

Coordination changes of trace elements in silicate melts with pressure

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Natural silicate magmas contain networks of Si^{4+} and Al^{3+} cations in tetrahedral coordination with oxygen. With increasing pressure, higher coordination numbers become stable. This has major implications for the physical properties of the melt, but there are also chemical implications. If the coordination number of an element increases, the element's partial molar volume in the melt decreases, which changes the way that element partitions between the melt and other phases. Studies of partitioning, particularly of trace elements, are widely used for understanding geochemical processes. Despite this, there has been very little research on coordination changes of trace elements in melts; so far, only Ni^{2+} , Co^{2+} and W^{4+} have been investigated. No change was observed for W^{4+} up to 4 GPa [1], whereas Co^{2+} undergoes a 50% 4- to 6-fold coordination change by 10 GPa [2], and Ni^{2+} completely changes from 4- to 6-fold by 4 GPa [1].

In this study, we investigated the coordination of Ge^{4+} and Ga^{3+} at trace levels in CMAS glasses quenched from up to 6 GPa and 1650 °C. X-ray absorption near edge structure (XANES) spectra changed systematically with pressure for both elements in these glasses, which is consistent with a partial change in coordination. The most dramatic change was seen for both elements between ~3-4 GPa in one melt composition, suggesting that changes in the major element structure might be affecting the local environment of both trace elements. To investigate this, nuclear magnetic resonance spectroscopy will be used to study the environments of Si, Al, Mg and Ga in similar glasses.

Such a coordination change is expected to cause a change in partitioning for Ge^{4+} and Ga^{3+} , and this has two potential applications. Firstly, Ge^{4+} partitioning between silicate melts and minerals has potential to be used as a tool for determining the depth of magma origins. Secondly, partitioning between silicate melt and metallic melt is the basis of geochemical models of Earth core formation, and as moderately siderophile elements, an understanding of the partitioning data for Ge^{4+} and Ga^{3+} at high pressures is necessary for these models.

- [1] Jones (2012), PhD Thesis, Australian National University.
[2] Keppler and Rubie (1993), *Nature* **364**, 54-56.