

DIFFUSION-DRIVEN FRACTIONATION OF IRON ISOTOPES IN OXIDIZED AND REDUCED SILICATE MELTS. M. Roskosz¹, C.M.O.D. Alexander², J. Wang², N. Dauphas³, B.O. Mysen⁴. ¹LSPES, UMR 8008, Université Lille 1. E-mail: Mathieu.roskosz@univ-lille1.fr. ²DTM, Carnegie Institution of Washington, Washington, DC. ³Department of the Geophysical Sciences, The University of Chicago. ⁴Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC.

Introduction: Chemical diffusion of cations and atoms in silicates and metals can promote large isotopic fractionation [1]. An empirical formula relates the diffusion coefficients of two isotopes of an element to their mass ratios through $D_1/D_2=(m_2/m_1)^\beta$, where 1 and 2 refers to the two isotopes, $D_{1,2}$ are diffusion coefficients, $m_{1,2}$ are atomic masses and β is an empirical coefficient. Despite the limited data available for β , it is likely that its value depends on the structural and chemical properties of the element and of the medium in which diffusion takes place. In this study, we evaluate experimentally the effect of the redox state of Fe on diffusion-driven isotopic fractionation. We focused on Fe isotopes because they probe various critical differentiation processes in meteorites and planetary bodies [2].

Experimental: Diffusion couples were prepared from CaMgSi₂O₆ and Fe-bearing CaMgSi₂O₆ glasses previously prepared from isotopically normal, high-grade purity oxide and carbonate powders. Experiments were performed in a piston-cylinder apparatus at 1 GPa pressure to prevent convection in the melts. The run temperature was 1630°C, a temperature that ensures that samples were entirely molten at any redox condition and for any Fe content. Soret effects on Fe content could not be observed even after runs of 12 hours for initially homogeneous Fe-bearing melts. Typical experimental runs were much shorter (less than one hour). Samples were either loaded in graphite capsules to produce very reduced melts or a double Pt capsule with solid PtO₂ buffers that was developed to produce oxidized melts and avoid diffusion of Fe into the Pt capsules because this produces large isotopic fractionations [3].

Results: After quenching, samples were mounted in epoxy for EMP analyses. Diffusion profiles were quantified and modeled to extract diffusion coefficients for ferrous (Fe²⁺) and ferric (Fe³⁺) iron in diopside melts. Even at this high temperature, when diopside liquid has a very low viscosity, there is a significant difference in diffusion rates - Fe²⁺ diffuses faster than Fe³⁺ by a factor of 1.5. Fractionation of Fe isotopes along these compositional gradients are currently being measured by SIMS (Cameca 6f) and laser ablation ICPMS.

Discussion: The structural role of iron in silicate melts is relatively well known. Ferrous iron is a network modifying cation (like Ca²⁺ and Mg²⁺) and generally occupies octahedral sites. Conversely, ferric iron is a network forming cation (like Al³⁺ and Si⁴⁺) and occupies tetrahedral sites in the melt structure. Our results provide a direct quantification of the effect of the structural environment of iron on its diffusion. Because isotopes fractionation also critically depends of the coordination state and of the nature and strength of chemical bonds, our results allow us to provide physico-chemical significance of the β coefficients and therefore open the opportunity to predict β values for a wide range of elements.

References: [1].Richter F. et al. (2003) *GCA* 67, 3905-3923. [2].Dauphas N. and Rouxel O. (2006) *Mass. Spec. Rev.* 25, 515-550. [3] Roskosz M. et al. (2006) *EPSL* 248 (3-4), 851-867.