

**MÖSSBAUER AND SYNCHROTRON MICROXANES ANALYSIS OF NWA2737.** M.C. McCanta<sup>1</sup>, M.D. Dyar<sup>2</sup>, A.H. Treiman<sup>1</sup>, C.M. Pieters<sup>3</sup>, T. Hiroi<sup>3</sup>, M.D. Lane<sup>4</sup>, and J.L. Bishop<sup>5</sup>. <sup>1</sup>Lunar & Planetary Institute, Houston, TX, <sup>2</sup>Dept. Astronomy, Mount Holyoke College, South Hadley, MA, <sup>3</sup>Dept. Geological Sciences, Brown University, Providence, RI, <sup>4</sup>Planetary Science Institute, Tucson, AZ, <sup>5</sup>SETI Institute / NASA-Ames Research Center, Mountain View, CA.

**Introduction:** NWA2737 is a chassignite (a class of igneous Martian meteorites) consisting of olivine, two pyroxenes, chromite, and minor accessory minerals, in order of decreasing abundance [1]. This assemblage is similar to Chassigny, but with the notable distinction that the olivines in NWA2737 have distinct brown and visually colorless regions. This coloration suggests that Fe<sup>3+</sup> may be compositionally important in this meteorite. The research presented here uses Mössbauer and synchrotron microXANES techniques to analyze the distribution of Fe<sup>3+</sup> in the whole rock and mineral phases in NWA2737 in order to understand the oxidation environment the magma was subjected to during and after crystallization. More detailed papers on the petrology, origin, and spectroscopy of NWA2737 are presented elsewhere in this volume [2,3].

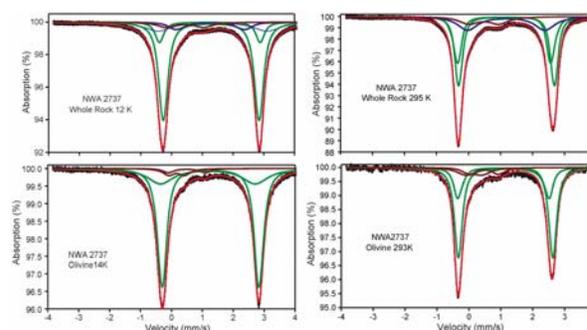
**Methods:** *Synchrotron MicroXANES Analysis.* Olivine Fe<sup>3+</sup> content was analyzed in thin section on the synchrotron microXANES (SmX) spectrometer at Brookhaven National Laboratory for Fe<sup>3+</sup>/ΣFe ratios using the calibration of [4] with the addition of aegirine as a Fe<sup>3+</sup> end member standard; the technique and apparatus are described in [5]. Analyses of both brown and visually colorless olivine regions were completed. The largest contribution to error in the analyses is the effect of crystallographic orientation as described in [6]; resultant %Fe<sup>3+</sup> errors are ±15% absolute for individual analyses.

**Mössbauer Analysis.** For Mössbauer analysis, approximately 10-20 mg of each sample were crushed to a fine powder with sugar under acetone before mounting in a sample holder confined by cellophane tape. Mössbauer spectra were acquired at 293K and 12K using a source of 30 mCi <sup>57</sup>Co in Rh on a WEB Research Co. model W100 spectrometer equipped with a Janus closed-cycle He refrigerator. Run times were 8-12 hours, and results were calibrated against α-Fe foil. Spectra were processed using the DIST\_3D program, an implementation of software described in [7]. The program uses quadrupole splitting distributions with Lorentzian lineshapes and an assumed average correlation between the isomer shift (IS) and quadrupole shift (QS) in each of two valence states. Widths, isomer shifts, and quadrupole splittings of the doublets were allowed to vary. Errors on IS and QS for well-resolved peaks are usually ±0.02 mm/s. Errors on

peak area depend on the extent of overlap with other peaks, but are generally ±3-5% absolute.

**Results:** *Synchrotron microXANES:* SmX data collected show olivine Fe<sup>3+</sup> content averaging 14%, within error of the Mössbauer analyses. The higher values may represent analyses that were contaminated by submicron oxides. Traverses across continuous regions of brown and visually colorless olivine show no variation in the Fe<sup>3+</sup> content. This suggests that the amount of Fe<sup>3+</sup> required for the brown coloration is at the ppm level, therefore undetectable with SmX.

**Mössbauer Spectroscopy:** Two different samples were analyzed using Mössbauer spectroscopy: the olivine separate and the whole rock. Each was run at 293 and 12K. All the spectra are quite similar except for the expected peak shifts at low temperature: both isomer shift and quadrupole splitting increase as temperature decreases.



**Figure 1.** Mössbauer spectra of NWA 2737 whole rock and olivine separates at room temperature and liquid helium temperature. Green doublets represent Fe<sup>2+</sup> in olivine, while purple represents Fe<sup>3+</sup>. Clinopyroxene peaks would lie at -0.36 and 2.64 mm/s and could not be resolved in either of these spectra. The red line represents the sum of all the component curves. Note the absence of peaks at high and low velocity, which might suggest a magnetically ordered phase (e.g., magnetite, pyrrhotite).

All of the spectra are dominated by two doublets associated with olivine, which occur near -0.40 and 2.75 mm/s (Figure 1). In both of the whole rock spectra, there was at least one additional doublet associated with Fe<sup>2+</sup>, but its interpretation is made difficult because of poor resolution due to the high degree of overlap with the other peaks. In the 293K spectrum, this Fe<sup>2+</sup> doublet has parameters similar to those reported [e.g., 8] for Fe<sup>2+</sup> in the M1 site of pyroxene (IS = ~1.19 mm/s, QS = ~2.35 mm/s). However, we did not observe the second doublet that usually arises from

$\text{Fe}^{2+}$  in the M2 site of pyroxene (with QS  $\approx$  2.00 mm/s). It is possible that such a doublet is present but with very low peak intensity – this idea is supported by the fact that the single pyroxene doublet is fairly broad (0.74 mm/s in the 293K data). Certainly, pyroxene peaks are expected on the basis of petrography and microprobe analyses. Thus, we conclude that pyroxene is present in small amounts in the whole rock sample.  $\text{Fe}^{3+}$  is represented in these spectra by one doublet in the whole rock sample and two doublets in the olivine separate. The Mössbauer data cannot really distinguish between octahedral  $\text{Fe}^{3+}$  in olivine, pyroxene, or oxide because the range of IS and QS for  $\text{Fe}^{3+}$  is quite small, and doublets corresponding to the octahedral sites in olivine, pyroxene, and spinel are similar enough to overlap nearly completely. The area of the octahedral  $\text{Fe}^{3+}$  doublet is 6-13% of the total peak area in the whole rock spectra, and 3-7% in the spectra of the olivine separate.

The olivine separate also has roughly half the  $\text{Fe}^{3+}$  in tetrahedral coordination. Of the phases identified in this meteorite, only a paramagnetic spinel like chromite can contain  $\text{Fe}^{3+}$ . Thus, we can assign the  $\text{Fe}^{3+}$  in the olivine separate to Fe oxide, probably chromite.

Finally, the flat baseline in the range from  $-4$  to  $-1$  mm/s on all of these spectra shows that there is no evidence for any Fe in any phase that is magnetically ordered, such as magnetite, hematite, or pyrrhotite.

The doublet areas of the different phases must be carefully interpreted because they do not relate directly to the relative abundances of the minerals involved. The Mössbauer technique “sees” only Fe atoms, such that the doublet areas of phases with variable Fe contents and unit cell volumes may be exaggerated or reduced relative to their true *modal* (i.e., volumetric) abundances. The average NWA2737 olivine has 0.43 moles  $^{56}\text{Fe}^{2+}$  per molar formula unit  $\text{M}_2\text{SiO}_4$  of  $\sim 44.3$   $\text{cm}^3/\text{mol}$ , giving 0.0097 mole- $^{56}\text{Fe}^{2+}/\text{cm}^3$ . The average pyroxene has 0.25 moles  $^{56}\text{Fe}^{2+}$  and 0.024 moles  $\text{Fe}^{3+}$  per formula unit  $\text{M}_2\text{Si}_2\text{O}_6$ , in an estimated volume of  $\sim 64.6$   $\text{cm}^3/\text{mol}$ , giving 0.0039 mole- $^{56}\text{Fe}^{2+}/\text{cm}^3$  and 0.0004 mole- $\text{Fe}^{3+}/\text{cm}^3$ . The average chromite has 0.693 moles  $^{56}\text{Fe}^{2+}$  and 0.100 moles  $\text{Fe}^{3+}$  per formula unit  $\text{AB}_2\text{O}_4$  of  $\sim 44.0$   $\text{cm}^3/\text{mol}$ , giving 0.0158 mole- $^{56}\text{Fe}^{2+}/\text{cm}^3$  and 0.0234 mole- $\text{Fe}^{3+}/\text{cm}^3$ .

Combining these data with calculated mineral volume proportions, one derives the distribution of iron among the minerals in NWA2737. Only 8.5% of the iron in NWA2737 is ferric, of which  $\sim 2/3$  is in tetrahedral sites in chromite, and  $\sim 1/3$  is in octahedral sites in chromite, pyroxene, and olivine. Ninety percent of the  $\text{Fe}^{2+}$  in NWA2737 is in its olivine, with the remainder divided between chromite and pyroxenes.

The Mössbauer spectra of NWA2737 (Figure 1) show clear contributions from  $\text{Fe}^{3+}$ , similar to those

seen in Earth mantle xenoliths that equilibrated at or slightly above QFM. Mössbauer spectra imply that roughly  $2/3$  of the  $\text{Fe}^{3+}$  in NWA2737 is in tetrahedral sites. Given the abundance of chromite [2] and its EMP chemical analyses, and the fact that  $\text{Fe}^{3+}$  in mantle olivine is consistently octahedral [9], we assign this doublet to  $\text{Fe}^{3+}$  in chromite or a related iron oxide. Unfortunately, the observed Mössbauer parameters are not in perfect agreement with those in the literature [e.g., 10] but the doublet is small and heavily overlapped, and its parameters are consistent with published chromite data within the expected standard deviation.

The remaining  $\text{Fe}^{3+}$  is in octahedral sites. In the whole rock spectrum, assignment of this doublet to pyroxene would be consistent with the EMP analyses that suggest  $\sim 15\%$  of the iron in its augite is  $\text{Fe}^{3+}$ . However, we note that this doublet also appears in both Mössbauer spectra of the olivine separate. Either this represents a contribution from  $\text{Fe}^{3+}$  in pyroxene (implying that  $\text{Fe}^{2+}$  in pyroxene is also present, though too heavily overlapped to be resolved) or it represents  $\text{Fe}^{3+}$  in either olivine or an oxide.

To resolve the latter issue, phase relations are useful. These data can be compared with Earth mantle xenoliths, for which  $f_{\text{O}_2}$  and  $\text{Fe}^{3+}$  contents of the phases are known independently. At  $f_{\text{O}_2}$  several log units above QFM, as in metasomatized hydrous (amphibole-bearing mantle xenoliths), olivine contains  $\sim 4\%$  of its iron as  $\text{Fe}^{3+}$ , and augite generally contains  $\sim 30\%$  of the total Fe as  $\text{Fe}^{3+}$  [8, 11]. More typically, unmetasomatized spinel peridotites equilibrated near QFM – the iron in their olivine is  $< 1\%$   $\text{Fe}^{3+}$ , and iron in their augites are typically 10-20%  $\text{Fe}^{3+}$ . These ranges are consistent with recent experimental work [12], in which augite equilibrated at  $f_{\text{O}_2} \sim \text{QFM}$  ( $\sim \text{IW} + 3.5$ ) has  $\sim 12\%$  of its iron as  $\text{Fe}^{3+}$ . If the octahedral  $\text{Fe}^{3+}$  in the olivine separate was in the olivine crystal structure, then it would imply a very oxidizing environment, like the source regions of metasomatized xenoliths. An oxidizing environment such as this on Mars may have arisen through shock processes, specifically shock heating resulting in loss of hydrogen from the olivine (see [2] for a more detailed description of this process).

**References:** [1] Beck et al. (2006) *GCA* 70, in press [2] Treiman et al (2006) this volume [3] Pieters et al (2006) this volume [4] Bajt. et al. (1994) *GCA* 58, 5209-5214. [5] Dyar et al. (2002) *AmMin* 87, 514-522. [6] Dyar et al. (2002) *CanMin* 40, 1347-1365. [7] Wivel and Mørup (1981) *JPhysESciInstr* 14, 605-10. [8] Dyar et al (1989) *AmMin* 74, 969-980. [9] McGuire et al (1991) *CMP* 109, 252-264. [10] Kuno et al (2000) *JRadNucChem* 246, 79-83. [11] Dyar et al (1992) *GCA* 56, 2579-2586. [12] McCanta et al (2004) *AmMin* 89, 1685-1693.