

### XANES AND FERROUS-FERRIC RATIOS IN THE NAKHLITE SECONDARY PHASES.

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**Introduction:** X-ray Absorption Near Edge Structure (XANES) observes spectra created by the energies of the 3d orbitals in transition metals like iron [1]. Our aim is to report observations and analyses of the Fe K XANES in standards and nakhlite samples in order to gain a calibration between the XANES and the ferrous-ferric ratio of the measured material. This will allow us to constrain the oxidation state, and how it changes, within the nakhlite alteration minerals such as phyllosilicate [2].

**Method and Samples:** We have used the I18 Beamline for Microfocus Spectroscopy at the UK *Diamond* Synchrotron. This enabled a spatial resolution of 2 x 2.5  $\mu\text{m}$ , measuring energy spectra ranging from 6900-7500 eV with a resolution of 0.25 eV, but concentrating on the XANES region from 7092-7122 eV with an energy resolution of 0.1 eV. The nakhlite samples have also been analyzed with Scanning Electron Microscopy at 15 kV. The nakhlite samples are NWA817, Y000593, Y000749, Nakhla, NWA5790, Governador Valadares, Lafayette, NWA998, and Miller-Range 03346, along with standards of goethite, haematite, nontronite, magnetite, augite, pyrrhotite, San Carlos olivine, and Barwell olivine.

The pre absorption edge centroid position was calculated by measuring the average position of the normalized intensity summed over the XANES pre-peak region subtracted from a curve-fitting baseline. Thus, the calculated position is greatly influenced by the structure of the L<sub>2</sub> and L<sub>3</sub> edges observed as pre-peak features, with the L<sub>3</sub> edge typically consisting of two significant peaks which vary in intensity between the left peak (~7112.2 eV) and the right peak (~7113.7 eV) attributed to the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> respectively [3].

**Results and Conclusions:** Barwell L6 olivine (Fe<sup>3+</sup>/ $\Sigma$ Fe = 0) has K-edge positions and calculated pre-edge centroid positions of 7118.8 eV and 7112.3 eV. With an increased oxidation state, as seen in hematite and goethite (Fe<sup>3+</sup>/ $\Sigma$ Fe = 1), the edge positions and pre-edge centroid were 7122.2 eV and 7114.7 eV respectively. There is a clear shift seen in these and other standards, in the pre-edge features and edges associated with increasing ferrous-ferric ratios.

XANES measurements across veins, observed in the nakhlites, showed increases in energy for the K-edge and centroid position towards the central gel feature of the vein. Across one particular Lafayette vein, ten points each 2  $\mu\text{m}$  apart were analyzed, the K-edge and centroid increased from 7118.6 eV and 7112.1 eV, in the surrounding olivine, to 7121.0 eV and 7114.8 eV in the central gel of the vein. Based on these observations, the central gel feature has K-edge and centroid positions between those of the magnetite and haematite standards, indicating an approximate Fe<sup>3+</sup>/ $\Sigma$ Fe ratio between 0.67 and 1.0. Observing the XANES spectra throughout these measurements, there is also a distinct change in the pre-edge structure in the outer-vein material from that of the surrounding olivine. This outermost vein material is phyllosilicate, measuring a ratio Fe<sup>3+</sup>/ $\Sigma$ Fe  $\approx$  0.4 and becomes more ferric with each measurement towards the central gel of the vein. Other vein minerals found in Lafayette include siderite, where XANES suggests a Fe<sup>3+</sup>/ $\Sigma$ Fe ratio between 0 and 0.2.

By observing the approximate normalized intensities of the two pre-edge peaks, a left/right peak intensity ratio reveals a trend from a high left peak changing to an increasing right peak associated with an increased Fe<sup>3+</sup>/ $\Sigma$ Fe ratio from 0 to 1, as measured in the standards. Such a trend is also observed in the veining features from the surrounding olivine into the vein and to the central gel, again indicating an increase in oxidation state towards the centre of the vein.

**References:** [1] Bunker G. (2010) In *Introduction to XAFS*. p. 137. [2] Changela H. G. and Bridges J. C. (2011) *Meteoritics & Planetary Sci.*, 45, 1847-1867. [3] Cressey G. *et al.* (1993) *Phys. Chem. Minerals*, 20, 111-119. [4] Marion G. M. *et al.* (2003) *Geochimica et Cosmochimica Acta*, 67, 4251-4266.