$Fe^{3+}/\Sigma Fe$ RATIOS IN PIGEONITE AS A FUNCTION OF f_{O2}: A PRELIMINARY INVESTIGATION. M. C. McCanta[1], M. J. Rutherford,[1] M.D. Dyar,[2] and J.S. Delaney[3]. [1]Brown University Department of Geological Sciences, Box 1846, Providence, RI 02912, molly_mccanta@brown.edu, [2]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, [3]Dept. of Geological Sci., Rutgers University, Piscataway, NJ 08855.

Introduction: Magmatic oxidation state reflects the degree of oxidation of the source region and, possibly, the additional effects of magma interaction with near surface rocks and/or fluids. The physical parameter which controls oxidation state is oxygen fugacity (f_{O2}). f_{O2} influences the crystallization sequences of magmas, as well as the composition of the resulting minerals [e.g. 1,2]. If the intrinsic f_{O2} of a planet is known at depth (i.e. the magma source region), insight can be gained into magmatic and non-magmatic processes which may have overprinted the primary f_{O2}.

Silicate melt $Fe^{3+}/\Sigma Fe$ ratios and Fe-Ti oxide equilibria are the best studied and most commonly used oxybarometers in terrestrial igneous rocks. It's long been known that the $Fe^{3+}/\Sigma Fe$ ratio in silicate melts is a function of oxygen fugacity [3,4]. This ratio has been calibrated experimentally and can be used to measure the crystallization f_{O2} of a magma. The dependence of Fe-Ti oxide equilibria on f_{O2} has also been quantified experimentally for use as a oxybarometer [e.g. 5].

Mafic minerals and possibly plagioclase have $Fe^{3+}/\Sigma Fe$ ratios that are a function of two factors: 1) crystal chemistry and 2) their crystallization f_{O2}. Olivine and low-Ca pyroxene, 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_{O2} [6,7]. The chemistry of high-Ca pyroxene, however, allows for extensive incorporation of Fe^{3+} in its crystal structure, making it a useful oxybarometer [8,9]. To date, there has been no systematic experimental study of the variation of the $Fe^{3+}/\Sigma Fe$ ratio as a function of f_{O2} in mafic silicates (or feldspar). If a systematic variation of mafic mineral $Fe^{3+}/\Sigma Fe$ with f_{O2} is discovered, this could provide a valuable new way of measuring f_{O2} in rocks which lack residual glass or in which the oxides are not present or in equilibrium.

A good candidate rock set to investigate is the group of basaltic Martian meteorites, which are holocrystalline and contain oxides which exhibit complex subsolidus reequilibration features. The measurement of crystallization f_{O2} in these samples is notoriously difficult and a new oxybarometer would be of great use. This study seeks to address the lack of a calibration of the variation of mafic mineral $Fe^{3+}/\Sigma Fe$ ratio with f_{O2} through a series of experiments and analyses of the products.

We have completed a sequence of controlled f_{O2} experiments on a synthetic basaltic shergottite starting composition, crystallizing the low-Ca pyroxene pigeonite (Pgt) [10,11]. The $Fe^{3+}/\Sigma Fe$ ratios have been measured in these pyroxenes in a first attempt to actually quantify their possible variation with f_{O2}.

Methods: *Experimental.* Dry crystallization experiments were performed on a starting composition composed of a synthetic shergottite melt in equilibrium with liquidus pyroxenes [12]. Samples were suspended on Re-loops in 1-atm, CO-CO_2 gas mixing furnaces at Johnson Space Center. Experimental f_{O2}'s ranged from IW+3.5 (QFM) to IW-1 (Table 1). Measured f_{O2}'s are accurate to ± 0.5 log units. Runs were heated to above their liquidus temperature for 0.5 hours and then cooled to run conditions at 60°/hr. Experiments were held at final conditions for 24 hours. Samples were rapidly quenched in water and thin sectioned for further analysis.

Table 1. Experimental run f_{O2} conditions and products.

	f_{O2}	Run Products
MSNJ-7	IW+3.5	Pgt+melt
MSNJ-3	IW+2	Pgt+melt
MSNJ-6	IW+1	Pgt+melt
MSNJ-4	IW	Pgt+melt

Analytical. All run products were analyzed on the synchrotron microXANES (SmX) spectrometer at Brookhaven National Laboratory for their $Fe^{3+}/\Sigma Fe$ ratios using the Bajt et al. [13] calibration with the addition of aegirine as a Fe^{3+} end member standard; the technique and apparatus are described in [14]. The largest contribution to these errors is the effect of crystallographic orientation as described in [15]; resultant $Fe^{3+}/\Sigma Fe$ 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 $Fe^{3+}/\Sigma Fe$ in (isotropic) glass are estimated at +/- 0.05.

Results: The first results for pigeonite and glass $Fe^{3+}/\Sigma Fe$ ratios produced in this study are given in Table 2; standard deviations are calculated based upon repeated analyses of different grains and/or locations in the glass.

Table 2. Fe^{3+} and standard deviations in pyroxene and melt

	Fe^{3+}_{Pgt}	Fe^{3+}_{melt}
MSNJ-7	0.12(06)	0.07(02)
MSNJ-3	0.04(10)	0.03(01)

PYROXENE IRON VARIATION WITH f_{O2}: M. C. McCanta *et al.*

MSNJ-6	0.14(05)	0.09(04)
MSNJ-4	0.13(08)	0.05(01)

Combined with electron microprobe analyses of the glass and pigeonite, mass distribution coefficients can be calculated (Table 3).

Table 3. Fe^{3+} concentrations in pyroxenes and melts.

	Fe^{3+}_{Pgt} p.f.u.*	Wt% Fe^{3+}_{Pgt}	Wt% Fe^{3+}_{melt}	Mass D*
MSNJ-7	0.070	1.76	1.03	1.71
MSNJ-3	0.024	0.59	0.44	1.34
MSNJ-6	0.086	2.11	1.30	1.62
MSNJ-4	0.077	1.92	0.72	2.67

*Fe^{3+} contents of Pgt calculated based upon 6 O. Mass D = Wt%Fe^{3+}_{Pgt}/Wt%Fe^{3+}_{melt}.

Discussion: These preliminary results indicate that the $Fe^{3+}/\Sigma Fe$ ratio in both pigeonite and glass is consistently very low, such that little or no correlation between f_{O2} and the $Fe^{3+}/\Sigma Fe$ ratio of the pigeonite is observed. This result might have been predicted because the f_{O2} range of the experimental run conditions is limited to relatively reducing conditions. The amount of Fe^{3+} in a melt can be calculated over a range of f_{O2} using an algorithm from [4]. The results of this calculation are shown in Figure 1.
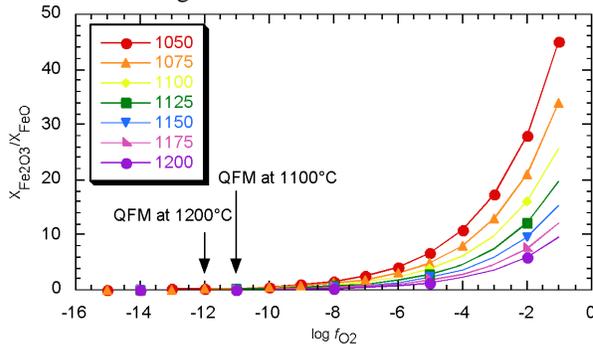

Figure 1. Plot showing the variation of silicate melt Fe^{3+} (i.e. Fe_2O_3 content) with f_{O2} over a range of temperatures. Note the lack of Fe^{3+} in the melt at and below QFM.

All current runs were completed at f_{O2}'s   QFM. As is clearly illustrated in Figure 1 and in our results, very little Fe^{3+} is present in the melt at these f_{O2} values. It is only at ~NNO (QFM+1) that Fe^{3+} begins to appear in the melt in significant quantities. Therefore, our experiments have probed a region of phase space where Fe^{3+} is in extremely low abundance.

It is noteworthy, however, that both the percentage of Fe^{3+} and the wt% Fe^{3+} in Pgt are higher than in the melt. However, since many of the values are within error of each other this result requires further verification.

A second issue that arises is the capability of pigeonite to respond to changes in f_{O2} given its crystal chemistry. In the survey of terrestrial pigeonite com-

positions presented in [16], it is apparent that the oxidation state of Fe in this mineral is generally in the range of 0-5% Fe^{3+}, and the highest reported %Fe^{3+} content for any pigeonite analysis in [16] is 16%. Thus, we may see only a very small change in the %Fe^{3+} in pigeonite over any f_{O2}. Such steric limitations on substitution of Fe^{3+} have been cited in the terrestrial literature to explain why the oxidation state of the upper mantle is higher (because Fe^{3+} is excluded from the major phase, olivine, and its concentration is thereby increased in the minor phase, spinel) than in the transition zone, where Fe^{3+} is distributed among the major phases [e.g. 17,18]. In the bulk composition studied here, crystal chemistry may favor exclusion of Fe^{3+} from pigeonite, increasing the concentration of Fe^{3+} in the melt as pigeonite crystallizes. Additionally, these experiments were doped with weight percent levels of trivalent rare earth elements (Eu, Gd, Sm), which may also have an effect on the amount of Fe^{3+} substitution into the pigeonite.

Conclusions and Future Work: In conclusion, this first look at pyroxene $Fe^{3+}/\Sigma Fe$ variation with f_{O2} shows no systematic trend, probably because the experimental conditions included only low-f_{O2}'s. It is clear that future experiments at f_{O2}'s higher than QFM are imperative. At these higher f_{O2}s significant amounts of Fe^{3+} are present in the melt and would be expected in the pyroxenes, allowing for an investigation of systematic changes. These new experiments will also extend the $Fe^{3+}/\Sigma Fe$ vs. f_{O2} data set to higher f_{O2} regions that may be relevant to terrestrial igneous rocks. It will also be important to study bulk compositions with high-Ca pyroxene on the liquidus so that the effect of crystal chemistry on oxidation potential can be fully assessed. With their resolution, the potential variation of pyroxene $Fe^{3+}/\Sigma Fe$ with f_{O2} can be explored and quantified.

References: [1] Eugster (1957). *J. Chem. Phys.*, *26*, 1760. [2] Frost and Lindsley (1991). *RevMin, 25,* 433-468. [3] Sack et al (1980) *Contrib. Mineral. Petrol., 75*, 369-376. [4] Kress and Carmichael (1991) *Contrib. Mineral. Petrol., 108, 82-92.* [5] Buddington and Lindsley (1964) *J. Pet., 5*, 310-357. [6] Nakamura and Schmalzreid (1983) *Phys. Chem. Mins.*, *10*, 27-37. [7] McGuire et al. (1991) *Contrib. Mineral. Petrol.*, *109*, 252-264. [8] Dyar et al. (1986) in *Mineral Spectroscopy*, GS Spec. Pub. 5, 273-289. [9] Luth and Canil (1993) *Contrib. Mineral. Petrol.*, *104*, 56-72. [10] McCanta and Rutherford (2001) *Lunar Planet. Sci., 32*. [11] McCanta et al. (2002) *Lunar-Planet. Sci.*, *33*. [12] Johnson et al (1991). *Geochim. Cosmochim. Acta, 55*, 349-366. [13] Bajt. et al. (1994) *Geochim. Cosmochim. Acta*, *58*, 5209-5214. [14] Dyar et al. (2002) *Amer. Mineral.*, *87*, 514-522. [15] Dyar et al. (2002) *Canad. Mineral.*, *40*, 1347-1365. [16] Deer et al. (1978) *Rock-Forming Minerals*, vol. 2A, Longman Grp. [17] O'Neill et a. (1993) in Evolution of the Earth and Planets, *Geophys. Monogr. 74*, IUGG, vol. 14, 73-88. [18] Canil et al. (1994) *EPSL, 123*, 205-220.