

**Comparison of Synchrotron microXANES determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  with Mössbauer values for clean mineral separates of pyroxene from Martian meteorites.** J.S. Delaney<sup>1</sup> and Dyar, M.D.<sup>2</sup>. Geological Sciences, Rutgers University, 610 Taylor Road, Piscataway, NJ08854 [jsd@rci.rutgers.edu]. <sup>2</sup> Geology and Geography, Mt Holyoke College, South Hadley, MA01075 [mdyar@mtholyoke.edu],

**Introduction:** The oxidation state of Fe in Martian meteorites is a parameter of great interest and the ability to determine this value in micrometer scale samples is important [1]. Intense, tunable x-ray sources at large synchrotron storage rings are being exploited to examine the Fe K-absorption edge with energy resolution of ~1-1.5eV in spots of 10x15  $\mu\text{m}$  on thin sections of a wide variety of materials including several Martian meteorites [2-5]. Synchrotron microXANES (SmX) spectroscopy is the technique that provides the most flexible capability for investigating  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . Variation of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  is manifested as a function of the energy of the pre-edge to the Fe absorption edge produced by the sample. SmX is at present the only technique that can be used with conventional polished thin sections [6]. Data for a broad spectrum of minerals have been produced and indicate that SmX can be used with a large variety of samples types [1].

Results for the Martian meteorites have been available since 1998 [3] but the implied oxygen fugacities for the SNC's derived early results were believed to be inconsistent with independent techniques [8,7]. Detailed examination of the results for several mineral groups demonstrated that the 'universal' calibration [6] used for earlier results was systematically overestimating the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in minerals such as pyroxene and feldspar in which the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  is low (<~10%). As a result, very detailed investigations of the relationship between SmX spectral features and large suites of independently characterized pyroxenes and other minerals were initiated. These studies led to revision of the Martian values [4] and the recognition of two major sources of error: (a) calibrations based on oxides and olivine were not suitable for pyroxene, amphibole, micas and feldspars; (b) the strong linear polarization of incident x-ray beam used to excite the samples is manifested in spectral variations caused by grain orientation in several minerals including pyroxene [4]. In addition, minerals with Fe in symmetrical sites typical of octahedral coordination, have very weak pre-edge structures. The low intensity of the peaks induces errors because the associated statistical fluctuations can be significant. For this reason, very significant improvements have been made to the beamline geometry used for the measurements. These improvements are continuing with the recent (2003) installation of a nine element Ge detector to replace the single Si(Li) detec-

tor previously used. This should provide at least a factor of 3 improvement in precision and probably better because of the significantly lower deadtime associated with modern digital detectors.

Revisions to the synchrotron microXANES technique involve the use of both mineral-group-specific calibration lines based on arrays of standards for which  $\text{Fe}^{3+}/\Sigma\text{Fe}$  data are available from Mössbauer spectroscopy and wet chemical analyses. The effect of crystal orientation is still under investigation. Systematic studies of the spectral response as a function of the optic axial plane in carefully selected arrays of minerals, have demonstrated that the effect varies from very strong in some micas to very weak in many feldspars. The orientation studies are continuing with the aim of developing a suite of techniques that will allow orientation effects to be eliminated. The optical orientation of the target grain can be determined in some cases. In other cases it may be necessary to make selected area XRD measurements and, finally, in many cases the use of a modified geometry for the x-ray microprobe beamline known as Magic Angle XANES has been shown to suppress much of the orientation dependence of the spectral signature.

**Martian Pyroxene:** The microXANES results remain at the high end of the expected range. To further test the validity of the synchrotron microXANES results, mineral separates of the constituent minerals of Martian meteorites were prepared and their  $\text{Fe}^{3+}/\Sigma\text{Fe}$  determined directly by Mössbauer spectroscopy. The average microXANES and Mössbauer results are compared in Table 1.

**Table 1:  $\text{Fe}^{3+}/\Sigma\text{Fe}$ (%) in Martian Pyroxene**

Meteorite	Möss	SmX
Shergotty	1.3	11.2
Zagami	1.3	2
QUE94201	2.5	8
Nakhla	3.4	0-5
Chassigny		0.21
ALH77005		0
EET79001	5.8	10-15
LEW88516	1.8	na
ALH84001	0	0

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In general the comparison is fairly good, although some samples still have high  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values. Both Shergotty and QUE94201 have zoned pyroxene so that average values for these minerals need to be treated very carefully. In the extreme case, pyroxene in QUE94201 displays zoning of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from a maximum of about 15% in the core to 0% at the rims. In this case, the volumetric relationships of the core and rim of the pyroxene need to be considered. Although the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of the cores is high, the area of each grain and, by extension, the volume of the core pyroxene relative to the total volume of crystal is low (10-15%), whereas the relatively narrow, reduced rims are volumetrically the major fraction of the pyroxene (>50% vol). A comparable relationship is seen in the zoned (heavily shocked) olivine of ALHA77005 and LEW88516. In both meteorites the olivine shows patchy brown areas with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values ranging from 5-25%. However, the volume of these areas relative to the bulk olivine is small and easily reconciled with bulk olivine results by [9] and now confirmed by [10].

**Discussion:** The 'evolution' of the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values toward the current numbers is clearly approaching a level that appears to be consistent with most available tests of the measurements. However, the significance of relatively high values that persist in the data despite these corrections is unresolved. Two aspects of this need to be investigated. (1) The partition coefficients of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  remain essentially unknown. In particular, steric effects, as manifested in inter-element correlations, need to be investigated experimentally. It remains to be demonstrated whether  $\text{Fe}^{3+}$  will behave like other trivalent species (Al, Cr) in crystal-liquid partitioning experiments or if it will passively follow  $\text{Fe}^{2+}$ . In addition, nothing is known about the effect of cooling rate on  $\text{Fe}^{3+}$  partitioning. Will it resemble those multivalent species that appear to substitute metastably into pyroxene crystallized under rapid cooling conditions but are effectively retained in the liquid at more sedate cooling rates? This is of particular importance in samples such QUE94201. The extreme compositional zonation in the pyroxene of this sample is clearly consistent with basalt that crystallized rapidly at or near the surface of Mars. Metastable formation of  $\text{Fe}^{3+}$  in such compositions must at least be considered.

(2) In addition to the internal processes that modify the Martian samples in the crust of Mars and at its surface, the importance of shock as a potential modifier of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  needs to be considered. Color variations in some pyroxene grains may reflect localized shock pressure effects, but nothing is currently known about the influence of simple shock events on the redox state of iron in pyroxene. New results for shocked feldspar

however, suggest that shock modification of Fe oxidation state occurs [11].

**Into the Future:** The techniques for synchrotron microXANES analysis of oxidation/coordination states are still under active development and further tests of consistence are being actively sought. A significant limitation of the technique remains in the relative difficulty of carrying out measurements at facilities that are currently maintained only in National Laboratories and for which demand is rising rapidly. The increase in demand for these facilities is rapidly outstripping the availability of new beamlines that require decade-long commitments before they become available. An alternate approach would be to find a new method of producing the intense tunable x-ray beams that are required for the x-ray microprobes whether they are used for SXRF, SXRD, XANES, XAS or other modes. Rapid developments in the physics of laser-electron interactions that can be harnessed as x-ray sources are very encouraging and suggest that these x-ray spectroscopic techniques will be usable, in the foreseeable future, with instruments that can be accommodated in a typical university setting.

**Acknowledgements:** NAG5-12148, NAG5-9528 (jsd), NAG5-10424 (mdd); SR Sutton & A Lanzirotti, and Beamline Team at NSLS X26A have made this possible:

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