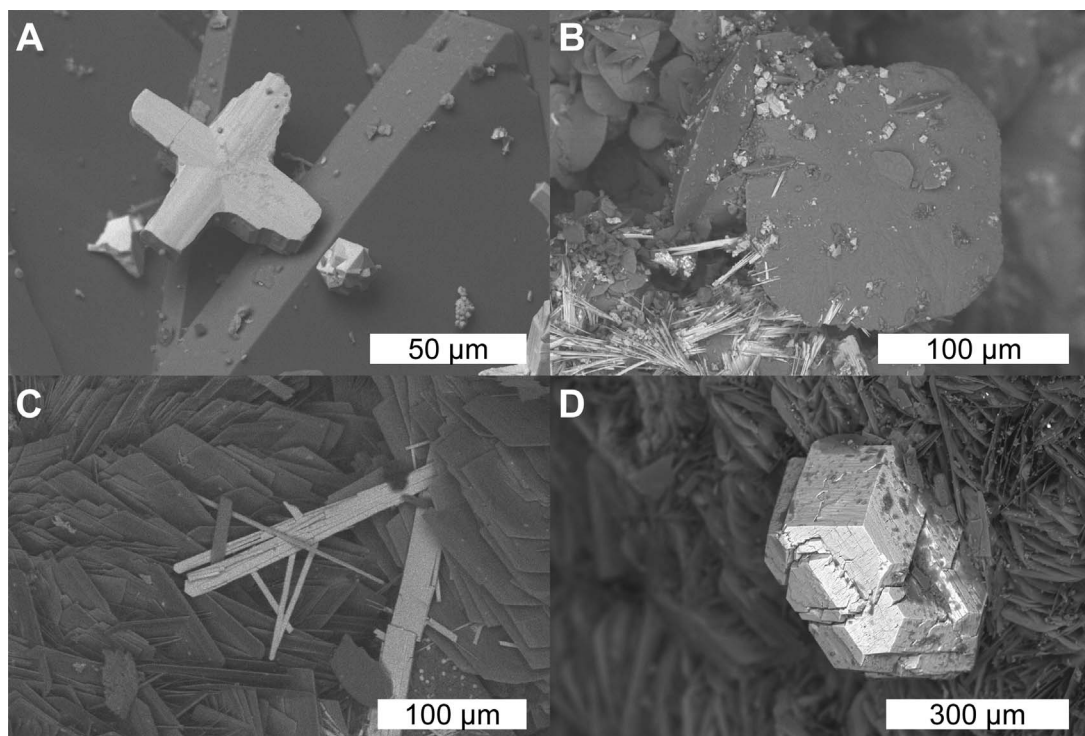


Fig. 2. SEM images of (A) a lueshite twin and a pyrochlore penetration twin on natrolite, (B) small octahedra of pyrochlore and needles of fersmite on hydroxylgugiaite, (C) a fersmite group mineral on chiavennite, and (D) peterandresenite on chiavennite. (A) and (B) are from the Ilímaussaq alkaline complex, South Greenland, and (C) and (D) are from Tvedalen, Norway. Note that in all images the Nb minerals are the lighter grey in color.

Figure 2A shows a twinned lueshite perched on a natrolite crystal from an altered pegmatite in the Ilímaussaq alkaline complex, South Greenland (WGS 84 GPS coordinates: N 60° 53.720', W 45° 50.881'). The pegmatite has been blasted, so the exact relation of the natrolite material to the unaltered part of the pegmatite is unknown. Lueshite appears to be one of the last-formed minerals and can be very abundant, covering most of some natrolite cavities. The same natrolite paragenesis also hosts tapersuatsiaite and aegirine. A pyrochlore group mineral and fersmite on hydroxylgugiaite from an altered pegmatite on Mount Nakkaalaaq are shown in Figure 2B. The pegmatite at Nakkaalaaq, Ilímaussaq, South Greenland (WGS 84 GPS coordinates: N 60° 58.909', W 45° 54.769') is rich in cavities and has experienced at least two alteration events that are evident from albite pseudomorphs after analcime and the beryllium mineralogy. The cavities are rich in late-stage phases, in particular beryllium minerals. Hydroxylgugiaite covers the walls of cavities and is among the last minerals to form. However, as Figure 2B shows, Nb minerals such as

pyrochlore and fersmite formed even later than the secondary Be-minerals. Figure 2C shows fersmite on the Be-zeolite chiavennite from an altered pegmatite within the Larvik Plutonic Complex (LPC) in Norway (WGS 84 GPS coordinates: N 59° 2.353', E 9° 51.413'). Peterandresenite occurs in the same paragenesis as fersmite and chiavennite. Peterandresenite is often associated with hanesmarkite; both minerals occur on zeolites and are the last minerals to form. Furthermore, it appears they have formed from a fluid caught in depressions associated with a fracture or have slowly run over a surface (Fig. 2D). Despite describing just a few examples of late-stage Nb minerals, it is the experience of the authors that it is a widespread phenomenon within alkaline systems.

## DISCUSSION

### Temperature

The general view that Nb and Ta are immobile under geological processes is questionable given the late-stage mineralization observed in Figure 2. The

Nb-minerals lueshite and pyrochlore *sensu lato* formed on the zeolite natrolite during late-stage alteration of a pegmatite in the Ilímaussaq alkaline complex, South Greenland. Their presence on natrolite constrains the upper temperature limit. Natrolite dehydrates at 350 °C (van Reeuwijk 1972) whereas lueshite is typically a primary mineral (Chakhmouradian & Mitchell 1998). The mineral tapersuatsiaite, occurring in the same natrolite paragenesis as lueshite, is a hydrous phase which loses most of its water at 250 °C (Karup-Møller & Petersen 1984). The formation of two different Nb minerals at late stages indicates that Nb is mobile at, or below, the zeolite-facies conditions where the natrolite formed. Similarly, on the top of Mount Nakkaalaaq in the Ilímaussaq alkaline complex fersmite and pyrochlore are among the last minerals to form in a pegmatite, which has experienced several stages of alteration. Although there is no definite determination of the formation temperature for the Nb minerals at Nakkaalaaq, they form as the last minerals of the last alteration event, suggesting low temperature. Furthermore, pyrochlore and lueshite occur throughout Ilímaussaq as late-stage veins in all geological units, indicating high mobility of niobium at low pressure and temperature.

Fersmite-group minerals together with peterandresenite and hanesmarkite are also the last minerals to form in some altered pegmatites of the LPC. The primary Nb minerals at LPC are pyrochlore and wöhlerite, which show various degrees of degradation during late-stage alteration. As with other alkaline complexes, the alteration of the primary Nb minerals results in a series of secondary Nb-minerals, but as Figure 2 shows, these are not pseudomorphic, *i.e.*, Nb was transported from the primary minerals before forming the secondary minerals elsewhere in the pegmatite.

The fact that the examples above all include Nb minerals occurring as the last minerals formed as the result of alteration on top of or associated with zeolites and other low-temperature minerals suggest that Nb is mobile at low pressure and temperature. In fact, as these minerals are the last to form, Nb seems to be among the most mobile elements. Furthermore, thermal analysis of peterandresenite shows it starts to degenerate at temperatures of 85 °C, illustrating the low temperature of the fluid causing the formation of these secondary minerals (Friis *et al.* 2014).

#### *Transport mechanism*

Previous workers emphasized the importance of temperature in controlling niobium mobility (Timofeev *et al.* 2015, Timofeev & Williams-Jones 2015). Studies of late-stage alteration of natural

pyrochlores show that only the larger cations are remobilized at temperatures <150 °C by diffusion from sites within the niobium-oxide framework (Lumpkin & Ewing 1995, Geisler *et al.* 2004). Niobium remains intact in the structure at low temperatures. Structural modifications only occur at higher temperatures, resulting in the formation of new species, such as columbite-group minerals or fersmite. In other cases pyrochlore is formed as a high-temperature alteration product of lueshite (Chakhmouradian & Mitchell 1998). All of these observations support the general idea that high temperatures are required to structurally modify primary niobium-bearing minerals and remobilize the niobium. However, we know the secondary minerals formed at low and not high temperature; furthermore, the limited thermal stability of peterandresenite illustrates that it can only be formed at low temperature.

Two of the secondary minerals are of particular interest, namely peterandresenite and hanesmarkite (Friis *et al.* 2014, 2017). These minerals include large ions that belong to a group of compounds collectively known as polyoxometalates and more specifically as polyoxoniobates. Peterandresenite, hanesmarkite, and melcherite (Andrade *et al.* 2018) belong to the hexaniobate subgroup and all contain the  $[\text{Nb}_6\text{O}_{19}]^{8-}$  ion known as the Lindqvist ion. The Lindqvist ion is familiar to polyoxometalate chemists as one of the simplest and most robust of the polyoxometalate anions (Pope 1983, Nyman 2011). Figure 1 shows that the Lindqvist ion is stable at  $\text{pH} > 8$  and that the solid niobate hydrolysis product, niobic acid, forms when the ions are neutralized. The aqueous niobium concentrations can reach very high levels in alkaline solutions and the Brønsted acidity of the  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$  ion controls its solubility and mobility. The high pH requirement for the stability of the Lindqvist ion explains why it has only been found in minerals from alkaline rocks.

The discovery of Lindqvist ions in low-temperature secondary minerals indicates that polyoxometalate ions are undoubtedly the transport medium for aqueous niobium, contradicting previous suppositions about its immobility. This is consistent with experimental data. For example, it has been shown that the solubility of amorphous  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  increases by more than four orders of magnitude in the pH range 7–12, consistent with the data in Figure 1, and that the niobium in solution slowly forms hexaniobate ions that can be detected spectroscopically (Deblonde *et al.* 2015). Although these pH conditions ( $\text{pH} > 8$ ) appear high for common geological environments, measurements from mine waters at Kvanefjeld, Ilímaussaq, showed pH values  $>10$  (Asmund 2002) and from the



Kola Peninsula up to  $\sim 12$  (Kraynov *et al.* 1969). In addition, Markl & Baumgartner (2002) showed experimentally that alteration of primary feldspathoid minerals in Ilímaussaq would lead to  $8 < \text{pH} < 10$ . Therefore, higher pH values resulting in the formation of the polyoxoniobate ions in alkaline rocks are fully consistent with the familiar hydrolysis chemistry of the  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$  ion (Etxebarria *et al.* 1994, Deblonde *et al.* 2015). Experimental studies have shown that decaniobate ions are present at circumneutral or slightly basic pH conditions, but they will readily react and form large  $[\text{Nb}_{24}\text{O}_{72}\text{H}_8]^{16-}$  clusters, causing an increase in the pH of the fluid, which in turn can lead to a breakdown of the  $[\text{Nb}_{24}\text{O}_{72}\text{H}_8]^{16-}$  to form stable hexaniobates (Villa *et al.* 2008, Sures *et al.* 2018). Consequently, alteration of Nb minerals in fluids with  $\text{pH} \sim 7$  may form metastable polyoxoniobate ions, which upon disassembly cause an increase in pH of the altering fluid. Of course, other examples of mobility *via* large molecules are known from a series of decavanadate minerals that forms on the walls in old mine adits, such as those of the pascoite group (Hillebrand *et al.* 1914, Kampf *et al.* 2011).

The implication for geology is that a molecular view of weathering processes is important, as pointed out by Rustad (2010). Not only is the paragenesis of Nb-minerals more sensitive to acid-base chemistry than to small changes in temperature or pressure, but polyoxometalate solubilities are dramatically affected by specific counterions and differ between Nb and Ta in solution (Fullmer *et al.* 2014, Sures *et al.* 2017). Unlike in conventional geochemical speciation of natural waters, most monomeric cations (*e.g.*,  $\text{Ca}^{2+}$ ) and alkaline- and alkaline-earth counterions closely coordinate to the polyoxometalate anions and seem to be integral to their stability in solution (Antonio *et al.* 2009), to the kinetic labilities (Villa *et al.* 2010), and to the solubility of solid products formed by condensation of the ions. Ions that are usually considered to affect solubilities only *via* changes in ionic strength are not innocuous in the presence of large multimeric ions. Recently, whole new classes of actinyl-peroxide clusters, ranging up to several nanometers in size and composed of hundreds of atoms, have been discovered (Sigmon *et al.* 2009) from attempts to make the mineral studeite, a peroxo-bridged uranium mineral (Burns & Hughes 2003). From the work here on Group V metals, it is clear that these molecules exist in nature, both as large anions that are stable in solution and as structural units in a solid. Furthermore, it is apparent that a more complicated approach to solute speciation calculations is needed. These polyoxometalate ions are so dramatically affected by counterions that speciation with ternary or quaternary complexes is essential to capture their mobilities in

nature. This molecular view of geochemistry emphasizes actual structures and specific interactions that are missing from most current geochemical transport codes.

### *Invisible carrier*

More importantly, synthesis work at high pH shows that the Lindqvist ion is present in the reactions as an intermediate complex when producing synthetic equivalents of minerals such as lueshite, pyrochlore, and columbite at low temperature and autogenic pressures (*e.g.*, Wu *et al.* 2010, Zhang *et al.* 2010). The hexaniobate ion is extraordinarily soluble, yet the fact that it is rare to find it in minerals indicates that it dissociates during a crystallization step to release monomers to form minerals. Interestingly, synthetic work showed that at high pH a pyrochlore structure formed, but at  $\text{pH} \sim 8$  a columbite structure was stable (Zhang *et al.* 2010). The pH control on formed phases under the same pressure and temperature conditions further illustrates the importance of acid-base chemistry when inferring alteration conditions for Nb minerals in nature.

There is another important point to derive from these observations: the hexaniobate ion is a robust and common soluble form of niobium and the polymeric ions have been well-known for decades. Most niobium-bearing minerals, however, have no Lindqvist ion moiety in their structures, yet even in these cases, one can infer that the mobile form of niobium was probably the  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$  ion, and even some higher polymers (*e.g.*, decaniobate) are known (Nyman 2011). By analogy with the presence of the decavanadate anion in the pascoite mineral group, it is possible that decaniobate-containing minerals exist, as two heteropolyniobates minerals are known (Atencio *et al.* 2008, Cooper *et al.* 2012). There is no monomeric form of Nb(V) that has unequivocally been identified in aqueous solution, although fragments smaller than the hexaniobates have been observed in mass spectra; the dominant stable form even with submicromolar concentrations of metal is the hexaniobate ion. There are likewise no strong ligands anticipated for these natural solutions that could enhance solubility of a condensed niobate solid beyond that achieved by the simple polyoxometalate ion, which arises only from hydrolysis and acid-base chemistry.

### *Nb-Ta fractionation at low temperature*

The Nb/Ta ratio is often used as a proxy for evolution and crystal fractionation in igneous systems. However, the effect of alteration on the Nb/Ta ratio is rarely discussed, although studies of primary and

secondary pyrochlores from the Lueshe carbonatite have shown an increase of the ratio during alteration (Nasraoui & Bilial 2000). Increased HF content has shown to increase the solubility of Ta, but not as much as it increases the solubility of Nb (Timofeev *et al.* 2017). Consequently, low pH and fluorine in a fluid will facilitate fractionation of Nb and Ta, resulting in an increase of the Nb/Ta ratio in secondary compared to primary minerals. Similarly, under basic conditions the hexaniobate ion forms at lower pH than the hexatantalate ion (Deblonde *et al.* 2015) because of inherent differences in the acid-base chemistry. Accordingly, if the pH of a fluid interacting with a primary mineral is above the solubility of Nb, but below that of Ta, then Nb would preferentially be leached over Ta. Villesuzanne *et al.* (1998) showed that the Ta–O bond is more covalent than the Nb–O bond, which explains the lower solubility of Ta compared to Nb. A few papers have explored Lindqvist ions with mixed Nb/Ta content of the type  $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$  with  $1 \leq x \leq 5$  (e.g., Anderson *et al.* 2007), which illustrates that Lindqvist ions can record the Nb/Ta ratio of the primary mineral. If the pH of the fluid is beyond the solubility threshold for Ta, then no Nb-Ta fractionation between primary and secondary minerals should occur. However, if the pH in an alteration fluid is above the solubility of Nb, but below that of Ta, Nb would enter a fluid whereas Ta would be retained in the primary mineral, resulting in a different Nb/Ta ratio in the Lindqvist ion than in the primary mineral, *i.e.*, Nb and Ta can be strongly fractionated from each other. If a Lindqvist ion maintaining the original mineral's Nb/Ta ratio dissociates to form secondary minerals these may not reflect the original Nb/Ta ratio. When heating  $\text{Na}_8[\text{Ta}_5\text{NbO}_{19}]$  to form  $\text{Na}_2\text{Ta}_{1.67}\text{Nb}_{0.33}\text{O}_6$  a mixture of  $\text{Na}_2\text{Ta}_2\text{O}_6$  and  $\text{NaNbO}_3$  was formed (Anderson *et al.* 2007). The implication is that even if the Nb/Ta ratio is transferred to the Lindqvist ion during alteration, there is no guarantee that it will be present in the secondary mineral, as Nb and Ta may be completely fractionated.

Another difference between hexaniobates and hexatantalates is that the former can be protonated on bridging oxygens, whereas the latter cannot and will dissociate, forming Ta phases (Fullmer *et al.* 2014). In the circumstance where a fluid contains both hexaniobate and hexatantalate, the introduction of reactive protons would inhibit the transport of Ta as the hexatantalate ion would dissociate. Conversely, the hexaniobate ion that can accommodate three protons would continue to be in solution and can be transported further. Consequently, the Nb/Ta ratio would be different in the products than in the initial mineral, and Nb can be transported further than Ta.

## CONCLUSIONS

The observations described above indicate that Group V metals can be transported as large ions in geological fluids, and these large polyoxometalate ions are missing from all geochemical reaction-path calculations. In particular, the discovery of naturally occurring hexaniobates provides evidence for polyoxometalates as a transport mechanism for highly charged cations. Furthermore, transporting Nb and Ta as polyoxometalates provides an explanation for how secondary Nb-minerals can form at low temperature and pressures. These observations combined with syntheses also reveal that, although the hexaniobate ion was the means of transport, the resulting solid does not necessarily contain the hexaniobate ion. The lack of Earth Science studies into element mobility *via* polyoxometalates is surprising as pascoite, for example, was described more than a century ago (Hillebrand *et al.* 1914). Additionally, it has been pointed out that these nanometer-sized ions can be used to understand reaction pathways at the molecular level, and the term “Molecular Geology” was coined by Rustad (2010). These ions are the right size to treat comprehensively using computational chemistry and can also be used as experimental models to understand reactions affecting minerals. Here we show that understanding the molecular species in geological environments can explain how one of the least mobile elements, niobium, is transformed into one that is exceedingly mobile at surface conditions, simply *via* a change in pH. Accepting that molecules and clusters are important for geological processes opens new avenues for cross-disciplinary research between geoscientists and chemists, which appropriately could be called “Molecular Geology”.

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