

## Changes in the coordination and valence state of Ge in silicate melts at conditions relevant to core formation

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The Earth's core formed from the segregation of metal and silicate in a magma ocean. This magma ocean is thought to have been deep, and the oxygen fugacity ( $fO_2$ ) would have been low (pressures over 30 GPa and  $fO_2 \sim IW-2$ , where IW is the iron-wustite  $fO_2$  buffer) [1]. Many models of core formation rely on metal-silicate partition coefficients of trace elements. These can be affected by both  $fO_2$  and pressure, especially if there are changes in an element's valence state or coordination number (how many oxygens it bonds with).

This study investigates the valence state and coordination of Ge as a trace element in silicate melt. Ge is a moderately siderophile element that is used in models of Earth's core formation.  $Ge^{4+}$ , the stable oxidation state in the Earth today, is chemically similar to  $Si^{4+}$ . Since Si is known to undergo pressure-induced coordination changes in natural melts,  $Ge^{4+}$  might do the same. In addition, several metal-silicate partitioning studies have suggested that the valence of Ge might change from 4+ to 2+ at low  $fO_2$  [2].

A series of Ge-doped silicate glasses were prepared by quenching melts in a piston cylinder apparatus at various pressures and  $fO_2$ . Ge K-edge X-ray Absorption Near Edge Structure (XANES) spectra of the glasses were recorded at the Australian Synchrotron. Additionally, the partitioning of  $Ge^{4+}$  between olivine and melt was determined as a function of pressure, temperature and composition.

The XANES spectra indicate that the average coordination number of  $Ge^{4+}$  increases at pressures > 4 GPa. The partitioning experiments show that the distribution coefficient for  $Ge^{4+}$  and  $Si^{4+}$  between olivine and melt ( $K_d^{Ge-Si_{ol-melt}}$ ) decreases with increasing pressure, which is consistent with a change in coordination. A change in the XANES spectra of glasses prepared at low  $fO_2$  was also observed, which is interpreted as the first spectroscopic evidence of  $Ge^{2+}$  in silicate a melt. The partitioning behaviour of  $Ge^{2+}$  is not well known.

[1] Wood, Walter & Wade (2006) *Nature* **441**, 825-833. [2] Kegler & Holzheid (2011) *Eur. J. Mineral.* **23**, 369-387.