

CHROMIUM VALENCY IN INDIVIDUAL LUNAR OLIVINE GRAINS USING X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES) MICROANALYSIS S. R. Sutton^{1,2}, K. W. Jones², B. Gordon², M. L. Rivers^{1,2}, and J. V. Smith¹; ¹Department of the Geophysical Sciences and Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637 ²Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973.

Introduction: The oxidation states of minor and trace elements in lunar minerals provide important clues on the physio-chemical history of the Moon. Chromium in olivine has been particularly intriguing since lunar olivines are enriched in Cr compared with terrestrial olivines [1,2]. This enhanced partitioning could be due to crystallization conditions, crystal-chemical factors and/or reduction of Cr. Steele and Smith [1] suggested that minor element contents were most readily explained if both Cr^{II} and Cr^{III} are present, the latter residing in a couple with Al. Cr^{II} -containing orthosilicates have been synthesized [3]. However, direct evidence that Cr exists in a reduced chemical form in lunar olivine has been difficult to obtain. Optical absorption evidence has been inconclusive because of ambiguities in band assignments and potential overlaps [4].

X-ray Absorption Near Edge Structure (XANES) analysis is a useful technique for chemical speciation studies and is applied extensively in areas of materials science such as thin film studies (e.g., [5]). We report here our first attempts to apply this technique in a microprobe mode in order to obtain XANES spectra on individual co-existing phases in conventional rock thin sections. Our initial results on olivine in microgabbro 15555 support the hypothesis that Cr in lunar olivine exists both as Cr^{II} and Cr^{III} .

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., [6]) with the addition of a Si(220) channel-cut monochromator on the incident radiation. A beam size of 200 micrometers was used in the present experiments. Each XANES measurement consisted of scanning the incident beam energy from just below to just above the Cr K absorption edge and recording the Cr K alpha count rate at each incident energy. In general, such scans show an abrupt increase in fluorescence at the absorption edge energy but, in detail, the precise edge energy depends on the oxidation state and bonding, and structure in the above edge absorption profile reflects the positions of neighboring atoms. Typically, a total scan of 100 eV was made in 500 steps (0.2eV/step) and each energy was counted for 5 seconds for a total scan time of about 1 hour. The resulting spectra were then compared with those of reference materials to infer valence state as discussed below.

Results: XANES spectra for Cr^0 (metal), Cr^{II} (CrCl_2), Cr^{III} (Cr in synthetic forsterite) and Cr^{VI} (K_2CrO_4) in various reference materials are shown in figure 1. The energy reproducibility of features in these spectra was about 1 eV. The general trend is for the energy of the absorption edge to increase with increasing oxidation state. Thus, the K edge (defined here as the energy at which the Cr Ka normalized count rate is 0.5) for Cr^{VI} is 20 eV higher than that for Cr^0 . Cr^{VI} is a particularly important species as its XANES spectrum contains a sharp pre-edge feature at 5993 eV (+ 4 eV relative to the Cr^0 edge of 5989 eV) which can be used for calibration and resolution purposes.

Figure 2 shows XANES spectra for 15555 pyroxene, 15555 olivine and a synthetic forsterite containing 1.25% Cr_2O_3 . Since this synthetic olivine was grown in air, its XANES spectrum is an excellent benchmark for Cr^{III} in mafic silicates. As can be seen, the edge for the 15555 pyroxene is virtually identical to that of the synthetic olivine consistent with the view that Cr in pyroxene exists totally as Cr^{III} . Three XANES spectra on 2 separate olivine grains gave edges of + 10, + 10 and + 12 eV. The mean olivine edge of + 11 eV is intermediate to those of Cr^{II} in CrCl_2 and Cr^{III} in the synthetic olivine (+ 5 and + 15 eV, respectively). These observations suggest that Cr in olivine exists as both Cr^{II} and

Cr^{III} . Application of the lever rule on the edge energies suggests the $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$ ratio is close to unity but Cr^{III} may be preferred. Additional high resolution work will be needed to quantify this ratio.

These initial results are promising but several potential complications exist which need further attention. First, inclusions are always a problem when working at low concentrations and at the present time we cannot rule out the possibility that some Cr is in inclusions such as spinel. The areas analyzed appeared optically clear in transmitted light but only 1% inclusions by mass could account for the observed Cr abundance. Second, the tails of the x-ray beam may excite Cr in neighboring pyroxene grains. The low Cr count rates obtained from small epoxy regions in the thin sections suggest such effects are minor. Third, absorption edge energies vary slightly with matrix - lower atomic number materials tending to have lower edges. Variations among silicates should be small but we currently lack a good Cr^{II} standard in a silicate matrix. The validity of using Cr^{II} in CrCl_2 as an endmember needs to be tested.

Nonetheless, these results demonstrate the potential of an exciting new technique for tackling lunar and meteoritic petrogenesis. It may, for example, eventually be possible to determine $f\text{O}_2$ from $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$ ratios after studies of crystals grown under controlled conditions. In principle, such determinations should be possible on zones of individual crystals. The chemical states of other elements such as Ti, V, Fe, Mn, and Ni should also be measurable using micro-XANES.

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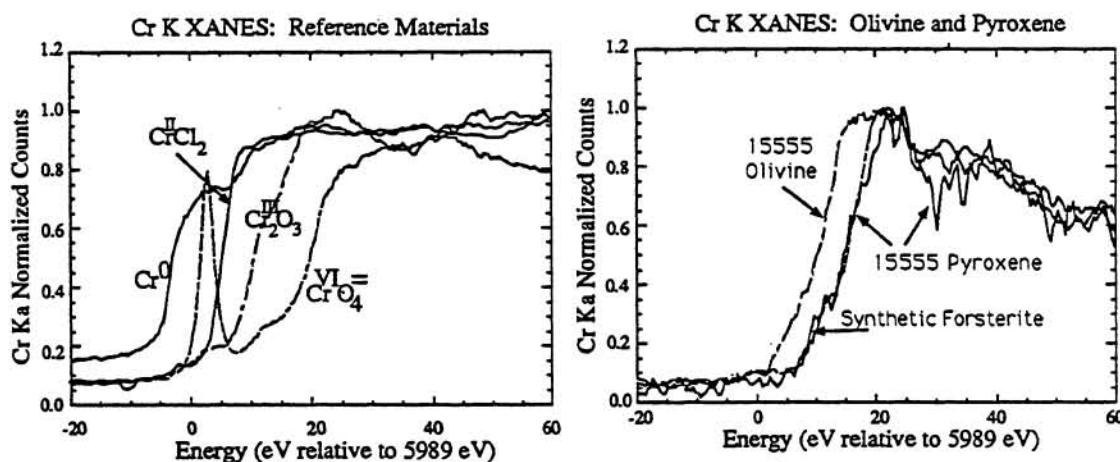


Figure 1: Cr K XANES spectra for reference materials: (a) Cr^0 (Cr metal), (b) Cr^{II} (CrCl_2 ; G. Frankel, A. Davenport and H. Isaacs, private communication), (c) Cr^{III} (Cr_2O_3), (d) Cr^{VI} (K_2CrO_4).

Figure 2: Cr K XANES spectra for 15555 olivine, 15555 pyroxene and synthetic forsterite. The lower absorption edge of the lunar olivine suggests the presence of Cr^{II} .