Correction of the calibration of ferric/ferrous determinations in pyroxene from Martian samples and achondritic meteorites by synchrotron microXANES spectroscopy. Delaney, Jeremy S[1]., and Dyar, M.D[2], (1) Geological Sciences, Rutgers University, 610 Taylor Road, Piscataway, NJ08854 [jsd@rci.rutgers.edu] (2) Geology and Geography, Mt Holyoke College, South Hadley, MA01075

Introduction: The determination of $Fe^{3+}/\Sigma Fe$ in micrometer scale areas using synchrotron micro-XANES spectroscopic (SmX) measurements of Fe pre-edge peak energies, pioneered by Bajt et al. [1], has been successfully demonstrated and applied to a variety of major rock-forming mineral groups [2]. This technique uses a straightforward peak fitting procedure and relies on an empirical calibration based on fayalite, magnetite and hematite for the determination of $Fe^{3+}/\Sigma Fe$ in a wide variety of minerals and glasses. The technique has been subjected to tests of its usefulness by comparison of SmX results for many mineral grains with numerous independent analyses of the same samples by wet chemical techniques and by Mössbauer spectroscopy. The correlation coefficient of linear regression of $Fe^{3+}/\Sigma Fe$ determined by SmX with that by either wet chemical techniques or by Mössbauer spectroscopy is typically in excess of 90% for mineral groups showing the entire range of $Fe^{3+}/\Sigma Fe$ (as %age) from 0 to 100%. For tourmaline, this coefficient is 96%. Clearly the empirical SmX technique as applied is successfully producing consistent results.

In addition to producing a high correlation coefficient for analyses from any mineral group, the results of the technique must also show precise reproduction of the "true" $Fe^{3+}/\Sigma Fe$ values across the entire composition range when sufficient "standard" samples are available. For several mineral groups, (pyroxenes, amphiboles, micas and feldspars) sufficient data have been collected that it is possible to demonstrate the existence of a systematic bias that artificially elevates the $Fe^{3+}/\Sigma Fe$ ratios determined by SmX in samples with dominant ferrous iron. Since many geologically interesting problems involve samples with relatively low $Fe^{3+}/\Sigma Fe$ values, the observed bias is very important and a reliable method for removing it must be developed.

This study reports a study of well characterized pyroxene samples for which bulk analytical results, mostly determined by Mössbauer spectroscopy, are compared with SmX results using the Bajt et al. Procedure and applies the results of this test to previously analyzed pyroxene from the Martian meteorites, lunar samples and basaltic achondrites.

Samples Studied: A suite of terrestrial pyroxenes from a broad range of environments were analyzed by Dyar et al [3] and provide the initial sample set for creating the initial calibration test across the range of $Fe^{3+}/\Sigma Fe$ in pyroxene. These results show a strong correlation between the bulk analyses and the SmX microanalyses. The data are however somewhat scattered, especially at low $Fe^{3+}/\Sigma Fe$ by a variety of factors, including contributions from Fe-bearing inclusions the bulk pyroxene analysed. Electron microprobe studies of the SmX samples demonstrated that spinel, ilmenite and olivine inclusions all contribute to uncertainty in the bulk $Fe^{3+}/\Sigma Fe$ values. Systematic SmX studies of several of these samples has also demonstrated that the XANES spectra of pyroxene can vary as a function of the crystallographic orientation. Because of these complexities, further pyroxenes were located in which the iron is entirely ferrous, to study the relationship between the current SmX calibration and the independent bulk results and to provide data on which to base a correction to the earlier technique. These samples include ortho- and clino-pyroxene from the achondritic meteorites: Serra de Mage, Tatahouine, EET90020; lunar meteorites ALH76005, EET87521, and Apollo basalt 15555. In addition, orthopyroxene use for site occupancy studies by optical spectroscopy [4] were measured. These results are then used to apply a correction factor to the previously published pyroxene analyses from the Martian meteorites [5]

Results: The data demonstrate that for pyroxene, the original SmX calibration procedure in which the ferrous iron end member is represented by pure fayalitic olivine shows systematically high $Fe^{3+}/\Sigma Fe$ values for both ortho- and for clinopyroxene. In addition for pure ferric pyroxene (acmite) the predicted value is systematically low, For low ferric orthopyroxene a reduction of $Fe^{3+}/\Sigma Fe$(as %) by ~10-15% is necessary to eliminate the bias. For clinopyroxene this value is 15-20%. The effect of this current form of the correction is to rotate the observed correlation line between SmX and Mössbauer data on to the 1:1 line. Differences in shape and position of the Fe K-edge pre-edge peaks were not detectable in earlier data because of low x-ray count rates. These can now be documented reliably and these results suggest that the differences of the bond strength and coordination environment between the olivine standard and pyroxene group minerals can be recognized in the spectral pre-edge data. Application of crystal-field constraints to the observed electron transitions and

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comparison with optical spectra based on the Z+1 model for x-ray generation provide a new constraints for interpreting the pre-edge spectra [6] allowing results to be taken beyond the previous empirical calibration. Measurements based on this new approach are now in progress and will supercede the current values. The procedures currently used for interpreting SmX microanalytical data are being modified to incorporate these new constraints.

Pyroxene in Martian meteorites: $Fe^{3+}/\Sigma Fe$ determinations in pyroxene from Martian meteorites has revealed significant variation including the presence of zoning in grains from QUE94201. The absolute values obtained for these samples have ranged from 16% to 40% ferric iron. Based on the present discussion, we provide a corrected table of data for these meteorites to compensate for the recognized bias. It is emphasized that this correction applies only to the pyroxene as olivine results are consistent with independent results. Feldspar results will be treated elsewhere.

Table 1: Revised $Fe^{3+}/\Sigma Fe(\%)$ for Martian Pyroxene.

Meteorite	Original	Revised
Shergotty	0.28 +/- 0.05	0.112
Zagami	0.212 +/- 0.08 (0.171 +/- 0.04)	0.02
Nakhla	0.09 +/- 0.01 clean '0.17-0.35' cloudy	0
Chassigny	0.35	0.21
ALH77005	0.09-0.30	0
EET79001	0.27-0.3	0.10
		0.15
LEW88516	*na*	0
ALH84001	0.14 +/- 0.01	0

References: [1] Bajt et al(1994) *GCA*, 58,5209 [2] Delaney et al (1998) Geology, 26,139; [3] Dyar et al. (1989) Am. Min., 74, 969; [4] Goldman & Rossman (1977) Am Miner.62,151; [5] Delaney et al. (1998)LPSC XXIX, 1241 ;[6] Dyar et al (2000) this volume.