MINERALOGICAL $\text{Fe}^{3+}/\Sigma\text{Fe}$ MEASUREMENTS AS PROXIES OF VOLATILE BUDGETS: II. COMPARISON OF MICRO- AND MACRO-SCALE DATA, AND APPLICATIONS SUCH AS $K_d$ DERIVATION. M. D. Dyar, J. S. Delaney and S. R. Sutton; 1Dept. of Geography and Geology, Mount Holyoke College, South Hadley, MA 01075, mddyar@amherst.edu, 2Dept. Geol. Sci., Rutgers University, Piscataway, NJ 08854, 3Dept Geophysical Sci., Univ. Chicago, Chicago IL 60637

Introduction: The ability to measure the oxidation states of Fe in coexisting phases in extraterrestrial rocks has long been problematic because direct measurements were only possible on bulk samples. The new technique of synchrotron microscale X-ray (SmX) absorption near-edge spectroscopy (XANES) now allows microscale discrimination of Fe$^{3+}$ and Fe$^{2+}$ on spot sizes of <10x15 µm. This method permits examination of redox zoning in minerals, allows realistic characterization of these cations for thermodynamic modeling, permits study of oxidation kinetics at microscales, and would have the potential, when coupled with ion probe measurements of H, to distinguish between dehydrogenation and oxidation processes.

Over the past five years, we have accumulated >300 pairs of analyses comparing Fe$^{3+}/\Sigma\text{Fe}$ measured by bulk techniques (i.e., Mössbauer spectroscopy and wet chemistry) with microscale measurements by XANES [1, 2, 3]. We have also compared the results of these direct measurements with Fe$^{3+}/\Sigma\text{Fe}$ values calculated on the basis of electron microprobe stoichiometry. Our most recent work has focused these comparisons on lunar samples, Martian meteorites, eucrites, and terrestrial basalts and cumulates. We present here a comparison of Fe$^{3+}/\Sigma\text{Fe}$ values measured or estimated by various techniques, and give examples of how the ability to measure Fe$^{3+}/\Sigma\text{Fe}$ at microscales lends insight into understanding (1) partitioning of Fe$^{2+}$ and Fe$^{3+}$ between crystal-liquid and mineral-mineral pairs, and (2) zoning of Fe$^{3+}$ and its ability to document changing conditions during crystalization.

Methods for Determination of Fe$^{3+}/\Sigma\text{Fe}$:

Calculated Fe$^{3+}/\Sigma\text{Fe}$. At present the most common method of determining Fe$^{3+}$ and Fe$^{2+}$ in minerals is to use charge balance based on assumed perfect stoichiometry. All of the errors associated with each element analyzed are propagated onto the calculated Fe$^{3+}/\Sigma\text{Fe}$ In silicates, Fe$^{3+}$ recalculation schemes are especially strongly biased by their dependence on measured Si content because SiO$_2$ contributes a large percentage of the total oxide content, such that its standard deviation contributes a large amount of the total uncertainty in the analysis. Because Si$^{4+}$ is a highly charged cation, even small errors in its abundance have a large effect on calculated total charge. Furthermore, Si has a relatively narrow first order K$\alpha$ peak, such that minor misalignments in peak discrimination can result in large errors on Si content. The strong effect of Si content on calculated %Fe$^{3+}$ is shown in Figure 1 for a number of important silicates. Note that only for Si-poor spinel does the comparison even come close to 1:1.

Wet Chemistry. When abundant, homogeneous samples are available (rarely true of extraterrestrial materials), wet chemical analyses still provide the highest quality analyses. However, few labs perform these analyses, and opinions on optimal procedures vary. For this study, we have selected samples previously analyzed using to chemistry for comparison to the other methods.

Mössbauer spectroscopy. MS is also a bulk technique requiring homogeneous (or at least free of competing Fe-containing phases) samples with optimal results generated by sample sizes >100 mg. Results presented here were measured on the Mössbauer spectrometer in the Mineral Spectroscopy Labs at the University of Oregon and West Chester University.

Synchrotron micro-XANES. The SmX technique uses a synchrotron X-ray beam that can be focused and collimated to produce a true microbeam, permitting the use of petrographic constraints in the selection of the areas to be analyzed. Both the K and L absorption edges of Fe, Fe$^{3+}$ and Fe$^{2+}$ are usable [4,5] but we routinely use K-edges. The position of features associated with the X-ray K-absorption edge of Fe has been shown to be a sensitive and quantitative indicator of Fe$^{3+}$/Fe$^{2+}$ in the phase being studied [6,7]. The data presented here were made using beam line X26A at the National Synchrotron Light Source, Brookhaven National Laboratory, New York. Polished thin standard
thin sections were used. Previous in situ measurements of the Fe\(^{3+}/Fe\) ratio in minerals were used to establish a calibration line based on the derived pre-edge peak energies of synthetic fayalite (Fe\(_2\)SiO\(_4\)), natural magnetite (FeO\(_2\)), and hematite (FeO\(_3\)) as a function of their known Fe\(^{3+}/2\)Fe ratios [4].

**Results:** We use these data to show three main points:
1) Fe\(^{3+}/Fe^{2+}\) values determined by SmX methods yield excellent agreement with more traditional bulk methods.
2) Complete analyses allow calculation of partitioning coefficients for Fe\(^{2+}\) and Fe\(^{3+}\) between coexisting phases.
3) Fe\(^{3+}/Fe^{2+}\) zoning is observed in almost all mineral species studied to date, and it results in an unsurprising discrepancy between SmX and other methods.

**Agreement between bulk and micro-XANES methods.**

Figure 2 shows a comparison of Mössbauer and wet chemical data on two different mineral groups: amphibole (from [11]) and pyroxene. These trends are also reproduced for other mineral groups including olivine, tourmaline, and spinel. Deviations from the 1:1 line result mostly from inhomogeneity in the bulk samples, as is caused by the presence of impurities, inclusions and/or zoning.

**K\(_D\) Calculations.** Among the most exciting applications of the new XANES data is the study of partitioning coefficients for Fe\(^{2+}\) and Fe\(^{3+}\) between coexisting minerals and mineral/melt pairs (Table 1). These data probably record variations in crystallization temperatures. R\(^{\text{3+}}\) and R\(^{\text{2+}}\) partition coefficients (Fe\(^{3+}\)-Al\(^{3+}\), Fe-Mg) between feldspar and pyroxene are given as examples. Because there are few experimental data on these parameters, it is presently difficult to evaluate our results. However, in general Earth and Mars have the highest Fsp-Px K\(_D\) values for both Fe\(^{3+}/Fe^{3+}+Al^{3+}\) and Fe\(^{2+}/Fe^{2+}+Mg\), while the sample from the HED Planetoid has the lowest K\(_D\)'s for Fe\(^{3+}/Fe^{3+}+Al^{3+}\) and Fe\(^{2+}/Fe^{2+}+Mg\) reflecting the decreasing role of Fe\(^{3+}\) in reduced bodies. In the most reduced samples studies of Cr\(^{3+}/Cr^{2+}\) can complement these data.

**Zoning of Fe\(^{2+}\) and Fe\(^{3+}\).** Because nearly all other major elements are observed to be zoned at thin section scales, it is no surprise that we see gradients in both Fe\(^{3+}\) and Fe\(^{2+}\) contents in our samples. For example, pyroxene in shergottite QUE94201 shows dramatic zoning, with Fe\(^{3+}\)-rich cores and Fe\(^{2+}\) rich rims. Strong suggestions of correlation between Fe\(^{3+}\) zoning and D/H in metasomatized amphibole are being investigated and suggest a direct link between isotopic and chemical effects of dehydrogenation reactions.

**Summary:** Comparisons of bulk and microscale measurements of Fe\(^{3+}/Fe^{2+}\) show excellent agreement; deviations result largely from impurities in the bulk samples. Documentation of partitioning reactions involving oxidation state changes is in progress and will provide a major new constraint on the petrogenesis of many bodies. The synchrotron micro-XANES technique can also being fruitfully applied in complementary studies using ion probe measurements of isotopic ratios to correlate with Fe\(^{3+}/Fe^{2+}\) changes with absolute spatial control on sampling.