

POTENTIAL EFFECTS OF MELT COMPOSITION ON REDOX RATIO: IMPLICATIONS FOR OXYGEN FUGACITY MEASUREMENTS. M. C. McCanta, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, Texas 77058 (McCanta@lpi.usra.edu).

Introduction: The ability to measure the intrinsic oxygen fugacity (f_{O_2}) of a system (e.g., magma storage region, planetary body, etc.) is essential to understanding elementary geologic processes such as crystallization and differentiation. Of all the major elements, only iron commonly exists in multiple valence states. Thus, accurate knowledge of the Fe^{3+}/Fe^{2+} ratio provides the best proxy for the amount of oxygen present in a crystallizing system and allows for estimation of magmatic f_{O_2} . To quantify f_{O_2} , a variety of oxybarometers are utilized. An oxybarometer commonly applied to terrestrial igneous rocks is based on the ratio of Fe^{3+}/Fe^{2+} present in the melt phase [1]. This ratio is believed to reflect the crystallization oxygen fugacity of the system and can be quantified, in a crystal-free glass, taken to represent a quenched melt, using the algorithm of [1] as follows:

$$\ln [X_{Fe_2O_3}/X_{FeO}] = a \ln f_{O_2} + b/T + c + \sum X_i d_i$$
where a , b , c , and d_i are experimentally determined constants and X_i is the mole fraction of the i^{th} oxide.

Earlier studies have suggested that the Fe^{2+}/Fe^{3+} ratio of a melt can be influenced by melt composition, specifically the structural role the various cation species fulfill [2,3,4], as well as f_{O_2} . *Dickenson and Hess* [2,3] investigated this effect over a range of melt compositions (peraluminous $\{K_2O < Al_2O_3\}$ to peralkaline $\{K_2O > Al_2O_3\}$) at a constant f_{O_2} and temperature. Under these conditions, they found a large compositional effect in the Fe^{2+}/Fe^{3+} ratio in peraluminous melts and essentially none in peralkaline melts (Figure 1).

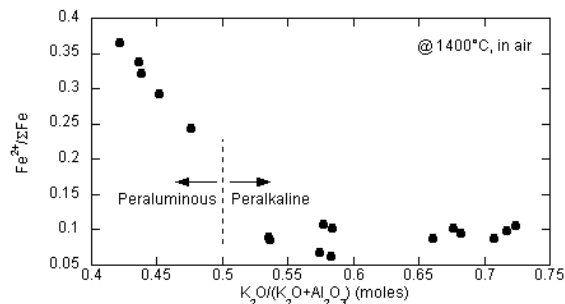


Figure 1. Melt Fe^{3+} vs. composition data from [2]. Note the distinct break in slope at $\sim(K_2O/K_2O+Al_2O_3)=0.5$. This approximates the peraluminous-peralkaline melt compositional boundary.

These effects were attributed to the presence of tetrahedrally coordinated Fe^{3+} in the melt, charge balanced with K^+ . In peraluminous melts, the results indicate that tetrahedral Fe^{3+} is less stable than in peral-

kaline melts. [2,3] suggest that increased competition between Fe^{3+} and Al^{3+} for the scarce charge-balancing cations in the peraluminous melts results in the compositional variability seen in Figure 1. However, their experiments were run only at a single high f_{O_2} (i.e., in air) and therefore any effects that changes in f_{O_2} may also have on melt Fe^{3+} content were not addressed.

The potential exists for compositional differences to influence melt Fe^{3+} content which may, in turn, influence f_{O_2} measurements. Therefore understanding the interplay between the compositional effects and f_{O_2} is imperative. This study presents new experiments to quantify the effects that composition may have on the Fe^{3+} content of the melt as a function of crystallization f_{O_2} .

Methods: Experimental. A series of experiments were carried out in the 1-atmosphere, gas-mixing furnaces at Johnson Space Center and the vertical tube Deltech furnace at Brown University. Four starting compositions, synthesized from reagent grade oxides and carbonates, were used to cover the range of melt compositions in the original study (Table 1). Starting compositions consisted of simplified melts in the $SiO_2-Al_2O_3-K_2O-FeO^*$ system. The only variable parameter was the K_2O/Al_2O_3 ratio, spanning compositions from peraluminous to peralkaline. The high SiO_2 of the starting composition was chosen due to previous studies which demonstrated that at SiO_2 values greater than 75 mol%, the redox ratio is sensitive to melt composition [5] and that this sensitivity decreases in melt compositions at lower values. Additionally, data from melts created in previous experiments on a Martian-type starting composition were included for comparison.

Table 1. Starting compositions.

wt. %	PM1	PM2	PK1	PK2
SiO ₂	69	69	69	69
Al ₂ O ₃	18	15	11	8
K ₂ O	11	14	18	21
FeO	2	2	2	2
K ^{*a}	0.38	0.48	0.62	0.72

^aK^{*} = $K_2O/(K_2O+Al_2O_3)$

Peraluminous compositions were run in the gas-mixing furnaces utilizing Re- and Pt-wire loops. The f_{O_2} was controlled using a predetermined mixture of CO and CO₂ gases and monitored with an external ZrO₂ sensor. The use of either Re or Pt loops was

predicated by the run f_{O_2} . Under high f_{O_2} conditions ($>$ quartz-fayalite-magnetite [QFM]) Pt-wire was used as Fe loss to the Pt-metal was minimized under these conditions. Re-wire does not take up Fe under low f_{O_2} conditions [6] and therefore was used in the low f_{O_2} experiments.

Peralkaline compositions were run in the vertical tube Deltech furnace. The high alkalinity of the peralkaline compositions necessitated a different experimental setup. To minimize alkali volatilization in these experiments, samples were placed inside lightly crimped Re-foil containers and sealed in evacuated silica glass tubes. The Re-foil was used to fix f_{O_2} at the Re-ReO₂ buffer (\sim Ni-NiO+2).

Temperature was held constant at 1450°C in all experiments. Charges were held for 12 hours at run conditions, the minimum time determined necessary to achieve constant Fe^{3+}/Fe^{2+} values by [2]. All experiments were quenched in water.

Analytical. All run products were analyzed for their major element composition on the Cameca SX-100 at Johnson Space Center and for their Fe^{3+} content on the Mössbauer spectrometer in the Mineral Spectroscopy Laboratory at Mount Holyoke College.

Results: Experimentally produced melts of a single, Martian-type, composition show significant increases in Fe^{3+} content with f_{O_2} (Figure 2). The measured Fe^{3+} content of these melts ranges from 0.03 wt.% at f_{O_2} values of QFM and lower to 8.51 wt.% in samples equilibrated at an f_{O_2} of \sim IW+8.6 [7]. This represents a percent $Fe^{3+}/\Sigma Fe$ range of zero to 59.5. Additionally, the glass compositions appear well correlated with the predicted $X_{Fe_2O_3}/X_{FeO}$ calculated using the algorithm of [1]. It is evident from these experiments that f_{O_2} variations have a significant effect on the ferric iron content of a single composition melt.

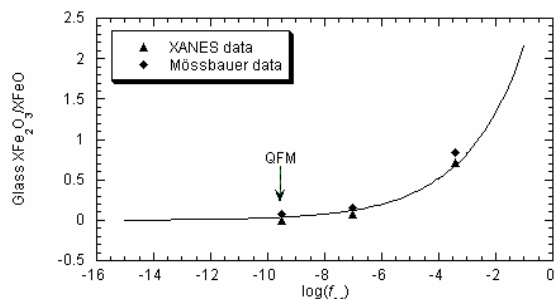


Figure 2. Comparison of experimental glass Fe^{3+} data (both XANES and Mössbauer) and f_{O_2} . The solid curve represents the calculated $X_{Fe_2O_3}/X_{FeO}$ from [1] for a melt at 1235°C, the temperature of these experiments.

The new glass data presented above was then plotted with data from [2] to compare compositional effects with crystallization f_{O_2} effects on redox ratio (Figure 3). Although these early experiments were run on a significantly different starting composition (lower SiO_2 , low Al_2O_3 , high FeO), the spread in the iron ratio as a function of f_{O_2} appears to be larger than that caused by compositional variations. The variation in $Fe^{2+}/\Sigma Fe$ in a single composition over a wide range in f_{O_2} is nearly double that seen as a function of compositional variability.

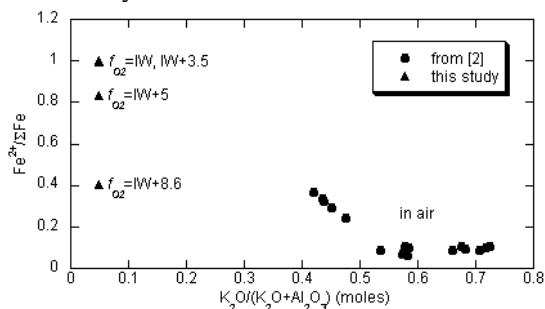


Figure 3. Comparison of glass data from [2] and new experiments on a single composition over a range of f_{O_2} values (shown on plot).

Ongoing Research: In peraluminous compositions, the variability in redox ratio with f_{O_2} appears significantly greater than that resulting from compositional differences. This suggests that melt measurements of Fe^{3+} for use in oxybarometry are not unduly effected by compositional differences. To further test this hypothesis, new experiments on peralkaline melts are planned. Additionally, experiments to characterize the effects of Ca addition to the melts are being completed. The study of [3] showed the compositional effects to be similar to that seen in the SiO_2 - Al_2O_3 - K_2O - FeO^* system, but more muted.

References: [1] Kress V. and Carmichael I. S. E. (1991) *Contrib. Mineral. Petrol.*, 108, 82-92. [2] Dickenson M. P. and Hess P. C. (1981) *Contrib. Mineral. Petrol.*, 78, 352-357. [3] Dickenson M. P. and Hess P. C. (1986) *Contrib. Mineral. Petrol.*, 92, 207-217. [4] Thornber C. R., Roeder P. L. and Foster J. R. (1980) *Geochim. Cosmochim. Acta*, 44, 525-532. [5] Paul a. and Douglass R. W. (1965) *Phys. Chem. Glasses*, 6, 207-211. [6] Borisov A. and Jones J. H. (1999) *Am. Mineral.*, 84, 1528-1534. [7] McCanta M. C., Dyar M. D., Rutherford M. J. and Delaney J. S. (2004) *Am. Mineral.*, 89, 1685-1693.