

Experimental and theoretical constraints on the chemical evolution of the outer core

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The chemical evolution of the outer core is controlled by chemical transfer across its upper and lower boundaries. Chemical exchange at the upper boundary with the mantle may be driven by a variety of processes, including an initial disequilibrium between core and mantle at the high pressure and temperature of their interface. A key question is whether chemical transport across the core-mantle boundary (CMB) is rapid enough to allow significant exchange over Earth's history. During the last several years, experimental evidence has accumulated for substantial solubility of Si and O in liquid iron at core-mantle boundary conditions [e.g. 1, 2]. Dissolution of these elements into the outer core may have left behind an insoluble layer of nearly pure periclase (MgO) that regulated further exchange. Silicate liquids also may have played an important role in exchange between the core and mantle, especially early in Earth history. Recent experimental and theoretical work on diffusion in periclase and silicate liquids under high pressure provide constraints on the magnitude of chemical exchange that may be possible across the CMB.

Precipitation of solid metal at the lower boundary of the outer core also may have important consequences for its chemical evolution. The inner core is small, accounting for only 5% of the core's mass, but may sequester some highly siderophile elements in high enough concentration to alter their proportions in the outer core. Such fractionations may impart a distinctive geochemical signature on the outer core [3]. Partitioning of elements between solid and liquid metal alloys depends on pressure, but even more so on the composition of light elements in the liquid. Experimental studies of partitioning in the relevant systems are beginning to paint a picture of how siderophile elements might behave during inner core crystallization, and the geochemical signatures that may result.

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Titanium complexation in Cl- or F-bearing high pressure-temperature aqueous fluids: New results from *ab initio* molecular dynamics

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The behaviour of high field strength elements (HFSE) in high pressure (P) high temperature (T) aqueous fluids remains poorly understood. Traditionally considered to remain immobile, recent experiments show elevated solubility of for example rutile in aqueous fluids in the presence of Na-Al-Si oligomers and polymers [1]. Likewise, field observations from high pressure metamorphic terranes show ample evidence for enhanced Ti mobility, possibly mediated through complexing halides [2].

To provide atomic-scale insight into the effects of halides on HFSE behaviour, we use *ab initio* molecular dynamics on small systems containing 64 water molecules. Here, we present new results showing, for the first time, direct observations of the extent of fluoride and chloride association with titanium in pure water at $T = 1000$ K and fluid densities in the range 880-1265 kg m⁻³ ($P \sim 0.9$ -3.7 GPa).

An important result is that direct Ti-Cl or Ti-F bonding is never observed in these simulations, but that association occurs through an intermediate, shared hydration shell containing hydroxide ions. Titanium to halide distance analyses show that at high pressure, a shared hydration shell configuration with fluoride is more persistent than is the case for chloride. Discrete HCl and HF species are not observed under these conditions. Previously, we showed that the first shell Ti-O coordination number in pure water at $T = 1000$ K increases from below five at low density to six at intermediate to high density [3]. The addition of halide ions suppresses this change of coordination number with density at 1000 K such that lower coordination prevails over a larger density range.

The more marked association of titanium with fluoride than with chloride make fluoride complexation a suitable candidate to explain enhanced titanium mobility in metamorphic aqueous fluids.

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