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Pressure-induced coordination change of Ge^{4+} and Ga^{3+} in silicate melts

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In geochemical systems, the relative stability of a given element in one phase or another is known as its partitioning behaviour, and many models of Earth processes are based on the changes in partitioning with pressure (and/or other intensive variables). Since higher pressures favour smaller volumes, changes in partitioning with pressure can be predicted if the pressure-dependence of the volume of each phase in the system is known. Volumes of mineral phases can be measured at high pressure, but partial molar volumes of melt components can only be measured at 1 atm. The partial molar volume of a melt component may change with pressure because of the mechanisms of melt compression, such as coordination changes. Si^{4+} and Al^{3+} , major cations in natural melts, are tetrahedrally coordinated by oxygen at ambient pressure but convert to octahedral coordination at higher pressure. Similar coordination changes may occur for trace cations, yet few have been studied. In this work, x-ray absorption near edge structure (XANES) spectroscopy was used to show a partial coordination change beginning at ~3-4 GPa for trace Ge^{4+} and Ga^{3+} in synthetic silicate glasses, quenched from high-pressure melts. Such coordination changes will affect the partitioning behaviour of Ge and Ga between silicate melt and other minerals, and thus have implications for geochemical models such as the depth of formation of erupted magmas and the formation of the Earth's core.

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