

OXIDATION OF THE NAKHLITE MARTIAN METEORITES DURING AN IMPACT

HYDROTHERMAL EVENT. L. J. Hicks¹, J. C. Bridges¹, S. J. Gurman², and H. G. Changela¹, ¹Space Research Centre, University of Leicester, Leicester, LE1 7RH, United Kingdom, ²Dept. of Physics & Astronomy, University of Leicester, Leicester, LE1 7RH, United Kingdom. j.bridges@le.ac.uk

Introduction: Impact events can create a higher permeability in the shocked rocks of the near-surface zone, along with increased temperature, allowing the development of circulating fluids in a post-impact hydrothermal system [1]. Over time, the circulating fluids deposit minerals on the walls of the veins throughout the permeable areas of the rocks. Such deposition has been found within the nakhlite martian meteorites.

Previous studies have found that the variations in petrography and mineralogy, between the different nakhlites, represent variations in burial depth within a thick lava flow or shallow intrusion [2].

Hydrothermal fluids from subsurface ice suffused these rocks, at temperatures up to 170°C, possibly ≤620 Ma [3,4]. Studies of the vein material, deposited by the circulating fluids, have revealed the presence of siderite, smectite-serpentine, an amorphous silicate gel assemblage, as well as terminal deposits of evaporite salts, with the amorphous silicate gel being the most widespread of these deposits [5].

Our aim is to further constrain the nature of the fluid, and in particular its oxidation state, via observations and analyses of the Fe k, X-ray Absorption Near Edge Structure (XANES).

Method and Samples : Observations and analysis of the nakhlite sample sections were made using the I18 Beamline for Microfocus Spectroscopy at the UK Diamond Synchrotron. This enabled a 2 x 2.5 μm spatial resolution for the Fe k XANES and also Extended X-ray Absorption Fine Structure (EXAFS) within energy spectra ranging from 6900 eV to 7500 eV. Open source graphical, cross-platform programs have been used to process the X-ray Absorption Spectroscopy (XAS) and EXAFS. The measurements were processed through *Athena*, which uses the data reduction/fitting engine IFEFFIT. This was then followed by analysis in *PySpline1.2*.

Nine polished nakhlite samples have been analysed for Fe k XANES: NWA817, Y000593, Y000749, Nakhla, NWA5790, Governador Valadares (GV), Lafayette, NWA998, and Miller-Range.

The nakhlite samples have also been analysed via Scanning Electron Microscopy (SEM) at 15 kV, using a Phillips XL30 ESEM at the University of Leicester's Advanced Microscopy Centre.

Results: Spectroscopy from several regions and transects have been obtained, typically including at least one olivine core and one pyroxene core measurement from each nakhlite sample, along with other

observed features, in particular veining and possible occurrences of alteration and zoning within olivine and pyroxene grains. Appropriate mineral standards have also been measured for Fe k XANES and EXAFS.

By fitting a baseline to the overall pre-edge region within the XANES spectra, the intensity-weighted energies (or centroids) have been calculated. The energy value along the spectra for the centroid and normalised edge position are the key to defining the Fe k absorption edge and the pre-absorption edge energy positions. Variations in the oxidation state, or the ferric-ferrous ($\text{Fe}^{3+}/\text{Fe}^{2+}$) ratio, are observed in the variations of these absorption edge and pre-absorption edge energy positions, where an increase in energy position is associated with an increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio [6].

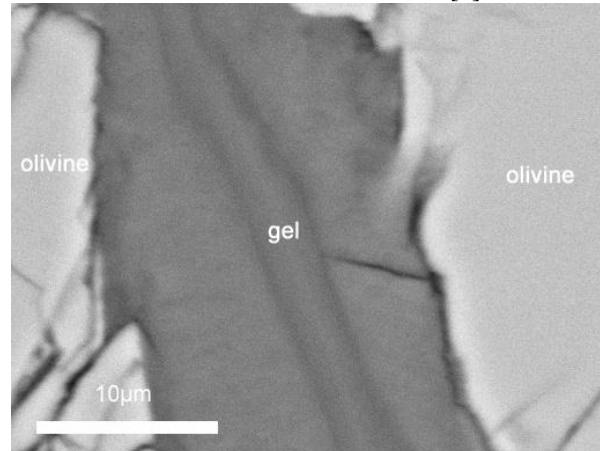


Fig. 1. Siderite-phyllsilicate-gel vein, found in the Lafayette sample, across which two transects of several points were measured for XAS.

Two transects of several points across a siderite-phyllsilicate-gel vein in the Lafayette sample (Fig. 1), were measured. Both transects reveal a well defined increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio into the central gel region of the vein, with the pre-edge centroid and normalised edge positions having energies of approximately 7113 eV and 7121 eV respectively, compared to the 7111.2 eV and 7118.5 eV values of the surrounding olivine.

The nature of the pre-edge peaks can be described as the combined fit of two pseudo-Voigt peaks, where both peaks vary dependent on the feature that is being studied. The transect across the phyllsilicate-smectite-gel vein showed a fall in the intensity of the left pre-edge peak to less than that of the right peak, away from olivine and in to the mid-vein gel (Fig. 2).

The central silicate gel of the vein has a $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio that closely resembles that of the magnetite standard that was also measured, including similar structure in the pre-edge peaks.

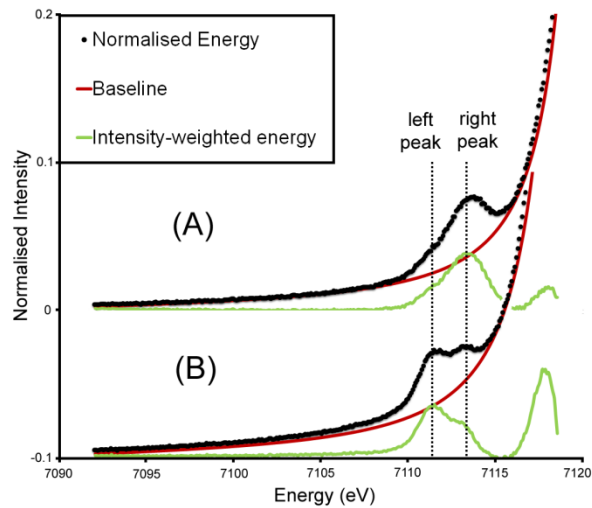


Fig. 2. Normalised Intensity of pre-edge peaks. (A) Analysis of the gel inner vein found in the Lafayette sample (Fig. 1) show a dominant right-peak compared to a barely visible left-peak. (B) The olivine surrounding the vein present pre-edge peak shapes similar to olivines found in all of the nakhlite samples, with a dominant left peak and smaller right-peak. Analysis of measurements taken as a transect from the the olivine (B) and into the vein (A) reveal the transition between the two as a gradual change in the pre-edge peak shape, with the left-peak falling and the right-peak rising.

A comparison of all the olivine measurements reveals some variation, especially noticeable in the EXAFS energy region (Fig. 3). All of the olivines, including the olivine standard, are typically observed to have pre-edge peaks with a stronger left peak compared to the right peak (Fig. 2B), with differences in the intensity between the samples. With average centroid and normalised edge positions of 7111.2 eV and 7118.3 eV respectively across all the olivines, there are some deviations in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio which will require further investigation. However, the pyroxenes present much more variation in the pre-edge peak structure between the samples, with some spectra revealing the pre-edge peaks to combine with equal intensities. The pyroxene measurements have average centroid and normalised edge positions of 7111.6 eV and 7119 eV.

Discussion: Early analyses of the measurements suggests that the secondary fluids flowing through the rocks were oxidizing relative to the surrounding material, as shown by an increase in oxidation state into the veining of the Lafayette sample. The low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the olivines is consistent with the olivines observed in chassignite NWA2737 [7]. Under highly

oxidising conditions, the oxidation of the Fe^{2+} in the olivines into Fe^{3+} can result in precipitation of the Fe smectite nontronite [8]. Accurate distinction between nontronite and saponite requires knowledge of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Iron smectite-serpentine phyllosilicates have been characterised in the veining of nakhlite samples [5], thus a nontronite standard was measured. The production of serpentine-bearing phyllosilicates, associated with oxidation of iron in cooling rocks, may have been associated with the release of methane [9].

Synchrotron micro-XANES spectroscopy is a very useful tool in determining oxidation states of iron, as the pre-main-edge absorption features directly relate to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the material. However, it is important to be aware of uncertainties caused by low ferric contents, crystal orientation effects, and the presence of nanophase iron metal [7]. Further studies into the Fe k XANES features will continue for all samples, with investigations into background fitting and Gaussian functions to the pre-edge peaks, to assess the structure in greater detail.

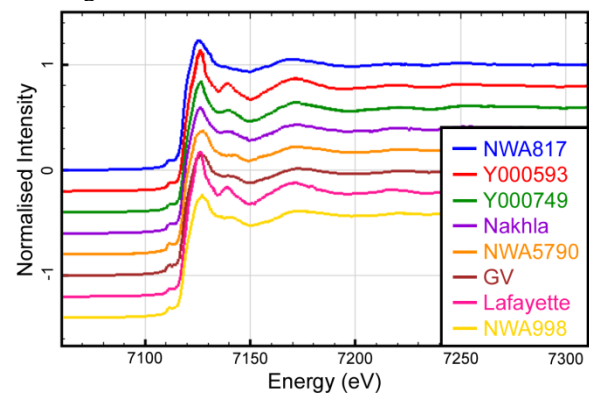


Fig. 3. XAS of selected olivine core measurements from each nakhlite sample. Offset for clarity, the spectra are stacked top-to-bottom in order of suggested increasing burial depth [2].

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