Measuring V-XANES in aluminum-rich chondrules to probe oxygen fugacity conditions in the early solar disk

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Motivation

Multivalence transition elements can be used to constrain the oxygen fugacity ($f_{O_2}$) of the solar nebula environment from which meteoritic components formed (Fig. 1). E.g., Ti³⁺/Ti⁴⁺ has been measured in CAIs, suggesting they formed under reducing, variable conditions as low as IW-8 [1-3]. Studies of Fe in ferromagnesian chondrules suggest they formed between IW-4 to IW-0.5 [4, 5].

The relationship between ferromagnesian chondrules and CAIs remains poorly understood. Al-rich chondrules may represent an important link between these components [6].

About Al-chondrules

- No single formation process can explain the variety of compositions observed in these objects [6]
- ~15% contain relict CAIs [9]
- O-isotope studies of Al-chondrules in OC and CR chondrites are conflicting:
  - Can $^{18}$O enrichment trend be produced by simple mixtures of chondrules and CAIs [11]? Or not [10]?

The V oxybarometer [7, 8, 12] may be particularly well-suited for Al-chondrules, as the V²⁺/V³⁺ buffer probes the fugacity region between Ti³⁺/Ti⁴⁺ and Fe⁰/Fe²⁺. The motivation for this research is to use oxidation state as a tracer for variations in the solar nebula environment, and to link such variations to the primitive components in chondrites.

Samples and Spectra

Pre-edge peak intensities and centroid energies of V-XANES spectra may be used to determine the valence in spinel and glass samples. Data were analyzed using the methods of [7, 8, 15]. Ti-XANES was measured in additional minerals for comparison.

K-edge XANES @ Beamline 10.3.2 ALS, Lawrence Berkeley National Lab

- Al-chondrules in Chainpur 1251-14, 1251-3 (LL3.4; Fig. 2)
  - V-XANES: Spinel in both chondrules, and glass in Chainpur 1251-3 (Figs. 3, 4).
  - Ti-XANES: Pyroxene and glass in Chainpur 1251-3
  - Previously studied for petrography, $^{26}$Al-$^{26}$Mg systematics, and O-isotopes [6, 13, 14]
- CAI in Renazzo NHMW-N1126 (CR2)
  - V-XANES: Spinel; signal/noise too low to resolve pre-edge region (Fig. 3)
  - Ti-XANES: Spinel

Pre-edge peak intensities and centroid energies of V-XANES spectra for Chainpur 1251-3 and 1251-14. Solid lines show the pre-edge peaks, and the dotted lines show the spline fit of the edge-jump. The edge-jump spline fit was subtracted from the region to quantify the pre-edge peak intensity. b. Pre-edge peaks were fitted with a single Lorentzian function.

V XANES spectra

Pre-edge peak intensities of Chainpur 1251-3-1; Intensity = 25.9

Pre-edge peak intensities of Chainpur 1251-3-1; Intensity = 25.9

Fig. 2: BSE images (left) and EDX maps (right) of Al-chondrules Chainpur 1251-14-1 (top), and Chainpur1251-3-1 (bottom). Mg, Ca, and Al are shown in red, green, and blue.

V XANES spectra

V₁ = 2.5 for Chainpur 1251-14
V₂ = 2.4 for Chainpur 1251-3

EXAFS analysis of the extended spectra suggests that the V is octahedrally coordinated.

Implications for Oxygen Fugacity

Reference:

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Fig. 1: Multivalence elements and fugacity, from [1].

Fig. 2: BSE images (left) and EDX maps (right) of Al-chondrules Chainpur 1251-14-1 (top), and Chainpur1251-3-1 (bottom). Mg, Ca, and Al are shown in red, green, and blue.

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Fig. 3: (Above) V XANES spectra for Chainpur 1251-3 (red line) and 1251-14 (blue dashed line) spinel. Inset: The signal/noise ratio of the glass data was too low to resolve pre-edge peak information for Chainpur 1251-3 glass (green) and Renazzo spinel (blue).

Fig. 4: (Left) a. Pre-edge region of the V XANES spectra for Chainpur 1251-3 and 1251-14. Solid lines show the pre-edge peaks, and the dotted lines show the spline fit of the edge-jump. The edge-jump spline was subtracted from the region to quantify the pre-edge peak intensity. b. Pre-edge peaks were fitted with a single Lorentzian function.

Fig. 5: Glass V peak intensity vs. log($f_{O_2}$) at 1400 °C from [7], compared to Chainpur Al-chondrules

V oxybarometer of Sutton et al. [7]

- Pre-edge peak intensity has linear correlation from -12 < log($f_{O_2}$) < -9
- Intensity of V²⁺ multiplet peak assumed to be zero due to near-perfect octahedral symmetry [7]
- At log($f_{O_2}$) < -12, amplitude of pre-edge peak goes to zero, V oxybarometer becomes poorly constrained (Fig. 5)

Using this oxybarometer, we can constrain the maximum Al-chondrule fugacity to log($f_{O_2}$) < -12 (approx. < IW-2).

Relevance to Solar System Formation

These results indicate that the Al-chondrules formed at lower fugacity than most ferromagnesian chondrules, potentially closer to the reducing conditions of CAIs [8]. This is supported by V XANES analyses of spinel and clinopyroxene (cpx) in Allende CAIs [2, 15], where they found the V* to range from ~2.3-2.7.

The Ti-XANES spectra of the Chainpur 1251-3 Al-chondrule also support formation in an environment similar to CAIs. While the glass spectrum is dominated by Ti⁴⁺, the cpx has a significant Ti³⁺ contribution (feature near 4969 eV), comparable to cpx measured in an Allende CAI [15] (Fig. 6).

Future efforts to extend the V oxybarometer to low $f_{O_2}$

- Developing L-edge oxybarometer not limited by the zero-intensity V²⁺ K-edge multiplet peak
- Creating low $f_{O_2}$ standards [18]
- Developing DFT models to yield physical insight into how valence affects the spectral properties of minerals

Fig. 6. Ti-XANES

Fig. 7. FIB section of spinel in Chainpur1251-14, prepared for L-edge XANES and development of V oxybarometer for low $f_{O_2}$ samples.