FERRIC IRON CONTENT OF NAKHLITE HYDROTHERMAL MINERALS. L. J. Hicks[1], J. C. Bridges[1], and S. J. Gurman[2], [1]Space Research Centre, Dept. of Physics & Astronomy, University of Leicester, LE1 7RH, UK, ljh29@le.ac.uk, [2]Dept. of Physics & Astronomy, University of Leicester, LE1 7RH, UK.

Introduction: Previous studies of the nakhlite Martian meteorites have observed veining material deposited by rapid cooling of subsurface hydrothermal brines at temperatures ≤100°C [1,2]. Studies of the veining material have revealed the presence of siderite, phyllosilicates (smectite-serpentine) prominent in the Lafayette nakhlite sample, along with a silicate gel found throughout most of the nakhlites [1].

Our aim is to compare varied techniques to measure and determine the ferric-ferrous ratio of the hydrothermal minerals in the nakhlites. Such analyses include X-ray Absorption Near Edge Structure (XANES), Extended X-ray Absorption Fine Structure (EXAFS), and the use of Electron Probe Microanalysis (EPMA) data. We show that the Fe-K absorption edge and pre-edge centroid positions can be related to the ferric-ferrous ratio of the nakhlite minerals. This will allow us to further constrain the identity of the phyllosilicates, oxidation state, and observe how it changes. The work will also provide complementary information about the secondary phases to that being obtained in our ongoing FIB-TEM analyses and fluid modelling of the nakhlites [2].
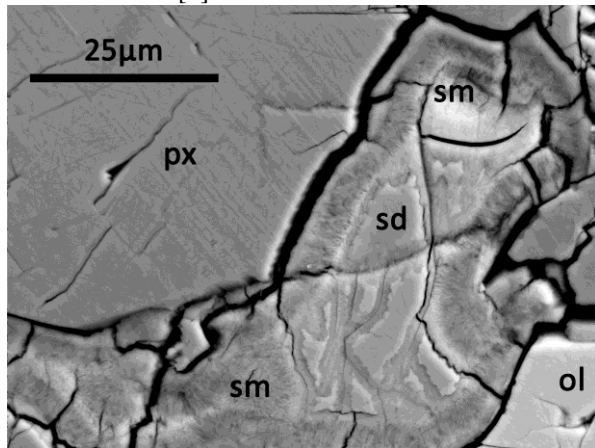

Figure 1. BSE image of secondary minerals including siderite (sd) and smectite (sm) surrounded by olivine (ol) and pyroxene (px) in the Lafayette nakhlite (BM 1958, 775).

Methods and Samples: Nakhlite sample sections and standards have been measured for Cr-K and Fe-K XANES and EXAFS using the I18 beamline for Microfocus Spectroscopy at the UK *Diamond* Synchrotron. High resolution XRF mapping of the nakhlite secondary mineral phase features, with spot size 2 x 2.5 μm observing elements of Z >20, make it possible to observe and locate the features accurately for XANES and EXAFS analyses. Spectra were measured over the XANES region from 7092 eV to 7145 eV with energy steps of 0.1 eV and the EXAFS region from 7145 eV up to ~7500 eV with varying energy steps of 0.2-0.4 eV. Once the data has been processed and normalized, the energy of the Fe-K XANES edge position is taken as the point where intensity is 0.5.

EPMA data were measured using a Cameca SX100 with an LTAP crystal spectrometer to observe mineral stoichiometry. Fe-L_α and Fe-L_β data have also been measured, at an accelerating voltage of 10 kV and beam current of 60 nA over the energy range 670-755 eV. This enables the 'flank method' of observing variations in peak shift and area correlated with ferric-ferrous ratios [3].

Fourteen standards of varying iron content have been measured and analysed for Fe-K XANES, along with nine polished nakhlite samples including NWA 5790, Miller Range 03346, NWA 817, Y-000593, Y-000749, Nakhla, Governador Valadares, Lafayette, and NWA 998.

The ferric-ferrous ($Fe^{3+}/\Sigma Fe$) ratios of the standards have been calculated from the mineral chemical composition and stoichiometry of the pyroxenes, olivines, hematite, magnetite and goethite [4,5].

Results: The dominantly ferrous olivines, including San Carlos, Barwell L6 and the Y-000749 nakhlite, are grouped in the lower energy edge positions 7118.4-7119.0 eV. In contrast, the ferric rich hematites and goethite have higher energy positions in the range 7121.1-7122.7 eV. Using this shift in edge position with increased ferric content, a linear fit has been applied (Fig. 2). This linear fit has been used as a calibration in order to estimate the ferric-ferrous content of the hydrothermal minerals in Lafayette.

Based on this fit, the estimated $Fe^{3+}/\Sigma Fe$ values (Table 1 and Fig. 2) show the central silicate gel of veins to have a ferric content of up to $Fe^{3+}/\Sigma Fe \approx 0.9$, compared to the phyllosilicates with $Fe^{3+}/\Sigma Fe$ values of 0.25-0.29. The siderite, as would be expected, has much less ferric iron, $Fe^{3+}/\Sigma Fe$ <0.1.

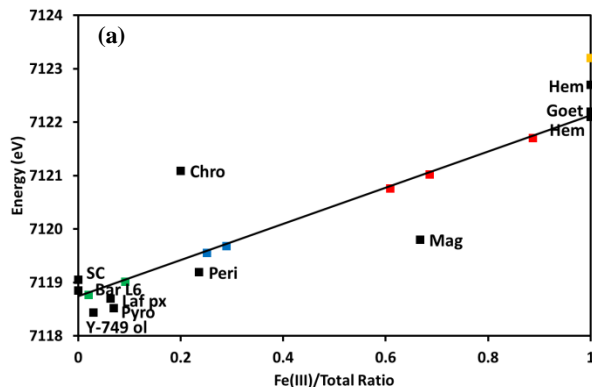*Figure 2.* Fe-K XANES edge positions correlated with $Fe^{3+}/\Sigma Fe$ (at%) ratios for standards. The 11 standards are San Carlos olivine (SC), Barwell L6 olivine (Bar L6), a nakhlite olivine (Y-749 ol), a nakhlite pyroxene (Laf px), pyroxenite (Pyro), chromite (Chro), peridotite (Peri), magnetite (Mag), hematite (Hem) and a goethite (Goet). The resulting linear calibration was used to determine the $Fe^{3+}/\Sigma Fe$ values for Lafayette siderite (green), phyllosilicates (blue), silicate gel (red), and a nontronite sample (yellow).

Table 1: Fe-K XANES measurements (eV) and $Fe^{3+}/\Sigma Fe$ ratio calculated from Fig. 2 calibration

Sample	XANES edge	$Fe^{3+}/\Sigma Fe$
Olivine	7116.9 – 7118.7	0.00
Pyroxene	7118.7 – 7120.0	≤0.37
Siderite	7119.0	0.09
	7118.8	0.02
Phyllosilicate	7119.7	0.29
	7119.6	0.25
Silicate gel	7120.8	0.61
	7121.0	0.69
	7121.7	0.89

Discussion: The Fe-K XANES spectra, from iron bearing minerals, provide a strong Fe-K edge suitable for determining an accurate (<0.05 eV error) energy position from the normalized data. We use the Fe-K edge positions of standards with known ferric-ferrous ratios, to calculate the ferric iron contents of minerals with unknown ferric content for which we have XANES data.

The $Fe^{3+}/\Sigma Fe$ values obtained for the Lafayette veining, show a definite trend of increased oxidation state from the surrounding ferrous olivines, through the siderites and phyllosilicates and into the mostly ferric central gel of the veins. A nontronite sample measured for Fe-K XANES, resulted in $Fe^{3+}/\Sigma Fe$ =1.0, which is consistent with studies of this mineral [5], and is high-

er than the ferric content for the phyllosilicate measured in this study. Another mineral saponite (smectite) has varying $Fe^{3+}/\Sigma Fe$ ratios of 0.11-0.85 [6]. With a ratio of $Fe^{3+}/\Sigma Fe$ ≈0.3, a saponite identity for the majority of the phyllosiliocates in the Lafayette olivine veins is consistent with the phyllosilicate measured here. The silicate gel has ratios of up to $Fe^{3+}/\Sigma Fe$ ≈0.9, and so clearly has the most oxidised, ferric composition of the hydrothermal silicates.

Conclusions: By using Fe-K XANES measurements we show a correlation between a shift in Fe K-edge position towards higher energies and an increased ferric content. This has proved to be an effective method for determining the oxidation state of iron within nakhlite cumulus and hydrothermal minerals. Our data suggest the that saponite is the main phyllosilicate in the olivine veins and that the amorphous gel found in the centre of veins is dominantly ferric.

References: [1] Changela H. G. and Bridges J. C. (2010) *Meteoritics & Planetary Sci., 45*, 1847-1867. [2] Bridges J.C. and Schwenzer S.P. (2012) *LPS XLIII* (subm.). [3] Hofer H. E. (2002) *Hyperfine Interations, 144/145,* 239-248. [4] Cawthorn H. G. and Collerson K. D. (1974) *American Mineralogist, 59,* 1203–1208. [5] Deer W. A., Howie R. A. and Zussman J., (1992) The Rock Forming Minerals (2nd Ed.) [6] Koyhama N., Shimoda S. and Sudo T., (1973) *Clays and Clay Minerals, 21*, 229-237.