

IN SITU DETERMINATION OF CHROMIUM OXIDATION STATE IN OLIVINE FROM CHONDRULES. S. R. Sutton¹, S. Bajt¹, and R. Jones²; ¹The University of Chicago, Chicago, IL 60637; ²University of New Mexico, Albuquerque, NM 87131

We report the results of our initial measurements of chromium oxidation state in olivine from chondrules using the microXANES technique. The synchrotron x-ray fluorescence microprobe on beamline X26A at the National Synchrotron Light Source (NSLS) was used. Cr XANES measurements were made on olivine from 4 chondrules: ALH77307 (CO3) type I and II and Semarkona (LL3.0) type I and II. The main conclusions are (1) both Cr²⁺ and Cr³⁺ are present in all chondrules measured and (2) Semarkona olivine contains more reduced Cr than ALH77307 olivine, consistent with the lower Fa composition of the former. These results are significant because, based on the fact that the transition between Cr²⁺ and Cr³⁺ occurs over a narrow range of fO₂, the microXANES approach may lead to a highly sensitive method for determining the redox conditions of formation for individual chondrules.

Introduction: Metal abundance and ferrous iron content provide evidence for the variation in oxidation states between different chondrules [1]. On these bases, type II chondrules appear to have formed under more oxidizing conditions than types I and III [2]. We have begun an x-ray absorption near edge structure (XANES) study of olivine from chondrules of different classification types and different meteorites. Our goal is to use in-situ microXANES to reveal the details of these variations in redox conditions.

MicroXANES is an attractive technique for this purpose for several reasons, in particular, (1) microXANES is a non-destructive, in-situ method applicable to conventional thin sections and is, therefore, well-suited for consortia type studies (including SEM, EMP, petrography, etc.) on individual chondrules and particular grains within them, (2) XANES determination of oxidation state is, in principle, applicable to all elements in the periodic table so it is conceivable to obtain redox information on an entire suite of elements in a particular mineral grain.

We report here the results of our initial measurements of chromium XANES in olivine. Chromium in olivine has been the focus of our initial efforts for several reasons, primarily because the results of previous microXANES work [3-5] suggest that the transition between Cr²⁺ and Cr³⁺ in olivine occurs close to the redox conditions under which chondrules are thought of have formed [6]. The Cr²⁺/Cr³⁺ ratio is, therefore, expected to be a sensitive indicator of redox variations among chondrule and meteorite types.

Chondrules: Cr XANES measurements were made on olivine from 4 chondrules: ALH77307 (CO3) type I and II and Semarkona (LL3.0) type I and II. The chondrules from ALH77307 are Fa5 (type I) and Fa29 (type II), and those from Semarkona are Fa1 (type I) and Fa13 (type II). Both type I chondrules contain small olivine phenocrysts (up to 100 microns), and low-Ca pyroxene on the rim. Fe, Ni metal blebs are more abundant in the Semarkona chondrule than ALH77307. Both type II chondrules contain large olivine phenocrysts and glassy mesostases.

Methodology: The synchrotron x-ray fluorescence microprobe on beamline X26A at the National Synchrotron Light Source (NSLS) was used in its normal configuration [7] including a Si(111) channel-cut monochromator. The monochromator had an energy bandwidth of 10⁻⁴ ($\Delta E/E$). A 25 μ m pinhole (larger than typical for the microprobe) was used to define the x-ray beam. An ion chamber was located down stream of the slit assembly for incident beam intensity normalization. A new, multielement, energy dispersive x-ray detector system [8] was used which permits us to collect the entire fluorescence spectrum from each of the individual detector elements (as opposed to the conventional single channel analyzer based electronics of previous systems). The advantage of this detector in the present application is the ten-fold increase in collection solid angle with sufficiently high energy resolution to extract the Cr K fluorescence intensity. The system was manufactured by Canberra Industries and consists of the following: 13, 1 cm diameter Ge detector elements; 13 NIM spectroscopy amplifiers with programmable gains; 4 analog multiplexors with maximum of 8 inputs each; 4 ADCs with programmable offsets and gains; 2 MCAs with Ethernet communications ports and 2 ADC inputs each. The amplifiers have shaping times from 0.5-12 microseconds.

XANES spectra were obtained by recording the Cr K α intensity at 0.5 eV intervals over the range approximately -20 to +50 eV relative to the main absorption edge energy. All energies were referenced relative to that of a sharp, pre-edge peak in a synthetic sodium chromate (Cr⁶⁺; 9). Each energy position was counted for between 1 and 60 seconds (depending on the total Cr content) for a total XANES spectrum acquisition time of typically 1 hr. Under these conditions, the minimum Cr concentration for which a useable K XANES spectrum could be obtained was about 100 ppm.

We report here semi-quantitative results for Cr²⁺/Cr³⁺ ratios based on the intensities and energies of peaks in the derivatives of the XANES spectra [3]. Standardization was obtained by comparison with two synthetic olivines: a Cr²⁺ bearing olivine (GRR-1690; G. Rossman, Caltech) and a Cr³⁺ bearing olivine (Ito forsterite; J. Ito, Univ. of Chicago). Calibration was obtained by computationally combining, in varying

proportions, the derivative XANES spectra for the two standards and then visually comparing the chondrule derivative spectra with these "theoretical standards" to determine a best match.

Results: Figure 1 shows the derivative Cr XANES spectra for the two standards. The Cr^{2+} spectrum is characterized by two dominant peaks, one at +2 eV and another at +8 eV. The Cr^{3+} spectrum also contains these peaks but shifted to 4.5 and 11 eV, respectively. This energy shift is due to the increase in valence electron level energies. A sample with both Cr^{2+} and Cr^{3+} will yield a spectrum containing all 4 peaks with intensities dependent on the oxidation state ratio. Figure 2 shows the measurements for olivine from ALH77307 and Semarkona type II chondrules.

Both Cr^{2+} and Cr^{3+} are present in all of the chondrule spectra. Comparison with the theoretical standards suggests a $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio of about 0.3 (i.e., mostly trivalent) for the carbonaceous chondrite ALH77307. Chromium in Semarkona type II is much more reduced with an estimated $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio of about 0.9 (i.e., mostly divalent). This difference is consistent with the fact that Semarkona olivine has a lower Fa composition. The data for Semarkona type I are somewhat problematic in that the XANES spectra are inconsistent with any conceivable olivine spectrum. Specifically, the Semarkona type I spectra possess a prominent derivative peak at about +15 eV. This peak has been observed by us only in XANES spectra obtained from lunar pigeonite [3] and was interpreted to be due to Cr^{3+} rich inclusions (e.g., chromite). Thus, we conclude that the Semarkona type I measurements were obtained on multiphase (i.e., olivine plus other phase(s)) regions in the chondrule.

The present data do not allow us to make any conclusive statements about the differences between various chondrule types. The small variations between type I and type II in ALH77307 were comparable to the observed variations within individual olivine grains. Additional work is needed to determine whether the intragrain variations are due to zoning and/or inclusions. For future work, we will concentrate on incorporating Kirkpatrick-Baez microfocusing mirrors in the apparatus to increase the x-ray intensity by a factor of 1000 into a 10 μm spot.

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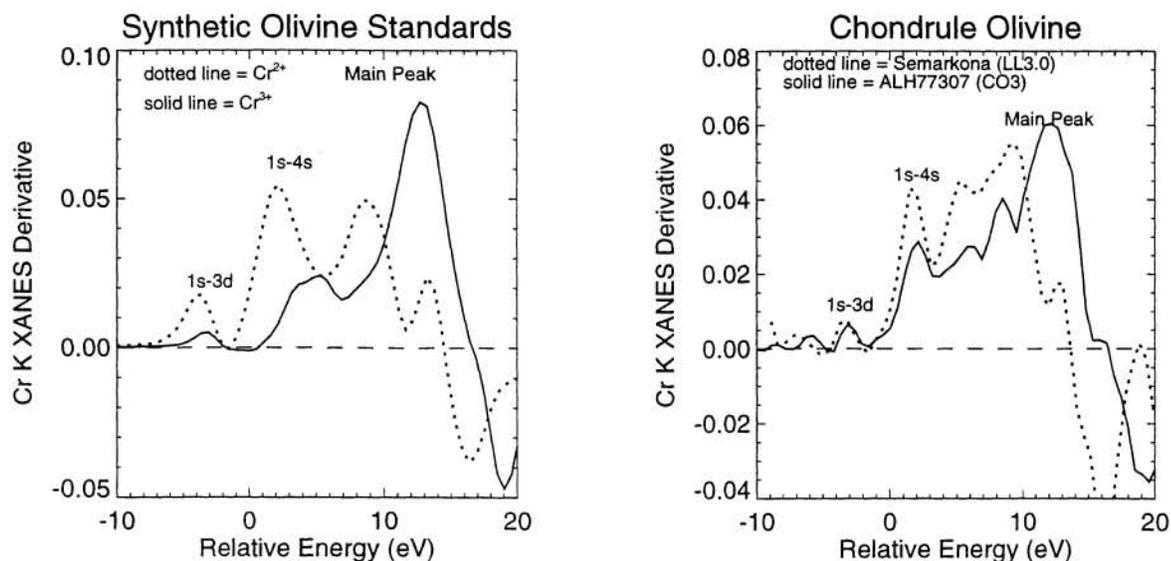


Figure 1 (left): Derivative Cr XANES spectra for the two standards: a Cr^{2+} bearing olivine (GRR-1690; G. Rossman, Caltech) and a Cr^{3+} bearing olivine (Ito forsterite; J. Ito, Univ. of Chicago). The energy shift of the peaks is due to the increase in valence electron level energies with increasing oxidation state.

Figure 2 (right): Derivative Cr XANES spectra for olivine from type II chondrules from Semarkona and a carbonaceous chondrite, ALH77307. Chromium is more oxidized in the carbonaceous chondrite olivine but both contain divalent and trivalent Cr.