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 ppm (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) versus 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$^{1+}$ 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 (Mc Donough, 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 ($fO_2 >$ IW-2) and trivalent (Ta$^{3+}$) in reducing conditions ($fO_2 <$ 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$^{5+}$. At present, Nb and Ta oxidation states under more reducing conditions have only been inferred from partitioning behavior as a function of $fO_2$. The aim of the present study is to determine directly 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.
EXPERIMENTAL

Experiments have been performed in multi-anvil apparatus at 5 GPa with variable oxygen fugacity at Laboratoire Magmas et Volcans (Clermont-Ferrand, France). The $fO_2$ was imposed by adding different amounts of metallic Si to the starting powders modifying the metal/oxide ratio of the sample. All experiments were performed using graphite capsules. The $fO_2$ values of the experimental charges have been determined following the thermodynamical formalism based on the Si-coesite equilibrium and fully described in Cartier et al. (2014b). In brief, we used the

$$\text{SiO}_2 = \text{Si} + \text{O}_2$$

equilibrium, wherein SiO$_2$ is coesite and Si is alloyed to Fe. The activity of Si in solution in the metallic alloy was determined using its concentration determined by electron microprobe, and the activity coefficient provided by the “metal activity calculator” of the Oxford petrology group. The activity of SiO$_2$ is 1 because coesite is present in the experiments. Finally, we write

$$fO_2 = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \cdot \left(\frac{a_{\text{SiO}_2}}{a_{\text{Si}}}\right),$$

with $\Delta G^\circ$ the standard free-energy change, T the temperature of the experiment and R the gas constant.

Three different starting materials were used. Samples #1198 and #1207 were investigated in the study of Cartier et al. (2014,a) who also conducted experiments on Nb and Ta partitioning as a function of $fO_2$ and proposed valence state for the two elements. Sample #1198 is a tholeiitic basalt doped with 200 ppm Nb and Ta and mixed with Fe metal and S. Sample #1207 consists of EL6 meteorite powder doped with 200 ppm Nb and Ta and mixed with 2 wt.% Si metal. Sample #1243 was synthetized for the present study and consists of EL6 meteorite material doped with
3200 ppm Nb and Ta and mixed with 42 wt.% Si metal (Table 1). All starting materials were
doped with Nb and Ta as AAS standard solutions.

Experimental charges were mounted in epoxy, ground and polished. The samples
comprised metallic quenched melt, silicate quenched melt (glass), enstatite, coesite and sulfide
melt in variable proportions. Chemical compositions have been analyzed using an electron
microprobe CAMECA SX100 and an Agilent 7500-cs induced coupled plasma – mass
spectrometer (ICP-MS) coupled with a Resonetics M-50 laser at the LMV (Clermont-Ferrand).

X-RAY ABSORPTION SPECTROSCOPY

Setup

Nb K edge and Ta L$_{III}$ edge XANES data were acquired at the X-ray absorption spectroscopy
(XAS) beamline BM23 of the European Synchrotron Radiation Facility (ESRF in Grenoble,  
France). Measurements were performed using a Si(111) double crystal monochromator coupled
to a micro-XAS station. This station is based on a set of Pt coated mirrors in a Kirkpatrick-Baez
(KB) geometry and a sample area specially designed for XAS measurements. The incident angle
of the two mirrors could be varied from 2 to 8 mrad allowing XAS operation up to 40 keV with a
maximum numerical aperture. The optical arrangement of the KB mirrors allows obtaining a
focal spot of 4 by 4 mm$^2$. The stability of the beam during a XAS energy scan is below 1
mm/keV in both transverse directions. The micro-XAS sample area part is based on a double
mechanical stage mounted in series. The first stage is designed to align the sample environment
part on the X-ray beam after the double reflection on the KB mirrors. The second stage, based on
a commercial hexapod, allows scanning the sample into the X-ray beam. The micro-XAS station
is equipped with mini ionization chambers developed in-house and a Vortex solid-state fluorescence detector. The setup is completed with a visible microscope with variable magnification.

Energy calibration

Given the need for thermal stability of the monochromator during the long time periods needed for an experiment, and the necessary precision needed on $E_0$ values to derive redox data, following procedure was established in order to model the monochromator drift. Figure 1 displays the threshold energies $E_0$ of Nb-foils measured during a week of beam time, and plotted as a function of time. One recalibration is visible after ~35h. The energy shift was parameterized as a polynomial function of time (intervals B and C) to correct every spectra acquired during the week from the drift.

Data acquisition and processing

For Nb, standard material was prepared in the form of pellets consisting of mixture of BN with NbO, NbO$_2$ and Nb$_2$O$_5$, for Nb$^{2+}$, Nb$^{4+}$ and Nb$^{5+}$ references, respectively. We also used an Nb foil, as a reference for Nb$^{0}$. In the same way, pellets made of mixture of Ta$_2$O$_5$ and BN were used as Ta$^{5+}$ reference, and a Ta foil was used as Ta$^{0}$ reference. We also used GaTa$_4$Se$_8$, which contains a mixture of Ta$^{4+}$ and Ta$^{3+}$ in equal amounts, resulting in a mean formal valence of 3.5. However the latter was only used for the quantitative valence versus $E_0$ (threshold energies) calibration (see later), and not for comparing the sample and reference XANES spectra because the Ta speciation in GaTa$_4$Se$_8$ is too different from the oxide structure. The niobium oxide
powders were purchased from Alfa Aesar and ground to 1-10 µm. The XANES data on oxide-BN pellets and metallic foils were acquired in transmission mode, and GaTa₄Se₈ was measured in fluorescence mode. All sample data (1198, 1207 and 1243) were collected in fluorescence mode, using the Vortex solid-state detector.

The experimental samples contain metal blobs immersed in the silicate melt. In order to avoid XANES signal contamination by metal fluorescence, we first acquired XRF maps of element distribution determined with the electron microprobe analysis of all the samples were used to select homogeneous and metal-free areas, as shown in Figure 2.

Because of the very low Nb and Ta concentrations of experimental samples (see Table 2), many spectra were accumulated for each experimental sample. These were subsequently stacked, thus improving counting statistics. Moreover, for each experimental sample, XANES data acquired on different points were used in order to check for potential contamination (from metal blobs) and heterogeneities in the melt. For both reference and sample XANES spectra, the different XANES analysis steps (inspection of individual spectra, merging, correction of E₀ and normalization) were performed with the ATHENA software from the Horae package (reference Ravel and Newville, 2005), based on the Ifeffit library (Newville, 2001). We defined the threshold energy E₀ as the first significant peak of the derivative (selecting the zero-crossing of the 2nd derivative curve with Athena software).

RESULTS
All details on the experimental conditions are given in Table 1. This study focuses on the silicate melt, of which the chemical compositions are given in Table 2. Table 3 summarizes the number of spectra that have been merged to produce the data presented below, together with the acquisition time for individual spectra. The data were obtained using a total acquisition time between 5.5 and 15 hours. We checked that spectra did not change during the acquisition period. Nb contents are comprised between 2.5 and 313 ppm, and Ta is in the range 21.9 – 282.7 ppm. At reducing conditions, Nb and Ta are siderophile and enter preferentially the metal phase (Cartier et al., 2014a). As a consequence the Nb and Ta concentration of quenched silicate melt of 1207 and 1243 are quite low (Nb: 8.4 and 2.5 ppm respectively; Ta: 201.5 and 21.9 ppm respectively, see Table 2). Nb oxidation state in experiment 1207 was not determined in this study.

As the region near the X-ray-absorption edge is scanned in energy, the ejected photoelectron sequentially probes the empty electronic levels of the material (Wong et al., 1984). XANES is strongly sensitive to the chemistry of the absorbing atom and various XANES spectral features can be interpreted in terms of local symmetry of the absorbing atom (Mottana, 2004). Pre-edge features of the X-ray-absorption edge spectra are caused by electronic transitions to empty bound states and give information on the oxidation state of the atom and local bonding characteristics (coordination). Finally the post-edge features of the XANES spectra are dominated by multiple-scattering resonance of the photoelectrons ejected at low energy. These features can be correlated with the atomic positions of the neighboring atoms. The present study is focused on the determination of Nb and Ta formal valence in various conditions. Thus we combined two methods. For the first approach, we compared qualitatively our samples spectra to reference spectra to find similarities (shape and edge position). In a second approach, we established a calibration curve for the edge position ($E_0$) versus formal oxidation state of the reference
compounds to determine the valence of our experimental samples. Most of the times, the chemical shifts (edge position) vary linearly with the valence of the atom, a phenomenon known as Kunzl’s law (Kunzl, 1932). In this study, we applied a calibration curve based on oxides compounds to quenched glasses. As discussed below, this should have little effect on the conclusions.

Niobium

Nb K-edge XANES spectra and corresponding first derivatives are shown on Figure 3. The four reference samples (standards) look similar to those obtained in previous studies (Burnham et al., 2012; Froideval et al., 2008). Niobium threshold energy $E_0$ is shifted from 18986 eV ($Nb^0$) to 19006 eV ($Nb^{5+}$) as Nb formal valence increases. As already noticed by Froideval et al. (2008), the white line intensity of the reference samples is also affected by Nb oxidation state, as well as the shape of the spectra. In $Nb_2O_5$, $NbO_2$ and $NbO$, Nb is octahedrally (and more or less distorted) coordinated, mainly due to the large radius of the element (Jehng and Wachs, 1990; Nico et al., 2011). Piilonen et al. (2006) showed that for $Nb^{5+}$, site distortion could result in shifting of $E_0$ position. For the purpose of the present investigation, the potential consequences of this shift are limited, and will be addressed below.

From all the spectra (samples and references) presented on Figure 3, we defined the threshold energy $E_0$ as the first significant peak of the derivative (selecting the zero-crossing of the 2nd derivative curve with Athena software). The results are given in Table 4 and are plotted on Figure 4. The reference samples were used to calibrate the dotted line. In order to evaluate the uncertainty associated to valence determination, we adopted the following approach. First we
determined the error on $E_0$ determination. Taking into account the beamline resolution, the approximation of taking $E_0$ as the first derivative peak on noisy spectra, the variability between the spectra that results in a deviation on the merged spectra, and the error associated to the normalization procedure, we estimate the global uncertainty on $E_0$ to be approximately $\pm 0.5$ eV. Due to the large energy shift between Nb and Nb$^{5+}$ (20 eV), the corresponding error on Nb valence is then $\sim 0.1$. As shown by Piilonen et al. (2006) in the case of Nb$^{5+}$, site distortion can shift the $E_0$ value by 2.6 eV at most. Taken this additional uncertainty yields error on Nb valence state of approximately $\sim 0.6$.

Sample #1198, the oxygen fugacity of which is IW-1, is similar to Nb$_2$O$_5$ (Fig.3), especially in pre-peak and edge features. When plotted on the valence calibration curve, Nb mean valence of #1198 has been found to be $4.4 \pm 0.6$ at IW-1. We conclude here that in this sample, Nb is mainly 5+ and is octahedrally coordinated. This result is consistent with previous studies that argue for Nb to remain pentavalent in silicate systems and between IW+7 and IW-4.2.

Sample #1243, with an oxygen fugacity of IW-7.9, looks similar to NbO. The oscillations (the first three low intensity peaks) in the pre-edge part of the derivative are mainly related to the noise on #1243 Nb spectra and have not to be taken into account (the Nb concentration is indeed very low at $\sim 2$ppm, Table 1). However the shoulder on the pre-edge position is not exactly the same for #1243 and NbO. In the same way the depression in the XANES region is very similar for the two spectra but seems to be shifted on the low energies for #1243. This should indicate that in this sample, Nb is mainly 2+, and its coordination is octahedral, although the surrounding atoms may not be only oxygen (O$^{2-}$) but also sulfur (S$^{2-}$) (see melt composition in Table 2). The calibration curve gives a mean valence of $1.9 \pm 0.6$, in agreement with the qualitative observations.
Tantalum

Ta LIII-edge XANES spectra and corresponding first derivatives are shown on Figure 5. The two reference samples are plotted on Figure 5 with the three experimental samples for comparison. From Ta$^0$ to Ta$^{5+}$, Ta $E_0$ shifts from 9881 to 9882.8 eV. This shift is relatively small (1.8 eV instead of 20 eV for Nb), and as consequence, the error associated to the determination of the valence is significantly high (1.3) compared to that of Nb (0.1), even though we estimate the error on $E_0$ determination to be the same than Nb ($\pm$ 0.5 eV).

Qualitatively, spectra of #1198 and #1207 are quite similar to that of Ta$_2$O$_5$, but seem to be slightly shifted toward the low energies. Likewise, the white line is split into two components peaks for both samples, unlike Ta$_2$O$_5$. This feature has already been observed by Burnham et al. (2012) and Farges et al. (2006). The white line in #1243 spectrum is located between those of Ta-foil and sample 1207. This indicates Ta formal valence in #1243 is less than 5.

For the valence versus $E_0$ calibration line, the same procedure as for Nb is employed here. Ta threshold energies have been defined as the first significant peaks of the derivatives for experimental samples and references. Results are given in Table 5 and displayed on Figure 6. The $E_0$ values of the standards define a linear calibration line with a good correlation. When plotted on this line, samples display the following mean valences for Ta: +4.6 ± 1.3 at IW-1, +3.1 ± 1.3 at IW-4.5, and +0.7 ± 1.3 at IW-7.9.

DISCUSSION
The results of the XANES measurements are summarized in Figure 7. Here, it should be noted that crystalline reference compounds were applied to the study of experimental glasses. As noted by Piilonen et al. (2006) in the case of Nb, the $E_0$ value depends on the crystalline structure and site symmetry around Nb, even for constant valence state. Therefore, the calibration curve obtained in the present study may be slightly affected. We note however that in the case of Nb, the shift due to crystallographic structure is about 2.5 eV (Piilonen et al., 2006), which is low relative to the total shift due to valence change from Nb$^+$ to Nb$^{5+}$. Moreover, the position of the white line is constant for the metal. Therefore, the uncertainty on valence determination arises solely from the position of the charged Nb ion edge energy. This difference is small compared to the observed shift among the samples studied, making the conclusion on Nb valence change robust. For the Ta case, it is known that the L-edge is due to the excitation of 2p electrons to d-state (Burnham et al., 2012) and the corresponding energy is usually less sensitive to the atom environment.

Although the number of data points is limited, the trend for both Nb and Ta is unambiguous: reducing oxygen fugacity from IW-1 to IW-7.9 yields valence reduction for both Nb and Ta. For the moderately reducing conditions (IW-1), Nb and Ta are predominantly in the 5+ state. The present study is compatible with Burnham et al., (2012) who found that, between IW+$+6.7$ and IW-4.3, niobium and tantalum are mainly pentavalent in silicate melts. For more reducing conditions (IW-4.5), Ta becomes trivalent. This finding is contradictory with Burnham et al. (2012) who conclude that Ta is pentavalent down to IW-4.3, but agrees with the interpretation of the oxygen fugacity dependent trace element partitioning results reported in Cartier et al. (2014b) as shown in Figure 7. The discrepancy between our results and those of Burnham et al. (2012) could be due to the fact that we used an $E_0$ vs. valence calibration curve, whereas Burnham et al.
only compared qualitatively the XANES spectra of samples equilibrated under various $fO_2$. We do not exclude that it could also be due to differences in melt compositions, but we note that both glasses equilibrated at ca. IW-4 have comparable SiO$_2$ concentrations and that their structure, expressed as the number of non-bridging oxygens per tetrahedrally-coordinated cations (NBO/T ratio, Mysen, 1987) are close (0.37 in our case vs. 0.25 in Burnham et al. (2012)).

At IW-7.9, Nb becomes divalent, whereas Ta is further reduced, maybe down to about 1+. The Ta results should be considered with caution because of the large error on mean valence determination. Nevertheless, as shown in Figure 7, our results are in good agreement with Cartier et al. (2014a) Nb and Ta valence estimation from experimentally determined metal – silicate partition coefficient versus oxygen fugacity relationship.

It is not clear from Figure 7 whether there is a crossover in the valence states of Nb and Ta. The data suggest that Ta is reduced to a formal valence of ca. +1 or less, which implies a crossover. However, Cartier et al. (2014a) found that the metal silicate partition coefficients of Nb and Ta merge at very low $fO_2$. This finding may imply that both elements have the same valence state at very reducing conditions. The low count number using the Ta L$_{III}$ edge combined with the small shift of Ta white line position across the range of valence states yields high uncertainties on valence state determination. Finally, both Nb and Ta become highly siderophile at very low $fO_2$ (Cartier et al., 2014a), which yields extremely low concentrations in the silicate melt for both elements. Low concentration is an additional difficulty when attempting to directly determine Nb and Ta valence state. Our approach, which consists of combining experimental geochemistry (using information from partition coefficients, Cartier et al., 2014a) with spectroscopic methods, appears to be a good tradeoff for valence determination at extreme conditions (pressure, temperature, oxygen fugacity) such as explored in the present study.
IMPLICATIONS

For elements whose valence varies across the range of the solar system oxygen fugacity values (IW-6 or less in enstatite chondrites to IW+8 in oxidized Earth’s rocks (Wadhwa, 2008; Larimer and Buseck, 1974)), it can be anticipated that their affinity with host minerals would change, depending on ambient conditions (Papike et al., 2005). Such may be the case for Nb and Ta.

Recently, the Nb paradox (that is, the Nb deficit in the bulk silicate Earth relative too Ta) has been re-evaluated in terms of the effect oxygen fugacity on metal – silicate partitioning during the Earth’s core segregation (Cartier et al., 2014a). Moreover, very recent studies report on anomalous Nb behavior in supposedly undifferentiated extraterrestrial material. Barrat et al. (2014) measured Nb negative anomalies in EL and EH5 enstatite chondrite silicate parts. Varela et al. (2014) discovered correlation between V and Nb depletions in chondrule cores of enstatite chondrite. These concentrations could be linked to the equilibration and/or removal of a metallic or sulphide phase occurring during the history of these objects, under conditions wherein Nb is siderophile and / or chalcophile. The latter behavior would be analogous to that of Ti, another HFSE, which was demonstrated as being chalcophile and divalent in Yamato 691 enstatite chondrite (Nakamaru-Messenger et al., 2012). Here, we have calibrated the valence of Nb and Ta in silicate melts as a function of $fO_2$. Although Nb and Ta concentrations in natural melts are very low, and consequently acquiring XANES spectra would be challenging, obtaining direct information on those element valence in solar system primitive objects could help in evaluating the oxygen fugacity that they recorded.
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REFERENCES


## TABLES

### Table 1. Experimental conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Pressure (GPa)</th>
<th>Temperature (K)</th>
<th>Starting material</th>
<th>Nb2O5 doped (ppm)</th>
<th>Ta2O5 doped (ppm)</th>
<th>Metal added (wt.%)</th>
<th>fO2</th>
<th>ΔIW</th>
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<tbody>
<tr>
<td>1198</td>
<td>5</td>
<td>2073</td>
<td>Tholeitic basalt</td>
<td>200</td>
<td>200</td>
<td>Fe + S</td>
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<tr>
<td>1207</td>
<td>5</td>
<td>2073</td>
<td>EH6 chondrite</td>
<td>200</td>
<td>200</td>
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<tr>
<td>1243</td>
<td>5</td>
<td>1973</td>
<td>EH6 chondrite</td>
<td>3200</td>
<td>3200</td>
<td>42 % Si</td>
<td>-7.9</td>
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### Table 2. Electron microprobe and ICP-MS analysis of the three experimental quenched melts.

<table>
<thead>
<tr>
<th>Experiment</th>
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<th>1207</th>
<th>1243</th>
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<tr>
<td>Electron probe (wt.%)</td>
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<td></td>
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<tr>
<td>Na=4</td>
<td>1σ</td>
<td>Na=4</td>
<td>1σ</td>
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<td>Al</td>
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<td>0.01</td>
<td>0.02</td>
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<tr>
<td>S</td>
<td>0.13</td>
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<tr>
<td>O</td>
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<td>Na=5</td>
<td>1σ</td>
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<td>Nb</td>
<td>312.9</td>
<td>11.0</td>
<td>8.4</td>
</tr>
<tr>
<td>Ta</td>
<td>282.7</td>
<td>12.6</td>
<td>201.5</td>
</tr>
</tbody>
</table>

Notes: * C content is calculated by difference between 100 % and the total. Na = number of analyses
Table 3. Details on data acquisition, with number of stacked spectra for each experiment, together with acquisition time (in minutes) for each individual spectrum.

<table>
<thead>
<tr>
<th>Exp. Sample</th>
<th>Nb of stacked spectra</th>
<th>Acquisition time (minutes/spectrum)</th>
<th>Nb of stacked spectra</th>
<th>Acquisition time (minutes/spectrum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1198</td>
<td>22</td>
<td>28</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>1207</td>
<td>no data</td>
<td>11</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1243</td>
<td>26</td>
<td>24</td>
<td>20</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 4. Nb threshold energies of references and experimental samples, and corresponding valences.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E₀</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb foil</td>
<td>18986</td>
<td>0</td>
</tr>
<tr>
<td>NbO</td>
<td>18994.7</td>
<td>2</td>
</tr>
<tr>
<td>NbO₂</td>
<td>19002.8</td>
<td>4</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>19006.0</td>
<td>5</td>
</tr>
<tr>
<td>1243</td>
<td>18994.1</td>
<td>1.9 ±0.6</td>
</tr>
<tr>
<td>1198</td>
<td>19004.09</td>
<td>4.4 ±0.6</td>
</tr>
</tbody>
</table>

Table 5. Ta threshold energies of references and experimental samples, and corresponding valences.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E₀</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta foil</td>
<td>9881</td>
<td>0</td>
</tr>
<tr>
<td>GaTa₂Se₆</td>
<td>9882.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>9882.8</td>
<td>5</td>
</tr>
<tr>
<td>1243</td>
<td>9881.2</td>
<td>0.7 ±1.3</td>
</tr>
</tbody>
</table>
Figure 1. Nb-foil measurements during the week of analysis. Black dots correspond to Nb-foil measurements, which E0 has been defined as the absorption spectra first derivative peaks. Nb-foil E0 is 18986 eV. The A period corresponds to monochromator stabilization. A recalibration was done between B and C periods. All sample analyses have been done between these Nb-foils measurements and we consequently applied to every point an energy shift correction corresponding to the ∆Shift on the figure. In detail, Nb spectra for sample 1198 have been acquired during the B period, and all other spectra, including experimental and reference samples, have been acquired during the C period.

Figure 2. Combined Nb and Fe map of sample 1243. The red part corresponds to the area with the highest Nb and Fe concentrations, i.e. an outcropping metal blob. The rounded green part is less concentrated in those elements and corresponds to a metal blob hidden beneath the surface. The blue area is Fe and Nb poor and corresponds to the quenched silicate melt. The structures (metal blebs, homogeneous melt area…) have been identified comparing the maps with SEM pictures of the samples.

Figure 3. Niobium spectra for standards and samples (left) and their derivative (right). Increase in Nb oxidation state causes an increase in E0. Sample 1198 (IW-1) is similar to Nb₂O₅ and sample 1243 is similar to NbO.
Figure 4. Niobium oxidation state versus E₀ calibration. The straight line is defined by a linear regression on the four standards (black filled circles). Then, the edge energies (E₀) of the samples (grey filled diamonds) have been plotted to estimate their mean valence. Sample 1198 Nb mean valence is 4.4 ± 0.1 and Sample 1243 mean valence is 1.9 ± 0.1.

Figure 5. Tantalum spectra for standards and samples (left) and their derivative (right). Increase in Ta oxidation state causes an increase in E₀. Sample 1198 is similar to Ta₂O₅. Samples 1207 and 1243 are increasingly shifted on the left but the lack of standards prevent us to define the Ta prevailing configurations.

Figure 6. Tantalum oxidation state versus E₀ calibration. The straight line is defined by a regression on the three standards (black filled circles). Then, the edge energies (E₀) of the samples (grey filled diamonds) have been plotted to estimate their mean valence. Sample 1198 Ta mean valence is 4.6 ± 1.3, Sample 1207 Ta mean valence is 3.1 ± 1.3, and Sample 1243 Ta mean valence is 0.7± 1.3. The rather large error is due to the very small energy shifts induced by the valence changes in Ta.

Figure 7. Nb (in blue) and Ta (in red) valence states as a function of oxygen fugacity. The results obtained in the present study (symbols at given fO₂ values) agree with values deduced from experimentally determined metal – silicate partition coefficients (Cartier et al., 2014a), shown as colored boxes, and with determination at IW-5.5 from enstatite / silicate melt partition (Cartier et al., 2014b) shown as hexagon. Open boxes with dotted contours represent the results of Burnham et al. (2012). Due to analytical constraints, the presence of Ta¹⁺ is uncertain, as discussed in the main text. Errors on valence state are discussed in the text. Uncertainties on oxygen fugacity (±0.5 log units) have been discussed in Cartier et al. (2014b).
Figure 1

Recalibration

$\Delta$Shift

Time (hours)

$E_0$ (eV)
Figure 2

Silicate melt

Metal blob (undersurface)

Metal blob (outcrop)
Figure 3
Figure 4

A graph showing the relationship between Nb oxidation state and $E_0$ (eV) for Nb, NbO, NbO$_2$, and Nb$_2$O$_5$. The graph includes data points for $E_0$ values of 18985, 18990, 18995, 19000, and 19005 eV.
Figure 6

![Graph showing Nb oxidation state vs. \( E_0 \) (eV) for \( \text{TaSe}_2 \), \( \text{GaTa}_4\text{Se}_8 \), and \( \text{Ta}_2\text{O}_5 \). The graph includes data points at \( E_0 = 9880.5 \text{ eV} \), \( 9881.0 \text{ eV} \), \( 9881.5 \text{ eV} \), \( 9882.0 \text{ eV} \), \( 9882.5 \text{ eV} \), and \( 9883.0 \text{ eV} \).]
Figure 7

Valence State vs. Oxygen fugacity (ΔIW) for Nb and Ta.