

Ferrous iron diffusion in ferro-periclase across the spin transition – A DFT study

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Diffusion is believed to control the viscosity of lower mantle minerals. While diffusion-experiments are limited to conditions of the shallow lower mantle, *ab initio* methods allow us to calculate absolute diffusion rates at any pressure and temperature [1,2]. The effect of the spin-transition in ferro-periclase on rheology is currently unknown.

We here present results of density-functional-theory calculations on absolute diffusion rates of high- and low-spin ferrous iron in ferro-periclase. The diffusivity of high- and low-spin iron depends on the physical conditions (pressure and temperature), iron concentration and the value of the chosen Hubbard U. We find that low-spin iron swaps back to high-spin during migration, such that the difference between high- and low-spin migration enthalpies only depends on the energy-difference of the ground-states.

We compared our absolute diffusion rates with experimental data of magnesium-iron interdiffusion in ferro-periclase at temperatures between 1873 K and 2273 K and at pressures ranging from 7 GPa to 35 GPa. All our diffusion rates are in excellent agreement with all the available experimental data.

Our results show that throughout the Earth's lower mantle, iron diffuses at a similar rate as magnesium. Thus, the spin transition of ferrous iron has no significant impact on the rheology of ferro-periclase in the Earth's lower mantle, and ferro-periclase remains much weaker than perovskite throughout. We conclude, therefore, that ferro-periclase can only control the viscosity of the mantle in regions where it becomes interconnected, such as areas of high strain around slabs or near plumes. At much higher pressures, such as in Super-Earths, low-spin iron diffusion is expected to become much slower than magnesium, making ferro-periclase more viscous than pure periclase.

[1] Ammann, Brodholt & Dobson, (2010), *Reviews in Mineralogy and Geochemistry* **71**, 201-224. [2] Ammann, Brodholt, Wookey & Dobson (2010), *Nature* **466**, 462-465. [3] Ammann, Brodholt, & Dobson (2011) *Earth Planet. Sc. Lett.* **302**, 393-402.

Chromium isotopes in the world's oceans: Potential tracers of redox environments

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We have developed a method for extracting and separating chromium (Cr) from a seawater matrix for isotope analysis using TIMS. We investigated a variety of ion exchange resins and co-precipitators to determine the optimal extraction method. Reported abundances of total Cr in seawater range from ~70 – 500ng/kg, depending upon seawater oxicity, water depth and proximity to continental land masses. A 500ml sample size permits ~10 duplicate analyses on TIMS which requires a minimum of 10ng of Cr. The reagent blanks are <2ng Cr and yields are high. Cr has four naturally occurring stable isotopes and therefore lends itself to double spiking for improved precision. We use a well constrained and optimized double spike of ⁵⁰Cr and ⁵⁴Cr [1].

Data will be presented on the distribution of Cr in major ocean basins, and the extent of isotope fractionation will be compared in oxic/anoxic waters, deep waters, and shelves. Building a global map of marine, Cr isotopes will facilitate a better understanding of the global geochemical and biogeochemical chromium cycle. Speciation analysis of seawater Cr is at odds with theoretical models and thermodynamic data. Both the trivalent and hexavalent ions (Cr(H₂O)₄(OH)₂⁺ and CrO₄²⁻) should be present in seawater in solubility equilibrium with the atmosphere, with a predominance of the +6 species. Observational analysis suggests that the system is in disequilibrium suggesting active cycling of Cr species [2]. The two naturally occurring oxidation states of chromium, +3 and +6, have distinct chemical properties and behaviour, with the potential for partitioning and isotopic fractionation between different reservoirs. Cr isotope fractionation in groundwater, of up to 6‰, have been attributed to redox changes [3].

[1] Galer (2007), *Geochim. Cosmochim. Acta*, **71** (15S), A303. [2] Elderfield, (1970) *EPSL*, **9**, 10-16 [3] Ellis *et al.*, (2002), *Science*, **295**, 2060.