

THE RELATIONSHIP BETWEEN CLINOPYROXENE Fe^{3+} CONTENT AND OXYGEN FUGACITY. M. C. McCanta¹, M. J. Rutherford,¹ M.D. Dyar,² and J.S. Delaney³. ¹Brown University Department of Geological Sciences, Box 1846, Providence, RI 02912, molly_mccanta@brown.edu, ²Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, ³Dept. of Geological Sciences, Rutgers University, Piscataway, NJ 08855.

Introduction: The intrinsic oxygen fugacity (f_{O_2}) imposed on a magma has the ability to influence the crystallization sequence of the melt, as well as the composition of the resulting minerals [e.g., 1, 2]. f_{O_2} is an easily controlled parameter in the lab, either through gas-mixing equilibria or with a solid-state buffer assemblage. In nature, the f_{O_2} of a closed system is imposed on the system internally through multivalent equilibria involving the phenocryst-melt assemblage. This results in a characteristic oxidation state.

The physical parameter used to quantify oxidation state is oxygen fugacity. Iron is the only major rock forming element in basaltic melts to exist in multiple valence states and, therefore, it is commonly used to assess f_{O_2} . Traditional methods to quantify f_{O_2} utilize the ferric content of glasses or coexisting Fe-Ti oxides. However, many rocks, such as the Martian meteorites, do not contain the necessary phases or have oxides which have suffered reequilibration, thereby rendering them unmeasurable by current techniques. For these rocks, new methods, utilizing other phases are needed.

Mafic minerals have $Fe^{3+}/\sum Fe$ ratios that are a function of two factors: 1) crystal chemistry and 2) their intrinsic f_{O_2} during crystallization. Olivine and orthopyroxene, for example, have steric constraints on the extent to which Fe^{3+} can be incorporated in their structures, and may not record changes in magmatic f_{O_2} in a way that can easily be measured [3, 4]. The chemistry of clinopyroxene, however, allows for extensive incorporation of Fe^{3+} in its crystal structure, making it a potentially useful oxybarometer [5, 6]. To date, there have been few, if any, systematic experimental studies of the variation of the $Fe^{3+}/\sum Fe$ ratio as a function of f_{O_2} in clinopyroxene. This study seeks to address this lack of data.

Methods: *Experimental.* Dry crystallization experiments were performed on a starting composition composed of a synthetic shergottite melt in equilibrium with liquidus pyroxenes [7]. Samples were suspended on Re-loops in 1-atm, CO-CO₂ gas mixing furnaces at Johnson Space Center. Experimental f_{O_2} values ranged from IW+~8.6 to IW-1 (Table). Measured f_{O_2} values are accurate to ± 0.5 log units. All runs were heated to above their liquidus temperature for 0.5 hours. Several runs (MSNJ-17, 23, 24, 25) were held at these conditions for 4 hours and quenched as glasses. The majority of runs were then cooled to run conditions at 60°/hr

to facilitate pyroxene nucleation and growth. These experiments were held at final conditions for 24 hours. Samples were rapidly quenched in water and thin sectioned for further analysis.

Name	T _{Final} (°C)	f_{O_2} (ΔIW)	Run Products
BS1-027	1190	4.0	aug+glass
BS1-019	1192	3.0	aug+glass
BS1-024	1190	1.0	aug+glass
BS1-005	1170	0.0	aug+glass
BS1-023	1190	-1.0	aug+glass
MSNJ-23	1235	~8.6	glass
MSNJ-25	1235	5.0	glass
MSNJ-17	1235	3.5	glass
MSNJ-24	1235	0.0	glass

*P(total) = 1 atm for all runs

Analytical. All run products were analyzed on the synchrotron microXANES (SmX) spectrometer at Brookhaven National Laboratory for their $Fe^{3+}/\sum Fe$ ratios using the Bajt et al. [8] calibration with the addition of aegirine as a Fe^{3+} end member standard; the technique and apparatus are described in [9]. The largest contribution to these errors is the effect of crystallographic orientation as described in [10]; resultant $Fe^{3+}/\sum Fe$ errors are ± 0.15 absolute for individual analyses. To reduce these errors, as many as 6 analyses were made on each phase at different locations with various orientations (for the pyroxene), reducing the errors to 0.05-0.10 absolute. Errors on $Fe^{3+}/\sum Fe$ in (isotropic) glass are estimated at ± 0.05 .

In addition, the holohyaline samples were subjected to Mössbauer analysis, a more traditional Fe^{3+} measurement method. These data were cross-referenced with the SmX data for the same experiments to be used as an independent check on the SmX method.

Results: *Glass-only experiments.* Mössbauer and XANES data record very similar Fe^{3+} contents for the holohyaline experiments [Figure 1]. All values fall close to the 1:1 line with an R^2 of 0.93, indicating a close correlation over a wide range of f_{O_2} values ($f_{O_2} = IW - IW + \sim 8.6$). Additionally, all measured glass $Fe^{3+}/\sum Fe$ values are consistent with values predicted by the method of Kress and Carmichael [11]. This suggests that the XANES method can provide consistent, reliable results and supports the data gathered

from the pyroxene-melt pairs, for which no Mössbauer data could be collected.

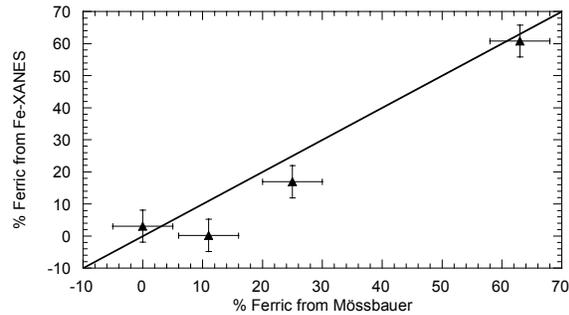


Figure 1. Comparison plot of Fe^{3+} percentage in experimental pyroxene-free glasses using XANES and Mössbauer techniques. Error bars are 5% error. Solid line represents a 1:1 correlation.

Pyroxene-melt pairs. Figure 2 plots the variation of augite Fe^{3+} content over a range of experimental f_{O_2} values. A clear increase in Fe^{3+} content is seen as the f_{O_2} increases to the quartz-fayalite-magnetite (QFM = IW+3.5) buffer and above.

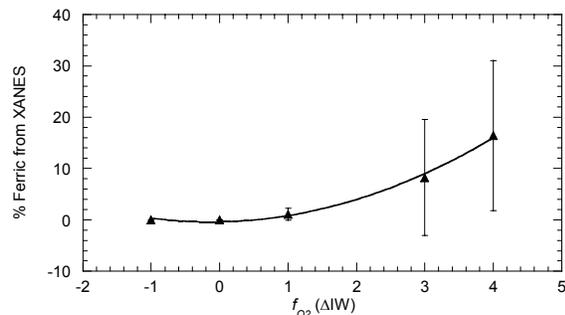


Figure 2. Variation of augite Fe^{3+} content with experimental f_{O_2} . Error bars are standard deviations between different crystals in a given experimental run.

Previous experimental work on the clinopyroxene pigeonite [12] shows that low-Ca clinopyroxenes do not accommodate much Fe^{3+} in their structures ($\sim <10\%$ of the total Fe); the same is true for orthopyroxenes. In contrast, Fe^{3+} contents of augites exhibit significant variation as a function of f_{O_2} (Figure 2). This may be due to the greater portion of large cations (i.e., higher Ca content) in augite, which results in less constrained Fe^{3+} - Fe^{2+} substitution. These trends are born out in the literature on wet chemical analyses of clinopyroxene, which indicates that the highest reported pigeonite % Fe^{3+} content is 16%, while augite % Fe^{3+} is found to vary from 0-100% [13].

Discussion: The holohyaline experiments suggest that the XANES technology accurately replicates Fe^{3+} measurements made with other methods and, therefore, can be applied with confidence to the augite-melt

pairs. This is important because other techniques cannot be used to quantify the Fe^{3+} of these crystallization experiments.

Our results indicate that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in augite and glass are consistently very low when f_{O_2} is below QFM. It is necessary to equilibrate at f_{O_2} values $>\text{IW}+3.5$, or $\approx\text{QFM}$, in order for significant Fe^{3+} to be present. Mass distribution coefficients ($\text{wt.}\% \text{Fe}^{3+}_{\text{pyroxene}}/\text{wt.}\% \text{Fe}^{3+}_{\text{melt}}$) were calculated for each pyroxene-melt experimental run. Values ranged from 0.00 to 0.77 for the augite, both suggesting some preferential Fe^{3+} partitioning over the range of f_{O_2} s studied. As with the percentage of Fe^{3+} in the mineral, the mass distribution coefficients for augite show a strong correlation with f_{O_2} . This relationship emphasizes the ability of augite Fe^{3+} contents to provide a record of the f_{O_2} during melt crystallization.

One of the starting motivations for this project was to provide insights into f_{O_2} values of SNC meteorites in which there are complications with interpreting results of other Fe oxybarometers. Recent work utilizing several phases suggests that the currently known SNC meteorites all crystallized under fairly reducing ($\leq\text{QFM}$) conditions, extending from IW-0.5 up to IW+3.5 [e.g., 14-17]. As discussed above, Fe^{3+} contents of clinopyroxenes that crystallized below QFM are small, and therefore they give no real insights into differences over that range of reduced f_{O_2} values. The relationships calibrated here might be useful, however, if more oxidized SNC meteorites are discovered.

Acknowledgments. Research funded by NASA grants NAG5-12225 (MJR), NAG5-10424 (MDD), NAG5-12848 (MDD), and NAG5-12687 (MDD) and the NASA Graduate Student Researchers Program NGT-963 (MCM).

References: [1] Eugster (1957) *J. Chem. Phys.*, 26, 1760. [2] Frost and Lindsley (1991) *RevMin.*, 25, 433-468. [3] Nakamura and Schmalzreid (1983) *Phys. Chem. Mins.*, 10, 27-37. [4] McGuire *et al.* (1991) *Contrib. Mineral. Petrol.*, 109, 252-264. [5] Dyar *et al.* (1986) in *Mineral Spectroscopy*, GS Spec. Pub. 5, 273-289. [6] Luth and Canil (1993) *Contrib. Mineral. Petrol.*, 104, 56-72. [7] Johnson *et al.* (1991) *Geochim. Cosmochim. Acta*, 55, 349-366. [8] Bajt *et al.* (1994) *Geochim. Cosmochim. Acta*, 58, 5209-5214. [9] Dyar *et al.* (2002) *Amer. Mineral.*, 87, 514-522. [10] Dyar *et al.* (2002) *Canad. Mineral.*, 40, 1347-1365. [11] Kress and Carmichael (1991) *Contrib. Mineral. Petrol.*, 108, 82-92. [12] McCanta *et al.* (2003) *LPS XXXIV*, Abstract #1361. [13] Deer *et al.* (1978) *Rock-Forming Minerals*, vol. 2A, Longman Grp. [14] Delaney *et al.* (1998) *LPS 29*, 1241-1242. [15] Hale *et al.* (1999) *GCA* 63, 1459-1470. [16] Herd *et al.* (2002) *GCA* 66, 2025-2036. [17] McCanta *et al.* (in press) *GCA*.