

## Divalent Germanium: Stable at Low Oxygen Fugacity and Highly Incompatible in Olivine

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In the Earth's upper mantle and crust, Ge is almost exclusively tetravalent (Ge<sup>4+</sup>). Divalent Ge (Ge<sup>2+</sup>) has never been observed in silicate or oxide minerals. However, it has been inferred that Ge<sup>2+</sup> may be stable in silicate melts under reducing conditions, based on metal-silicate partitioning experiments [1-4]. Whether this species was stable at conditions relevant to Earth's core formation has been unclear due to conflicting data from different studies.

In this work, we present X-ray absorption spectra of a series of silicate glasses quenched from melts equilibrated over a wide range of oxygen fugacity. The spectra show that the transition between predominantly Ge<sup>2+</sup> to predominantly Ge<sup>4+</sup> occurs over the range of relative oxygen fugacities from  $\Delta IW-2$  to  $\Delta IW+2$ , where IW is the iron-wüstite oxygen buffer in logarithmic units. Modelling of EXAFS gives the Ge<sup>2+</sup>-O bond length as  $1.89 \pm 0.03$  Å. Olivine-melt partitioning experiments were also conducted, which show that Ge<sup>2+</sup> is highly incompatible, with  $D_{\text{Ge}^{2+}}^{\text{olivine-melt}} < 0.005$ , whereas  $D_{\text{Ge}^{4+}}^{\text{olivine-melt}}$  is  $\sim 0.6$ .

The redox speciation of Ge must therefore be considered when modelling magmatic processes such as Earth's core formation and the generation of partial melts on other planetary bodies where prevalent oxygen fugacities are near saturation with Fe-rich metal, such as the Moon. In particular, the highly incompatible nature of Ge<sup>2+</sup> can provide a simple explanation for the anomalous enrichment of Ge in KREEP basalts, which was previously ascribed to lunar mantle metasomatism [5].

[1] Schmitt, Palme & Wänke (1989), *Geochim. Cosmochim. Acta.* 53, 173-185. [2] Capobianco, Drake & de'Aro (1999), *Geochim. Cosmochim. Acta.* 63, 2667-2677. [3] Kegler & Holzheid (2011), *Eur. J. Mineral.* 23, 369-378. [4] Siebert, Corgne & Ryerson (2011), *Geochim. Cosmochim. Acta.* 75, 1451-1489. [5] Dickinson, Taylor, Keil & Bild (1989), *Proc. 19<sup>th</sup>. LPSC.* 189-198.