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Niobium and tantalum in minerals: Siderophile, chalcophile or lithophile, and polyvalent

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ABSTRACT

Most geoscientists are convinced that minerals of both niobium and tantalum contain those elements in the 5+ state only. In fact, there are several well-documented minerals containing Nb^0, Nb^{2+}, Nb^{4+} and Nb^{5+}, and tantalum follows a similar pattern. Both elements can exhibit a siderophile, a chalcophile and a lithophile character, as well illustrated empirically, and as documented *via* XANES and XPS spectra. Of the XPS spectra that we report here on ferroniobium of metallurgical grade, pyrochlore, samarskite, niocalite, synthetic edgarite ($FeNb_3S_6$) and $NbTe_2$, only the samarskite and niocalite contain only one valence state of Nb (5+). Vladimir Vernadsky understated the situation when he placed Nb and Ta in the "dispersed" category. Columbite-group minerals are most unusual in exhibiting variable mutual disorder involving (Nb,Ta) and (Fe,Mn). Oddly, samples must be heated to become ordered. We raise the possibility that at the stage of primary crystallization, the relevant magmas contained mixed valences of Nb, Ta, Fe and Mn, which made a disordered distribution along the octahedrally coordinated cations energetically more acceptable. Owing to the relative insolubility of members of this solid-solution series in the ambient aqueous fluid, they have remained metastably frozen in a partly or completely disordered state.

1. Introduction

What are the oxidation states of niobium and tantalum? Surprisingly, the answer depends on the person being quizzed. A chemist will recall that niobium and tantalum are transition elements that belong to Group 5 of the periodic table; as in the case of vanadium, the element above them in Group 5, there are several valences. It is well known that minerals may contain V^0, V^{3+}, V^{4+}, and V^{5+}. Native vanadium has been found in a fumarole. Coulsonite, $Fe^{2+}V^{3+}_2O_4$, is a spinel-group mineral. Tetravalent vanadium is found in duttonite, $VO(OH)_2$, and in the sulfide patrónite, $V^{4+}(S_2^{2-})_2$, and pentavalent vanadium adopts a tetrahedral coordination in vanadinite, $Pb_5(VO_4)_3Cl$, an apatite-group mineral. Some minerals are known to contain V^{3+} and V^{4+}, and others contain V^{4+} and V^{5+}. Yet, where niobium and tantalum are concerned, most Earth scientists are convinced that minerals contain Nb^{5+} and Ta^{5+} only. In this article, we explain how this broadly accepted view came to be. We review the state of Nb and Ta in minerals of importance in ore assemblages and placers. We document the valence state of Nb in selected minerals by X-ray photoelectron spectroscopy. Finally, we discuss the case of columbite-group minerals, and the possible implications of the frozen-in positional disorder that they commonly show.

Even in his graduate student days, as he was being initiated to the mineralogical complexities of soils, Vladimir Ivanovich Vernadsky (1863–1945) invariably expressed an eagerness to probe more deeply into the mysteries of the structure of matter, especially minerals. He longed for broad generalizations (Balandin, 1982). Vernadsky's progress in answering the call to formulate such generalizations is documented by Wolf and Müller (2014–in this issue). He formulated a synthesis of his ideas concerning a classification of elements (Vernadsky, 1922). He assigned Nb and Ta to a category he called "dispersed elements", those that have a limited ability to complex with ligands (Vernadsky, 1922, 1933). He confessed, however, that so little was known about Nb and Ta in minerals at the time that he was quite unsure whether or not he had placed them in the correct category. It is thus most appropriate to link his name to our review of the complex crystal-chemical role of Nb and Ta in minerals, in a celebration of the 150th anniversary of his birth.

2. The view of most geoscientists about Nb and Ta

The main sources of information about the distribution of Nb and Ta in rocks and minerals remain the authoritative treatises of Rankama and Sahama (1950) and Goldschmidt (1954). To Rankama and Sahama

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(1950), both Nb and Ta "are purely and typically lithophile elements", typically found concentrated in pegmatites, either oversaturated (Nb and Ta) or undersaturated in SiO_2 (Nb). They pointed out a contrasting pattern of enrichment among the granitic pegmatites: the enrichment in Nb is manifested in early (*i.e.*, primary) parageneses, whereas Ta mineralization is a hallmark of hydrothermally modified pegmatites. This important observation points to differential mobility of the two elements in a hydrothermal fluid, an aspect that is still poorly studied and controversial. Most geoscientists today would agree with Vernadsky (1922, 1933), that these elements are dispersed and of limited mobility.

Goldschmidt (1954) stressed the "geochemical twins" aspect of Nb and Ta. The nuclear charge of Nb is 41, whereas that of Ta is 73; the atomic weight of Ta (180.9) is close to double that of Nb (92.9). Yet, the ionic radius of Nb^{5+} in octahedral coordination is 0.64 Å, the same as that of Ta^{5+} (Shannon, 1976). This phenomenon, well explained in courses on Inorganic Geochemistry, is due to the lanthanide contraction affecting the rare-earth elements, located between Nb and Ta in the periodic table. The contraction is illustrated by quoting the radii of the pentavalent ions in octahedral coordination, just as Goldschmidt (1954) did. The subliminal message is clear: Nb and Ta are found in nature as pentavalent ions in octahedral coordination. Goldschmidt mentioned the possibility of Nb^{4+} in passing, in one sentence: it "may exist at relatively low redox potentials in magmatic solutions".

The authoritative pronouncements quoted above, that Nb and Ta are strictly lithophile elements that occur as pentavalent ions octahedrally coordinated by oxygen in crustal rocks, have been relayed to generations of students. More recent investigations reinforce the message. In the opening statement in their article, Linnen and Keppler (1997) wrote: "Niobium and tantalum are both in the 5+ state for most geologically relevant redox conditions". They went on to investigate the solubility of columbite-(Mn) and tantalite-(Mn) in H_2O-saturated haplogranitic melts that simulate pegmatite-forming magmas. Piilonen et al. (2005) also investigated melts of granitic composition, with or without H_2O and F. They tentatively assigned an intense and well-defined pre-edge in EXAFS spectra of F-rich glasses to a decrease in the coordination of Nb^{5+} from 6 to 5 or 4. The presence of a pre-edge feature (I) observed in natural glasses and in some synthetic glasses (Piilonen et al., 2006, Figs. 5A, 6) was also interpreted to reflect distortion of the NbO_6 octahedra. They concluded that "niobium in natural minerals is always found as Nb^{5+} in octahedral coordination".

Experiments designed to simulate more basic magmas at conditions of the uppermost mantle (Burnham et al., 2012) led to the same inference. Piston–cylinder experiments at 1.5 GPa and 1610–1650 °C lasted between 9 and 48 min. X-ray absorption near-edge structure (XANES) spectra of all samples prepared over a range of oxygen fugacity from IW + 6.7 to IW −4.3 (IW: iron–wüstite) are virtually identical; note, however, that the haplobasaltic compositions have become contaminated (up to 65% SiO_2) by the incorporation of SiO_2 from the glass sleeve in the experimental assembly. Burnham et al. concluded that Nb^{5+} and Ta^{5+} in six-fold coordination occur under conditions typical of the upper mantle.

Wade and Wood (2001) evaluated in experiments the state of Nb in the Earth's core, inferred to show a weakly developed siderophile character. These authors argued that Ta behaves as a completely lithophile element in 25 GPa experiments at 2300 °C, whereas Nb seems to be as strongly siderophile as vanadium, and thus does concentrate to a limited extent in a metallic phase. They concluded that the Nb data are consistent with a 5+ oxidation state in the coexisting silicate fraction in their experiments; implicitly, they contend that valence states other than Nb^0 and Nb^{5+} are suppressed in some way at conditions typical of the core.

The message that only Nb^{5+} and Ta^{5+} are important in the crust, in the upper mantle, and in the core implies that more reduced states are at best mere curiosities. As we intend to show in the next section, clear evidence is at hand to show that reduced forms of Nb and Ta do occur in the crust and upper mantle. We contend that such reduced, more strongly chalcophile and siderophile Nb and Ta are prevalent deeper in the mantle and, presumably, also in the Earth's core.

3. A survey of minerals containing reduced Nb and Ta

At last count (January 2014 tally), there are 92 minerals in which Nb is the dominant occupant of the Nb-bearing site, and 45 minerals in which Ta is the dominant occupant of the Ta-bearing site. The majority of these minerals do illustrate the strongly lithophile character of Nb and Ta; they are found in granites and granitic pegmatites, as well as in silica-undersaturated syenites. In these minerals, Nb and Ta generally have a valence of 5+ and are [5]- and [6]-coordinated by oxygen. In what follows, we focus on the minerals that do not conform to the norm.

3.1. Nb and Ta in the metallic state

Jedwabite [$Fe_7(Ta,Nb)_3$], an alloy, is an example of Ta and Nb behaving as siderophile elements. It is a placer mineral found in the Nizhnetagilsky district of the Middle Urals, in central Russia (Novgorodova et al., 1997b). The mineral was shed from the Nizhniy Tagilsk Uralian–Alaskan zoned ultramafic complex, along with niobocarbide and tantalcarbide (see below). The polycrystalline grains are up to 0.15 mm across. Crystals of jedwabite abut against tantalcarbide. The bulk composition varies among grains, and jedwabite also contains Si, W, Sn and Mn. Its cell dimensions correspond to those of synthetic phase ε, Fe_2Ta (Coelho et al., 1995, Fig. 15), whose field of stability at 1 atmosphere ranges from 1875° to 575 °C. Inclusions of another alloy, Ru_xTa_{1-x}, are present in tantalcarbide (Jedwab, 1990); the alloy contains 7.56 ± 0.7 wt.% Ta ($n = 22$). The absence of other platinum-group elements and of niobium in the Ru–Ta alloy is noteworthy, especially as it coexists with inclusions of an alloy of Fe–Sn–Nb–W–Ta in tantalcarbide (Jedwab et al., 1992). Note that grains of native tantalum reportedly found in two Russian placers have been shown by Frondel (1962) to consist of tantalcarbide.

3.2. Carbides of Nb and Ta

Niobocarbide (NbC) and tantalcarbide (TaC) were discovered as placer minerals associated with jedwabite, shed from the Nizhniy Tagilsk Uralian–Alaskan zoned ultramafic complex, in the Middle Urals of Russia (Novgorodova et al., 1997a). The placer grains span a wide range of composition, from $(Ta_{0.95}Nb_{0.05})C$ to $(Ta_{0.20}Nb_{0.80})C$ (Fig. 1), such that the solid solution seems complete across the join TaC–NbC. Also present in solid solution are trace amounts of Fe, Sn, Mn and Ti, with the amounts increasing rimward. The grains are strikingly and complexly zoned and idiomorphic (Figs. 2A, B), but are devoid of a matrix. In Fig. 2A, the core is Ta-rich and rounded owing to repeated

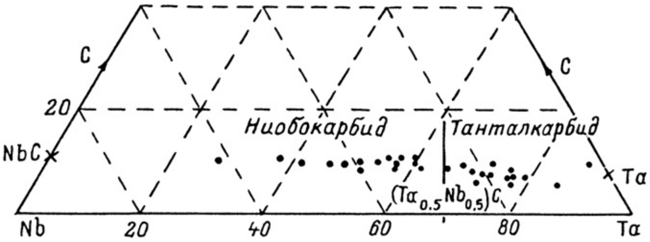

Fig. 1. Plot of compositions of the solid-solution series NbC–TaC, expressed in wt.% (Novgorodova et al., 1997a). The vertical line marks the 50 mol% boundary between niobocarbide, to the left, and tantalcarbide, to the right. Both minerals were discovered in a placer deposit in the Nizhniy Tagilsk complex, Middle Urals, Russia.