

The importance of iron mobility in magmatic-hydrothermal systems

ADAM SIMON^{1*}, LAURA BILENKER¹ AND AARON BELL²

¹Earth & Environmental Sciences, University of Michigan
[*simonac@umich.edu]

²Institute of Meteoritics, University of New Mexico

Iron is a ubiquitous component of arc-related magmas and porphyry-, high-sulfidation, iron-oxide-copper-gold (IOCG), and iron-oxide-apatite (IOA) ore deposits. Iron is present as an essential structural constituent in ferromagnesian silicate minerals, magnetite, sulfide crystals, and sulfide liquids, as well as aqueous fluids that exsolve from silicate melt. The observation that the oxidation state for different arc magma systems varies over approximately five orders of magnitude, from approximately one log unit below the FMQ (fayalite-magnetite-quartz) buffer to the HM (hematite-magnetite) buffer, indicates that iron exists in both ferrous and ferric forms in most arc magmas. The valence of iron is proportionally dominated by Fe²⁺ in most common ferromagnesian silicate minerals, is 2/3 Fe³⁺ and 1/3 Fe²⁺ in magnetite, is Fe²⁺ in sulfides, and is Fe²⁺ in Cl-bearing aqueous fluid. Interestingly, there does not appear to be a sliding scale for the oxidation state of iron in aqueous fluids, in contrast to silicate liquids. The observation that aqueous fluids contain only a single valence state of Fe across five orders of magnitude of fO₂ space is fundamentally different than sulfur, which exists as both H₂S and SO₂ in aqueous fluid and the relative proportion of each is dictated by the fO₂ of the system. These observations have critical implications for magmatic systems.

We continue to investigate experimentally the importance of the mass transfer of iron from melt to aqueous fluid, and the many reactions among aqueous fluid, silicate melt, magnetite, and sulfide phases. Our data confirm field-based hypotheses that the transfer of iron from melt to aqueous fluid increases the ratio of Fe³⁺ / Fe²⁺ in the degassed melt. This has implications for the composition of ferromagnesian silicates and the stability of sulfide phases during degassing. The mass transfer of iron affects the oxidation state of sulfur in the melt, driving sulfur from sulfide to sulfate, which in turn has implications for the mass transfer of ore metals (Cu, Au) from melt to aqueous fluid. This also may affect the fractionation of iron isotopes, and their ability to serve as geochemical fingerprints for source reservoirs of iron in IOCG and IOA deposits. We will present new data and discuss the incredible role that iron plays in moderating phase equilibria of silicate magmas, and the potential use of iron isotopes to assess the evolving oxidation state and source reservoir characteristics of arc magmas.

Insight to the local melt structures and their influence on the fractionation of rare earth elements (La, Gd, Yb, Y)

S.SIMON^{1*}, M. WILKE¹, S. KLEMME², W. A. CALIEBE³, R. CHERNIKOV³ AND K. O. KVASHNINA⁴

¹GFZ, German Research Centre For Geosciences, Potsdam, Germany (*correspondence: ssimon@gfz-potsdam.de)

²Westfälische Wilhelms-Universität, Münster, Germany

³Deutsches Elektronen-Synchrotron, Hamburg, Germany

⁴European Synchrotron Radiation Facility, Grenoble, France

Knowledge of the local structure around rare earth elements (REE) in aluminosilicate melts is of great interest for the geochemistry of magmatic processes, particularly for understanding the partitioning of REE between melt and the coexisting crystals in a more comprehensive way. Several studies already proposed a significant influence of the melt composition on REE fractionation [1 – 4]. In a fundamental study Ponader & Brown [5] showed that the local environment around La, Gd and Yb changes with polymerization of the melt, this was used to explain differences in element partitioning. However, no direct correlation between partitioning data and structural informations was provided.

In this study, melt compositions taken from Prowatke & Klemme [4] and various haplogranitic, -basaltic compositions were doped with La, Gd, Yb or Y and synthesized as glass. EXAFS was used to gather quantitative information on the local environment of Gd, Yb and Y and XANES for qualitative information on the local environment of La in the glasses. Additional high temperature (HT) in situ Y-EXAFS was performed to prove, if the local structure of Y above T_G corresponds to the local structure in the quenched melts. Analysis of the EXAFS data shows that the average bond length, the width and skewness of the REE-O pair distribution function increase with increasing polymerization of the melt for Gd, Yb and Y [6]. XANES spectra confirm a similar trend for La. The HT Y-EXAFS shows no significant change of the local structure above T_G. Finally, correlations of structural parameters and partitioning data from Prowatke & Klemme [4] were obtained.

[1] Blundy & Wood (2003) *Earth Planet. Sci. Lett.* **210**, 383-397. [2] Watson (1976) *Contrib. Mineral. Petrol.* **56**, 119-134. [3] Ryerson & Hess (1978) *Geochim. Cosmochim. Acta* **42**, 921-932. [4] Prowatke & Klemme (2005) *Geochim. Cosmochim. Acta* **69**, 695-709. [5] Ponader & Brown (1989) *Geochim. Cosmochim. Acta* **53**, 2893-2903. [6] Simon et. al. (2012) *Chem. Geol.*, **in press**.