

High *P-T* experiments and first principles calculations of the diffusion of Si, O, Cr in liquid iron

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Diffusion transport properties of molten iron and iron alloys at high pressures and temperatures are important for understanding large-scale geodynamic processes and thermochemical evolution of planetary interiors, such as the time and length scales of metal-silicate equilibration during core formation and chemical exchange across core-mantle boundaries during cooling. The density of the Earth's outer core is $\sim 10\%$ too low to be composed of pure Fe-Ni and is assumed to contain significant concentrations of light elements, such as Si, S, O, and/or C, in addition to siderophile transition metals (V, Cr, Mn, W) which are depleted in the Earth's mantle relative to chondrites. The chemical diffusivity of light and siderophile elements in liquid iron under *P-T* conditions of the Earth's core and its formation are therefore required to constrain the composition and potential chemical stratification of planetary cores, in addition to the kinetics of chemical buoyancy from inner core crystallization that partially drives the geodynamo. In order to better understand the effects of pressure and temperature on Si, O, and Cr diffusion in liquid iron, we have conducted (1) chemical diffusion-couple experiments combined with numerical modeling of diffusion profiles to account for non-isothermal annealing, and (2) first principles molecular dynamic (FP-MD) calculations from ambient pressure to 135 GPa and 2200-5500 K.

Experimental diffusion couples comprised of highly polished cylindrical disks of 99.97% Fe and metallic Fe alloy were contained within an MgO capsule and annealed within the *P-T* range 1873-2653 K and 1-18 GPa using a multi-anvil apparatus. A series of experiments are conducted at each pressure using variable heating rates, final quench temperatures (T_f), and time duration at T_f . Recovered capsules were cut and polished parallel to the axis of the cylindrical sample and measured using EMPA 10 μm -step line scans. To extend our dataset to *P-T* conditions of the Earth's core-mantle boundary, first principles molecular dynamics (FP-MD) simulations were performed based on density-functional theory and implemented using VASP code. Fe supercells of 150 atoms are overheated to induce melting, compressed to volumes along several isobars (0.0001-135 GPa) according to densities from the liquid iron equation of state, and allowing for changes in chemistry (Si, O, Cr). Diffusion coefficients are computed from atomic trajectories in the simulation cell via the Einstein relation.

Our findings corroborate theoretical estimates that diffusion coefficients are scalable to absolute melting temperature (T_m) yielding constant Si, O, and Cr diffusivities of approximately $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ along the melting curve from ambient to core pressures. A simple homologous temperature relation can therefore be used to predict diffusion rates relative to the melting curve. The homologous temperature activation term determined from FP-MD calculations for Si diffusion is larger by a factor of 1.3 than the value determined from experiments but diffusion coefficients at T_m are identical within error for both two methods. Verification of a homologous temperature relation for chemical diffusion in liquid iron implies that low-pressure experiments can be used as accurate analogues of mass transport properties of the Earth's outer core.