

Experimental determination of iron isotope fractionation during high temperature segregation of metal from silicate liquids: Evaporation or diffusion ? M. Roskosz^{1,2}, B. Luais² and M. J. Toplis³, Geophysical Laboratory, 5251 Broad Branch Rd., Washington, D.C., USA, m.roskosz@gl.ciw.edu, ² CRPG, 15 rue notre-Dame des Pauvres, 54501, Vandoeuvre-les-Nancy Cedex, France, ³ DTP (UMR 5562), 14, Ave. Edouard Belin, F-31400, Toulouse, France.

Introduction: Recent advances in mass spectrometry make it possible to measure isotopic variations of transition metals (Cu, Fe, Zn ...) in materials of interest to the Earth sciences. This rapidly developing field has given rise to several ground breaking studies, concentrated primarily on the characterization of natural materials, including extraterrestrial, igneous, biogenic and abiogenic sedimentary rocks [e.g.1]. In the case of Fe, these results have generated considerable interest because it has been inferred that isotopic ratios of this element might be a tracer of microbial activity, a conclusion supported by experimental studies of biological systems [2]. Iron isotopes may then be a powerful tool in the quest for signs of early life [2-3]. However, measurements on materials which are clearly abiogenic in origin, for example metal and silicate fractions of pallasite meteorites [4-6], demonstrate that Fe isotopic variability also occurs in this context. Similarly Fe isotope fractionation has been observed between clinopyroxenes and olivines in mantle xenolith nodules [4, 7]. Nevertheless, no experimental studies have been reported which quantify the degree of isotopic fractionation in high-temperature magmatic systems. The dependence of Fe isotope fractionation on thermodynamic properties such as temperature, pressure and oxygen fugacity has to be addressed.

Although the isotopic homogeneity of iron in the early solar nebula has been demonstrated [8], different groups of meteoritic materials clearly exhibit distinct iron isotopic ratios [6-8]. In almost all of these materials (from chondrites to iron meteorites), iron is present in both metallic and oxidized forms. Thus, experimental determination of the fractionation produced during metal segregation is essential to understanding the observed isotopic variability of extraterrestrial materials and to constrain the possible genetic links between different classes of meteorites. Furthermore, the Fe isotope fractionation induced by metal extraction may also give insights into the process of planetary core formation because iron is by far the most abundant component of the metallic phases present in planetary cores and meteorites [9]. As a first step toward an experimental determination of high pressure and temperature processes capable of fractionating iron isotopes, we present results of metal segregation from a silicate melt at various oxygen fugacities.

Materials and methods: The starting material is a glass of anorthite-diopside eutectic composition, classically considered to be a good analog of the 'silicate Earth', to which iron is added in oxidized form. Experiments were performed at high temperature and low oxygen fugacities such that a proportion of the iron was extracted from the silicate melt in metallic form. This was possible because reduced iron readily forms metallic alloys with noble metals such as Pt. This feature is used here to sequester metallic iron in a physically separable form from the residual silicate. In this way glassy and metallic components of the experimental charges can be easily identified and the isotopic fractionation of iron may be quantitatively determined in these two distinct geochemical reservoirs as a function of the redox state of the melt.

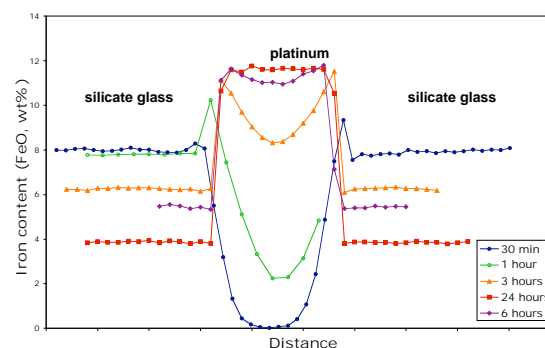


Figure 1: Iron content across a Pt-wire immersed in the silicate melt. Temperature was 1500°C and $\log(fO_2) = -5$. The iron fraction in Pt is homogeneous and constant after approximately 6 hours. The Fe content of residual glasses is a function of the contact surface between silicate and Pt which may change from a sample to another.

Experiments were performed at one atmosphere in gas-mixing furnaces in which the oxygen fugacity can be precisely controlled and the experiments rapidly quenched. The oxygen fugacity varied from $\log(fO_2) = -0.7$ (air), $\log(fO_2) = -8$ (just above the iron-wüstite solid buffer). The temperature was 1500°C. In these conditions, volatilization was not detected by electron-microprobe analyses. The run duration was 24 hours, a time sufficient to attain a good approach to equilibrium. Additional experiments with different run duration indicate that equilibrium is reached after approximately six hours.

and that no significant iron loss was observed after longer experiments (Fig.1).

After quenching, glass chips and platinum were mechanically separated. The silicate fraction was digested in concentrated HF+HNO₃, and the Pt-fraction was dissolved in aqua regia after HF leaching in order to remove any silicate contamination. Fe is purified from the silicate or the Pt matrix using AG-MP1 anion-exchange resin and extracted in HCl2M+H₂O₂ [10]. Elution curves and concentrations determined by ICP-MS indicate that yields are better than 99.6%. Fe isotopic analyses are performed on the hexapole MC-ICP-MS (Isoprobe Micromass, CRPG-Nancy). Argide interferences on masses 54, 56 and 57 are reduced to negligible levels by using the Aridus desolvating nebuliser (without N₂ flow) and Ar+H gases in the collision cell (for ArO and ArN), and by on-peak zero corrections (for ArOH). Instrumental mass bias is corrected using the standard-sample bracketing approach with respect to the IRM-014 Fe isotopic standard. Reproducibility on samples (n=3) is better than 0.1‰ on $\delta^{56}\text{Fe}$ (2 σ).

Results: Microprobe analyses indicate that the iron content decreases continuously in the silicate fraction with the oxygen fugacity (Fig.2) and 99% of the iron is segregated into the Pt-capsule at log(fO₂)=-8.

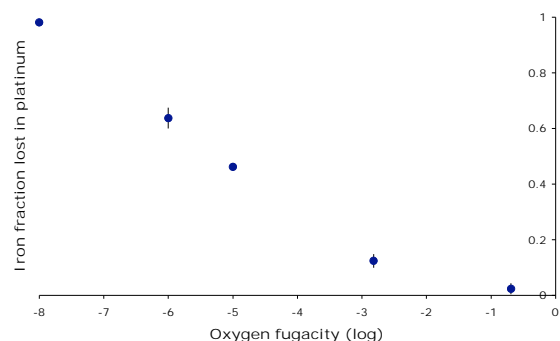


Figure 2: Iron fraction lost from the silicate melt into the platinum as a function of the oxygen fugacity .

Fe isotopic measurements performed on the silicate fractions show heavy $\delta^{56}\text{Fe}/^{54}\text{Fe}$ values ($\delta^{56}\text{Fe}/^{54}\text{Fe} = 0.1\text{--}4.8\text{‰}$, Fig. 3) which are positively correlated with the fraction of iron lost to the platinum. The silicate fraction is thus strongly enriched in heavy isotopes after the partial reduction of iron. By contrast, preliminary Fe isotopic measurements on the metal fraction indicate significantly lighter $\delta^{56}\text{Fe}/^{54}\text{Fe}$ values than in the silicate fraction. These results can be explained by diffusive iron reactions between silicate and metal, and perhaps minor evaporation. We cannot discard

additional evaporation processes because even volatilization not resolvable by microprobe analyses may significantly fractionate the silicate reservoir. Nevertheless, the volatility of iron at 1500°C at one bar pressure is extremely low. If this is confirmed by forthcoming data it should demonstrate that iron isotopes can be fractionated by change of redox conditions at high temperature.

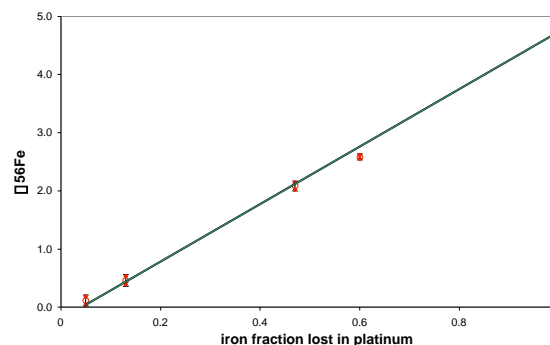


Figure 3: $\delta^{56}\text{Fe}$ in the silicate fractions as a function of the Fe fraction lost in platinum

Conclusion: Recent studies of the iron isotope geochemistry of planetary and meteoritic materials [9] report significant variability between Mars, Vesta, the Earth and the Moon. These variations have been interpreted in terms of partial evaporation processes. However, if our preliminary experimental results are confirmed, additional high temperature diffusive processes may also significantly fractionate iron isotopes. Such mechanisms must therefore also be considered when interpreting iron isotope data relevant to core-mantle segregation during planetary differentiation.

References: [1] Halliday A. N. et al. (1998) *Geochim. Cosmochim. Acta* 67, 2879-2891. [2] Beard B. L. et al. (1999) *Science*, 285, 1889-1892. [3] Dauphas N. et al. (2004) *Science*, 306, 2077-2080. [4] Zhu X. K. et al. (2002) *Earth Planet. Sci. Lett.* 200, 47-62. [5] Poitrasson et al. (2004) *LPS XXXV, Abstract #1634*. [6] Kehm K. et al. (2003) *Geochim. Cosmochim. Acta* 67, 2879-2891. [7] Beard B. L. and Johnson C. M. (2003) *Geochemical News* 117, 8-13. [8] Zhu X. K. et al. (2001) *Nature* 412, 311-313. [9] Poitrasson et al. (2004) *Earth Planet. Sci. Lett.* 223, 253-266 [10] Marechal et al. (1999) *Chem Geol* 156, 251-273.