

X-RAY MICROPROBE DETERMINATION OF CHROMIUM OXIDATION STATE IN OLIVINE FROM LUNAR BASALT AND KIMBERLITIC DIAMONDS S. R. Sutton, S. Bajt, M. L. Rivers, and J. V. Smith; Department of the Geophysical Sciences and Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637;

The synchrotron x-ray microprobe is being used to obtain oxidation state information on planetary materials with high spatial resolution. We report initial results on chromium in olivine from various sources including laboratory experiments, lunar basalt and kimberlitic diamonds. The lunar olivine was dominated by Cr^{2+} whereas the diamond inclusions had $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratios up to about 0.3. The simplest interpretation is that the terrestrial olivine crystallized in a more oxidizing environment than the lunar olivine.

Introduction: The oxidation states of minor and trace elements in minerals provide important clues on the physio-chemical history of the planets. Petrogenetic models generally assume oxygen fugacities based on indirect evidence. Since many of these assumptions involve low oxidation states that can stabilize reduced species, a technique that can directly measure valences could provide valuable constraints. The x-ray absorption near edge structure (XANES) technique used with the synchrotron x-ray microprobe, in principle, allows oxidation state determinations on individual co-existing phases in conventional rock thin sections. We report initial results on chromium in olivine from various sources including laboratory experiments, lunar basalt and kimberlitic diamonds.

Samples and Standards: Various reference materials were analyzed to establish the systematics of the Cr K XANES as a function of oxidation state. These materials were principally silicates but also included chromium metal (Cr^0) and potassium chromate (K_2CrO_4 ; Cr^{6+}). A suite of alkali borosilicate glasses (Savannah River Laboratory glass frit 131) was synthesized under various controlled oxygen fugacities by H. Schreiber (Virginia Military Institute). The oxidation states of Cr in these glasses were determined previously by conventional chemical procedures and optical spectrophotometry [1]. Three chromium-doped, synthetic forsterite standards (kindly supplied by G. Rossman, Caltech) contained either Cr^{2+} (GRR 1690), Cr^{3+} (Ito Forsterite), or Cr^{4+} (GRR 1587).

Lunar olivine grains from mare basalt 15555 were analyzed. The analyzed grains (5 olivines and 4 pyroxenes) were part of conventional thin sections mounted on pure silica slides. The olivine showed normal zoning with higher Mg in the cores than the rims. Fo numbers ($100 \cdot \text{Mg}/(\text{Mg}+\text{Fe})$) of the XANES-analyzed regions ranged from Fo 56 to Fo 68 (electron microprobe analyses by J. Delaney, Rutgers U.).

The diamond inclusions (100-300 μm) derived from three kimberlite regions - Premier and Koffiefontein (South Africa; kindly supplied by J. Harris, U. of Glasgow) and Kalimantan (Asia; kindly supplied by H. Meyer, Purdue U.). The Kalimantan olivine was an exposed inclusion and was analyzed while still embedded. The South African olivines were extracted from the diamonds and mounted individually for analysis. Each inclusion was analyzed with the electron microprobe to determine Cr content (200-800 ppm) and verify mineralogical identification. Fo numbers ranged from Fo 93 to Fo 97 (electron microprobe analyses by I. Steele, Univ. of Chicago, and H. Meyer).

Analytical Techniques: The synchrotron x-ray fluorescence microprobe on beamline X26 at the National Synchrotron Light Source (Brookhaven National Laboratory, NY) was used in its normal configuration [see e.g., 2-4] with the addition of a silicon (111) channel-cut monochromator on the incident radiation. A relatively large beam size of about 100-200 μm was used because of the trace level Cr contents of the olivine. XANES spectra were obtained by scanning the incident beam energy from just below to just above the Cr K absorption edge and recording the Cr K_α count rate at each incident energy. The detector was a Si(Li) energy dispersive instrument with an area of 30 mm^2 mounted at 90° to the incident beam (i.e., incident and takeoff angles = 45°). Cr K_α count rates were optimized by adjusting the distance between

the sample and the detector. The geometry of the apparatus limits the minimum sample-to-detector distance (i.e., largest collection angle) to about 1 cm corresponding to a solid angle of about 0.25 sr. A total energy scan of about 100 eV was typically made in 300 steps (0.3 eV/step) with each step counted for between 1 and 30 live seconds depending on the Cr content of the sample. Energies were defined relative to the energy of the prominent pre-edge peak in the XANES spectrum of chromate (Cr^{6+}). The Cr K XANES spectra typically contained three peaks: an isolated pre-edge peak, a bump on the absorption edge rise, and the edge crest, analogous to features observed in Fe XANES by Waychunas et al. [5]. Derivatives of the XANES spectra were used to determine the relative energies of these spectral features. XANES spectra of the reference materials (i.e., materials with Cr in known oxidation state) were used to determine the energy dependence of the edge position and resonance features and this information was used to infer Cr oxidation states in the lunar and kimberlitic olivine.

Results: Spectral features in the reference materials showed a good correlation with known oxidation state. Comparison of these data with those for the olivine indicate that Cr in the lunar olivine is predominantly divalent whereas the Cr in the diamond inclusions contains both Cr^{2+} and Cr^{3+} with the latter dominant [6]. For the diamond inclusions, the chromium in the Kalimantan inclusion was predominantly trivalent whereas a larger divalent component was present in the Premier and Koffiefontein olivine. Our first attempt to quantify the divalent content in these inclusions used a series of computational mixtures of XANES derivatives of the divalent and trivalent reference forsterites. The South African diamond inclusion spectra most closely match the theoretical spectrum with Cr^{3+} and Cr^{2+} in 2:1 proportions.

Discussion: These initial chromium oxidation state determinations on olivine from lunar basalt and terrestrial kimberlitic diamonds indicate that divalent chromium is a ubiquitous component of olivine crystallized under reducing conditions. The simplest explanation of the Cr speciation in 15555 is that the mare magma source originally contained Cr^{2+} and Cr^{3+} and that these species were preferentially incorporated into olivine and pyroxene, respectively. This conclusion implies that either the olivine D values for Cr^{2+} under lunar conditions are greater than suggested by laboratory partitioning studies [e.g., 7,8] or, more likely, the melt was dominated by divalent chromium at the time of olivine crystallization (caused, for example, by spinel crystallization). The diamond inclusions studied had $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratios up to 0.3. The obvious interpretation is that the terrestrial olivine crystallized in a more oxidizing environment than the lunar olivine [8]. However, additional research needs to be done to verify this conclusion.

MicroXANES has great potential for tackling planetary petrogenesis but more work is needed to refine the quantification of mixed valences. Particularly important are XANES analyses on synthetic olivine crystallized under controlled redox conditions. The present results suffer from several complications. First, the olivines have greatly different Fe contents and the effect on XANES spectra of Fe content needs to be studied in detail. Second, some and perhaps all of the olivines studied contain Cr-bearing micro-inclusions, notably, chromite. Smaller, more intense x-ray beams are needed to avoid these inclusions. And, third, the synchrotron beam is a linearly polarized x-ray source and XANES spectra depend somewhat on crystal orientation [9]. Polarization experiments will be pursued to study this effect.

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