Evidence for Nb$^{2+}$ and Ta$^{3+}$ in silicate melts under highly reducing conditions: A XANES study

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**ABSTRACT**

Niobium (Nb) K-edge and tantalum (Ta) L$_{III}$-edge XANES spectra were acquired at the part-per-million concentration level in silicate glasses quenched from chondritic melts equilibrated at 5 GPa and under moderately to highly reducing conditions (IW-1, IW-4.5, IW-7.9). Standard materials have also been analyzed for Nb and Ta, and the data were used to construct the calibration curves of $E_0$ (threshold energy) vs. valence. Under moderately reducing conditions our results are consistent with niobium and tantalum being mainly pentavalent in the silicate melts as also suggested by previous studies. We do not exclude that at IW-1, a small fraction of Nb and Ta could be reduced, leading to a mean formal valence slightly lower than five. At IW-4.5, Ta is mainly in the form Ta$^{3+}$, and at IW-7.9, Ta appears to be Ta$^{3+}$, whereas Nb is divalent (Nb$^{2+}$). The possibility for Nb and Ta to be present in reduced forms has implications for the behavior of the two elements during the processes of differentiation on planetary bodies formed in the reduced parts of the early Solar System. Element partitioning is a function of size and valence, and our results show that high field strength elements could be reduced, which could change their chemical affinity. This may also be important for the Earth and Moon formation and early differentiation, as exemplified by the “Nb paradox.”

**Keywords:** Niobium, tantalum, XANES reduction, silicate glass, Nb paradox

**INTRODUCTION**

Niobium and tantalum have been classified as high field strength elements (HFSE), because their ionic charge over ionic radius ratio is high. This electronic feature mostly defines Nb and Ta behavior in magmatic systems: as their sizes differ significantly from that of the available lattices in most of the common minerals, both elements tend to partition into the melt phase during melting. Moreover Nb and Ta are described as “geochemical twins”: they are known to occur only in pentavalent state and octahedrally coordinated (VI-fold) in geological systems, and share the same ionic radius (0.64 Å, Shannon 1976). For those reasons, Nb and Ta should behave similarly during the extraction of the core, which is the major differentiation process affecting young terrestrial planets. However, the Nb/Ta ratio of the bulk silicate Earth (BSE) is significantly lower than the chondritic value, unlike as expected (McDonough 1991; Münker et al. 2003; Rudnick et al. 2000). This observation is described as the “niobium paradox.” Recently, Cartier et al. (2014a) demonstrated that this geochemical contradiction could be explained by the fact that Nb and Ta can be reduced at very low oxygen fugacity ($f_{O_2}$). This changes the dependence of their metal-silicate partition coefficients on $f_{O_2}$, causing Nb/Ta fractionation relative to starting bulk chondritic value. Therefore, Nb and Ta behavior (partitioning) in metal-silicate systems is mainly controlled by oxygen fugacity ($f_{O_2}$).

There are several ways to estimate cation oxidation states in magmatic systems. Metal-silicate melt partition coefficients as a function of $f_{O_2}$, diagrams can be used to infer cation formal valence in the silicate melt. Such data are consistent with Nb being pentavalent (Nb$^{5+}$) in moderately reducing conditions ($f_{O_2}$ > IW-3, i.e., above 3 log units below iron-wustite buffer) and divalent (Nb$^{2+}$) in reducing conditions ($f_{O_2}$ < IW-4), whereas Ta is pentavalent (Ta$^{5+}$) in moderately reducing conditions ($f_{O_2}$ > IW-2) and trivalent (Ta$^{3+}$) in reducing conditions ($f_{O_2}$ < IW-4, Cartier et al. 2014a). Furthermore, the behavior of ions in crystal-melt systems is in part governed by how effortlessly they substitute for other ions in crystal lattices, and that this substitution is mainly controlled by the ionic radius and the ionic charge of the element (Brice 1975; Wood and Blundy 1997).

X-ray absorption near edge structure (XANES) spectroscopy can be an effective tool to study element’s oxidation states. For example, Burnham et al. (2012) found that at oxygen fugacity between IW-4.3 and IW+6.7 and pressures from ambient to 1.5 GPa, Nb and Ta occur exclusively as Nb$^{5+}$ and Ta$^{3+}$. At present, Nb and Ta oxidation states under more reducing conditions have only been inferred from partitioning behavior as a function of $f_{O_2}$. The aim of the present study is to directly determine valence states at conditions relevant to early planetary body evolution, i.e., highly reducing conditions. For this purpose, we equilibrated metal-silicate systems at 5 GPa and under various redox conditions (IW-1, IW-4.5, and IW-7.9), and then probed Nb and Ta environments in quenched silicate melts using XANES technique.