EFFECT OF FOCUSED ION BEAM (FIB) SECTIONING ON Cr AND Ti VALENCES IN SEMARKONA OLIVINE.

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Introduction: A major challenge in the study of returned samples from extraterrestrial bodies is unraveling the origin and evolution of the material from measured physical and chemical properties. Primitive Solar System materials, such as those from comets and asteroids, the primary targets of sample return missions, are largely-unequilibrated fine-grained objects [e.g., 1,2]. Thus, the component phases potentially have diverse origins and evolutionary histories.

Spatially-resolved X-ray-based analytical techniques are valuable in establishing the texture, mineralogy, crystal structure, and chemical state of returned materials and offer in-situ and non-destructive capabilities [3,4]. These techniques can be integrated with microstructural observations obtained using FIB-TEM techniques [5] to provide a comprehensive approach to the coordinated analysis of returned samples. The goal of this project is to develop high-energy, synchrotron-based analytical methods applicable to picogram ($\sim\mu m^3$) quantities of returned material, the mass sensitivity typically required to obtain data on single-phase aliquots.

One task is to develop X-ray absorption fine structure (XAFS) spectroscopy methods (notably, X-ray absorption near edge structure - XANES) for measuring multiple redox equilibria involving multivalent elements to constrain oxidation state, a valuable approach since conventional mineralogic oxybarometers are difficult to apply to these materials and because each redox couple is sensitive to different oxygen fugacity (fO_2) regimes so that together they provide a wide dynamic range in oxidation state conditions.

The spectroscopy work specifically focuses on valences of the first-row transition metals Ti, V and Cr, multivalent elements selected because they have redox couples that span the suspected range of fO_2 experienced by the igneous components of these materials [6,7]. The relevant redox couples are $Ti^{3+}\leftrightarrow Ti^{4+}$, $V^{2+}\leftrightarrow V^{3+}$(possibly $\leftrightarrow V^{4+}$) and $Cr^{2+}\leftrightarrow Cr^{3+}$. We are using FIB methods to produce mono-mineralic samples.

Methods: Our development work has focused on olivine from type I and type II chondrules in Semarkona (OC 3.00). Beginning with a thin section, candidate olivine regions for FIB sample extraction were identified by SEM and Cr and Ti XANES valence analyses were obtained within a few tens of μm of these spots prior to FIB sample preparation. Four XANES spectra were obtained on each spot, each with the thin section rotated by a 90° increment about the thin section normal, an approach that was intended to average out spectral differences that may arise due to X-ray pleochroism. The four spectra were merged for each spot to produce Cr and Ti valences. Valences were determined following the methods of [8] and [9] for Cr and Ti, respectively.

FIB sections (typically 10 x 20 x 1 μm) were then produced from these regions (one section from each of 6 regions) using conventional FIB sample preparation techniques, e.g. [10]. Sections were mounted to V-slots in Cu TEM grids (Figure 1 top) which in turn were clamped in SEM-compatible vices. XANES analyses were collected on the FIB sections in this configuration. This approach allowed us to evaluate the effect of FIB milling [11] on the Cr and Ti valences by comparing valence results for the FIB sections with those for the associated pre-FIB spots. For the FIB sections, the synchrotron beam analyzed a volume of olivine ~ 2 x 2 x 1 μm = 4 μm³ which is a mass of ~ 10 pg.

For each FIB section, an XRF map was first collected to locate the olivine material (Figure 1 middle). XANES measurements were obtained with the FIB sections in three different relative orientations (-20°, 0°, +20°) rotating about the vertical axis (i.e., within the grid plane). At each orientation, a XANES linescan was collected scanning from one side of the FIB section to the other collecting XANES spectra every 2 or 2.5 microns (e.g., red line in Figure 1 middle). The resulting profiles of Cr content were used to identify the olivine-FIB region in each line scan (Figure 1 bottom) and the Cr and Ti valence results were averaged over this region. Each spectrum in this region was processed individually and the resulting valences averaged. These averages for each of the three orientations were then averaged themselves to produce a single valence for each FIB section ("FIB Average" in Table 1). This overall average for the FIB section was then compared to the pre-FIB thin section valences and the difference computed (Table 1). For Ti, the same spatial regions identified in the Cr profiles were used.

Results: The valence differences between the FIB sections and the pre-FIB thin section analysis spots was small, averaging -0.06 ± 0.07 (reduction) and 0.12

± 0.07 (oxidation) for Cr and Ti, respectively (ignoring Ti in FIB#4 which contained some adjacent matrix). At least some of these small offsets are likely to be due to residual orientation differences since the FIB sections have only been rotated through 40° so far.

Our best comparison is for FIB#3 and FIB#6, two orthogonal sections within the same grain associated with two pre-FIB analysis spots (G and H). We can further correct for spectral differences that may arise due to X-ray pleochroism by averaging the valences for FIB#3 and FIB#6 and comparing that result to the average of the G and H spots. Doing this (see last row in Table 1), the Cr valences are essentially identical (2.12 ± 0.05) and the Ti valence in the FIB sections (3.26 ± 0.05) is slightly more oxidized than that in the TS (3.14 ± 0.05). Comparing these spectra shows that the Ti pre-edge multiplet has a small additional oxidized peak..

Table 1: Semarkona Olivine Valences

FIB #	Thin Section Spots	Chromium			Titanium		
		FIB Average	Thin Section Average	FIB-TS	FIB Average or Merge	Thin Section Average	FIB-TS
1	A,B	2.35	2.41	-0.06	nd	nd	nd
2	C	nd	2.21	nd	nd	3.26	nd
3	G,H	2.01	2.13	-0.12	3.20	3.14	0.06
4	C	2.20	2.21	-0.01	3.90	3.26	0.64
5	C,D	2.02	2.22	-0.20	3.35	3.25	0.10
6	G,H	2.23	2.13	0.10	3.33	3.14	0.19
average		2.16	2.22	-0.06	3.29	3.18	0.11
3,6	G,H	2.12	2.13	-0.01	3.26	3.14	0.12

precisions of average valences are +/- 0.07
nd = not determined

Conclusions: For Semarkona olivine, FIB sample preparation has no effect on Cr valence and the effect on Ti valence is close to negligible and possibly non-existent. The high-quality XANES spectra for our analyzed FIB masses (~10 pg) demonstrates that robust valence determinations can be obtained down to the "picogram" mass level.

References: [1] Brearley A. J. (1993) GCA 57, 1521-1550. [2] Dobrică E. and Brearley A. J. (2014) *MAPS* 49, 1323-1349. [3] Sutton S. R. et al. (2017) *JEQ* 46, 1158–1165. [4] Sutton S. R. et al. (2017) *GCA* 204, 313-330. [5] Singerling S. A. et al. (2016) Met. Soc. #6239. [6] Papike J. J. et al. (2016) *Am. Min.* 101, 907-918. [7] Righter K. et al. (2016) *Am. Min.* 101, 1928-1942. [8] Goodrich C. et al. (2013) *GCA, 122,* 280-305. [9] Simon S. B. and Sutton S. R. (2018) M&PS 53, 2138-2154. [10] Abreu N. M. and A. J. Brearley (2010) *GCA* 74, 1146-1171. [11] Rubanov S. and Munroe P. R. (2004) *J. Microscopy* 214, 213-221.
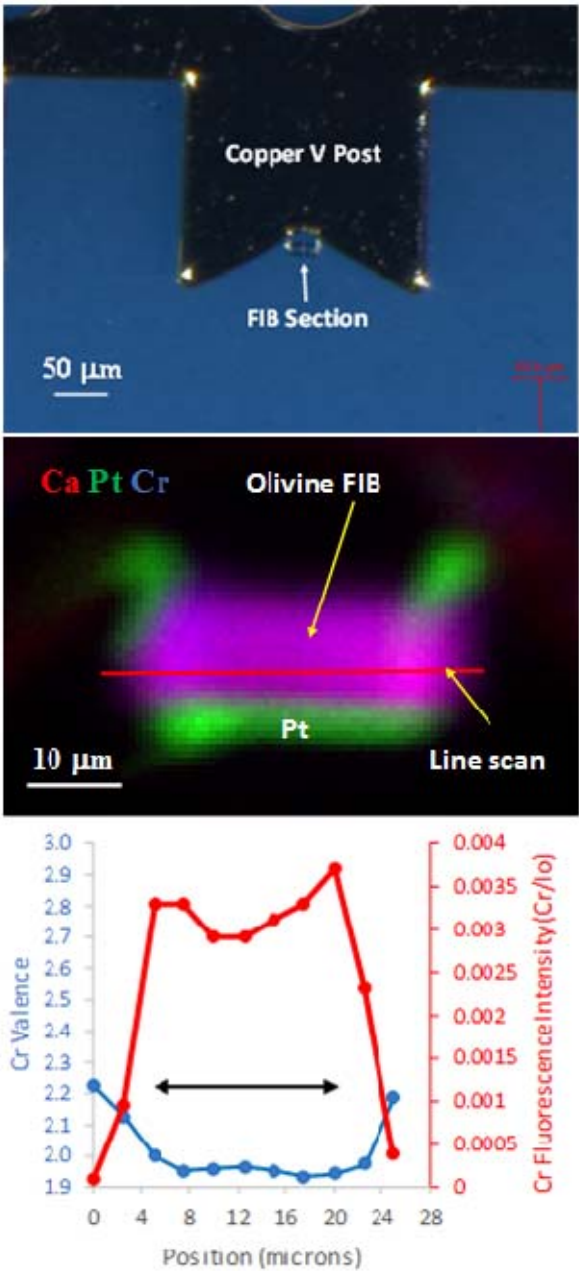

Figure 1: *Top:* FIB section mounting scheme showing close-up of copper TEM grid V-post holding FIB section. *Middle:* Three-color elemental map showing distribution of Pt (green), Ca (red), and Cr (blue) for a single orientation. The olivine in FIB#3 section contains both Ca and Cr and therefore corresponds to the purple region (~25 μm wide). *Bottom:* Plots of Cr valence and Cr concentration along the red line in middle image. The black arrow shows the region over which valence was averaged in this orientation.