Calculation of Chemical Shift for Ti via EELS White-Line-Ratio Method

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$3d$ transition metals occur in a wide range of mineral phases in primitive meteorites. Their oxidation states are directly affected by thermodynamic conditions, and so can provide constraints on the temperature and pressure under which their host phases formed or last equilibrated. Hibonite, thought to condense directy from the early solar nebula at high temperatures [1], can contain mixed valence Ti^{3+} and Ti^{4+}. [2] determined that the existence of reduced Ti^{3+} in hibonite was likely the result of oxygen-vacancy formation under reducing conditions, and experimentally related these valences to oxygen fugacity (fO$_2$). Ti and V have been found in mixed valence in planetary pyroxenes [3] which were also associated with fO$_2$. These measurements were of bulk material, and provided model-independent constraints on the thermal landscape of the early solar nebula. We hypothesize that atomic-scale measurements of the oxidation states of Ti and V could also provide new insights into the crystal chemistry and structure of planetary materials.

Electron energy-loss spectroscopy (EELS) has become a leading method in high spatial resolution and high energy resolution. EELS coupled to an aberration-corrected scanning transmission electron microscope (STEM) enables direct analysis of atomic columns [4-7]. There are primarily two EELS approaches to the quantification of oxidation state of $3d$ metals. Direct quantification of oxidation states can be achieved by fitting the energy-loss near-edge structure (ELNES) with linear combinations of reference spectra [7-9]. Alternatively, $L_{2,3}$ edges ('white lines') experience a chemical shift tied to oxidation state [10]. To quantify Ti^{3+}/Ti^{4+}, [11] applied a method developed by [12] whereby the ratio of oxidation states is directly proportional to the ratio of intensities of EELS white lines.

To establish the white-line-ratio method under our own calibrations, instrumentation, and optical conditions, we also acquired EEL spectra of Ti oxides of known Ti^{3+}/Ti^{4+} content (Table 1). Spectra were acquired using a 200keV aberration-corrected Hitachi HF5000 S/TEM equipped with a Gatan Quantum ER electron energy-loss spectrometer. Spectra were acquired in TEM mode using a 2.5 mm entrance aperture and a dispersion of 0.01 eV/ch. Spectra were processed using a Python script developed in house, which partially utilizes the hyperspy software package [13]. All spectra were corrected for channel-to-channel gain variation and dark current. Low-loss and high-loss spectra were calibrated via zero loss peak (ZLP) centering, an inverse power law (AE^{-r}) model was used to subtract background, and all spectra were independently normalized such that their highest intensities were set to 1. The average energy resolution calculated by the full-width-half-maximum intensity of the ZLP over all spectra is approximately 0.26 eV. The white-line ratio method requires knowledge of the chemical shift of reference materials, and the edge onset (critical ionization energy, E_c) serves as a marker for such shift. The E_c for our spectra were determined with a derivative approximation, such that the slope of the tangent line associated with edge onset was demonstrably positive when compared to local slope variation in the preceding noise (a minimum slope value of 9.1×10^{-4} achieves these conditions for our data set).

Using this approach, we have calculated a shift in edge onset as a function of oxidation state over multiple sets of reference spectra. Figure 1 shows a representaive sample of spectra from our data set. Calculated

shifts averaged between 0.10 eV and 0.47 eV among successive valencies from Ti^{2+} to Ti^{4+}. Direct comparison to literature required calculating shifts with respect to the lowest-energy edge maxima (the second maxima in the case of TiO_2 due to splitting), which can be seen in Table 1. These shifts, ranging from 0.17 eV to 0.85 eV, are comparable to our E_c calculations, but all shifts are smaller than previously reported by [11]. The shift between Ti_2O_3 and Ti_3O_5 specifically is consistently less than our energy resolution, and would appear to be statistically insignificant. Qualitative analysis of our ELNES dataset does not suggest contamination as a cause for a lack of significant shift. To increase statistics and decrease error, we will acquire more spectra for our working dataset. Analogous to [11], we will also calibrate spectra using additional ELNES other than the zero-loss peak, such as the amorphous carbon edge associated with the film on which our standards are prepared. This method should provide us with an additional check on spectral calibrations [14].

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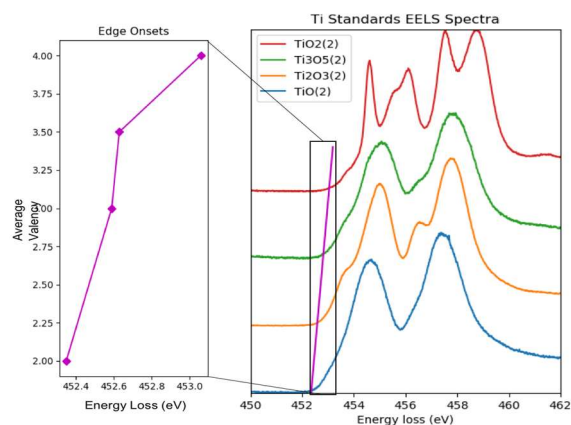
Oxide	Average L_3 peak	L_3 (b) edge peak
TiO	454.48 eV	457.4 eV
Ti_2O_3	454.99 eV	458.9 eV
Ti_3O_5	455.16 eV	459.0 eV
TiO_2	456.01 eV	460.0 eV

Table 1. Energy loss of left-most (L_3) peak maxima for all Ti standards, listed from smallest to largest average valency. Right column indicates peaks found in table 2 of reference [11].

Figure 1. Ti Standards EEL spectra with edge onset indicators overlaid. Edge onset chemical shift is nearly linear with a mean average valency vs. energy loss slope of 0.34.