

**MEASURING V-XANES IN ALUMINUM-RICH CHONDRULES TO PROBE OXYGEN FUGACITY CONDITIONS IN THE EARLY SOLAR DISK.** C. E. Jilly-Rehak<sup>1</sup>, A. L. Butterworth<sup>1</sup>, Z. Gainsforth<sup>1</sup>, and A. J. Westphal<sup>1</sup>. <sup>1</sup>University of California Berkeley, Space Sciences Laboratory, 7 Gauss Way, Berkeley, CA 94720. Email: [jillyrehak@ssl.berkeley.edu](mailto:jillyrehak@ssl.berkeley.edu).

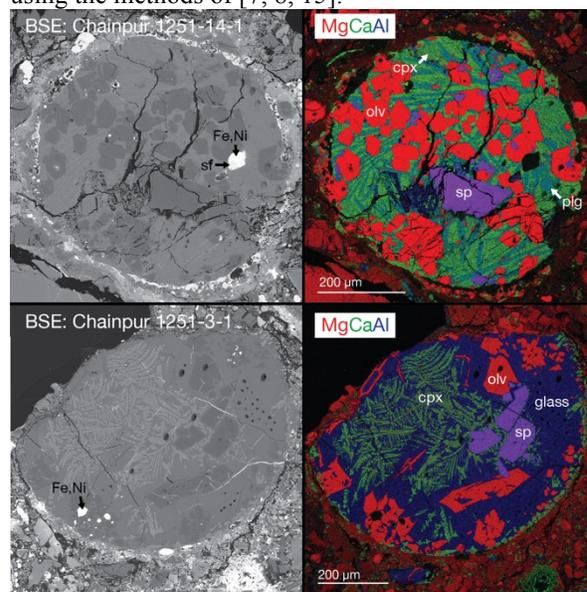
**Introduction:** Multivalence transition elements can be used to constrain the oxygen fugacity ( $fO_2$ ) of the solar nebula environment from which meteoritic components, such as chondrules and Ca-Al-rich inclusions (CAIs), formed. For example,  $Ti^{3+}/Ti^{4+}$  abundances in pyroxene, spinel, and hibonite in CAIs suggest that they formed in very reducing, variable conditions as low as IW-8 [1-3]. Studies of Fe equilibria and oxidation states in ferromagnesian chondrules suggest that they formed between IW-4 to IW-0.5 [4, 5]. While the oxygen fugacity environments of these components have been loosely constrained, the petrogenic relationship between ferromagnesian chondrules and CAIs remains poorly understood. Al-rich chondrules (Al-chondrules) may represent an important link, as they have mineralogical and chemical properties similar to both objects [6]. The V oxybarometer [e.g., 7, 8] may be particularly well-suited for Al-chondrules, as the  $V^{2+}/V^{3+}$  buffer probes the fugacity region between the  $fO_2$  of  $Ti^{3+}/Ti^{4+}$  and  $Fe^0/Fe^{2+}$ .

The formation mechanism of Al-chondrules is currently unknown; petrographic studies have shown that ~15% of Al-chondrules contain relict CAIs [9], suggesting a petrologic link, while mineralogical studies suggest that no single formation process can explain the variety of compositions observed in these objects [6]. The results of O isotopic studies of Al-chondrules in OC and CR chondrites are also conflicting, with the former arguing that the <sup>16</sup>O enrichment trend can not be produced by simple mixtures of ferromagnesian chondrules and CAIs [10], and the latter showing a different <sup>16</sup>O enrichment trend that supports a mixing scenario [11].

The motivation for this research is to use V oxidation state as a tracer for spatial and/or temporal variations in the solar nebula environment, and to link such variations to the primitive components in chondrites. To reach this goal, we aim: (1) to understand the formation mechanism and  $fO_2$  conditions for the enigmatic Al-chondrules; (2) to develop the V oxybarometer for reduced phases formed near the  $V^{2+}/V^{3+}$  buffer (~IW-4). Further details regarding the development of the V oxybarometer are discussed in detail in [12].

**Samples and Methods:** The two main samples used for this study were Al-rich chondrules Chainpur 1251-14-1 and Chainpur 1251-3-1 (LL3.4; Fig. 1). These Al-chondrules were chosen as they have been previously studied for petrography, O-isotopes, and <sup>26</sup>Al-<sup>26</sup>Mg systematics [13, 14, 6]. In addition, we targeted a CAI in Renazzo (CR2) thin section NHMW-N1126, and an Al-chondrule in NWA 7402 (L3.1) for comparison. V-XANES was measured in spinel from Chainpur 1251-14-1 and Chainpur 1251-3-1, and in

glass from Chainpur 1251-3-1. Count rates for V in NWA 7402 spinel were too low for analysis. Preliminary Ti XANES data were taken from multiple samples: clinopyroxene (cpx) and glass from Chainpur 1251-3-1, spinel and cpx from a Renazzo CAI, and spinel in the NWA 7402 Al-chondrule. Both elements were measured by K-edge XANES at Beamline 10.3.2, Advanced Light Source (ALS) synchrotron at Lawrence Berkeley National Lab. Data were analyzed with MATLAB, ALS beamline software, and Athena and Artemis software using the methods of [7, 8, 15].

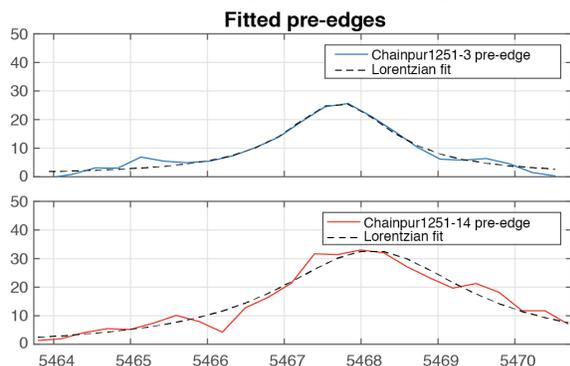


**Fig. 1.** BSE images (left) and EDX maps (right) of Chainpur 1251-14-1 (top), and Chainpur1251-3-1 (bottom). Mg, Ca, and Al are shown in red, green, and blue.

**Results:** The pre-edge peak intensities for spinels in Chainpur 1251-14-1 and 1251-3-1 were 32.8 and 25.9, with centroid energies at 5466.9 and 5466.5 eV, respectively (Fig. 2). These peak intensities and energies are lower than any of the glasses reported in [7]. The signal/noise ratio was too low for V in the Chainpur 1251-3 glass to accurately measure any pre-edge peak. Using the equation for the average valence  $V^*$  from [7],  $V^* = 2.5$  and 2.4 for Chainpur 1251-14-1 and 1251-3-1, respectively. EXAFS analysis of the extended spectra suggests that the V is octahedrally coordinated.

The preliminary Ti-XANES analyses are qualitative data, so we have noted the relative heights and shapes of the pre-edge peaks for comparison. All Ti pre-edge features are dominated by a large multiplet peak near 4971 eV, and a weaker multiplet peak at 4969 eV, consistent with meteoritic spinel and cpx from [2, 15].

Of the components measured, the Renazzo CAI spinel and the Chainpur 1251-3-1 cpx have nearly identical pre-edge peak intensities. The feature near 4969 eV in the Al-chondrule cpx is stronger than that in the CAI spinel, diagnostic of a  $Ti^{3+}$  contribution [2]. The Chainpur 1251-3-1 glass and the NWA 7402 spinel exhibit increasingly intense pre-edge peaks, suggesting they are relatively  $Ti^{4+}$ -rich compared to the other phases.



**Fig. 2.** V-XANES pre-edge peak analyses for Chainpur 1251-14-1 and 1251-3-1.

**Discussion:** Using a suite of V standards formed at variable  $fO_2$ , [7, 16] showed that the plot of pre-edge peak intensity vs.  $\log(fO_2)$  at 1400 °C has a nearly linear correlation from  $-12 < \log(fO_2) < -3$  ( $\sim IW-2$  through  $IW+8$ ). Using this V K-edge oxybarometer, we can definitively constrain the Al-chondrule fugacity to  $\log(fO_2) < -12$ , though it is likely much lower. The intensity of the  $V^{2+}$  multiplet peak is assumed to be zero based on the expectation of near-perfect octahedral symmetry [7]. As  $V^{2+}/V^{3+}$  increases at  $\log(fO_2) < -12$ , the amplitude of the pre-edge peak goes to zero and the current V oxybarometer becomes poorly constrained (Fig. 3). The energy-shift in the pre-edge for the Chainpur Al-Chondrules is consistent with a lower valence than the most reduced glasses measured in [7].

These results indicate that the Al-chondrules formed at lower fugacity than their ferromagnesian counterparts, potentially closer to the reducing conditions of CAIs. This is supported by V XANES analyses of pyroxene in an Allende CAI [2], where they found the  $V^*$  to range from  $\sim 2.3-2.7$ . In addition, the presence of reduced  $Ti^{3+}$ -bearing cpx in Chainpur 1251-3-1, suggests formation in a very reduced environment.

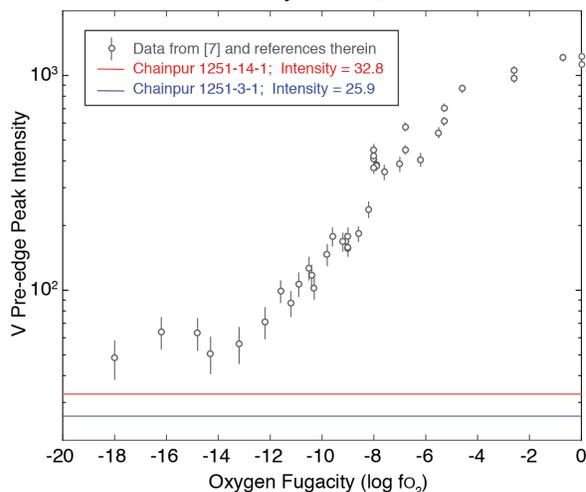
The distribution coefficient of V varies with valence and  $fO_2$ , therefore some caution must be taken when interpreting this data. Al-chondrules are well-suited to investigate this issue, as many contain both glassy and spinel phases, formed at low  $fO_2$ . In a single melt, [16] showed that the valences of the spinel and the glass were systematically different. This may be attributed to  $V^{2+}$  being more compatible in spinel than  $V^{3+}$  and  $V^{4+}$  [16, 17], leaving the glass enriched in the higher

valence species rather than reflecting variable  $fO_2$ . While the signal/noise ratio of the glass V spectra in this study was not sufficient to measure the pre-edge peak, we plan to explore this issue in future studies with other Al-chondrule samples.

To improve the results of this research, and to extend the V oxybarometer to low  $fO_2$ , we are taking the following steps: (1) developing an L-edge oxybarometer that is not limited by the zero-intensity  $V^{2+}$  K-edge multiplet peak; (2) creating low  $fO_2$  standards [18] (3) developing DFT models to yield physical insight into how valence affects the spectral properties of minerals.

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**Fig. 3.** Glass V peak intensity vs.  $\log(fO_2)$  at 1400 °C from [7], compared to Chainpur Al-chondrules.