

## Chemistry of the Earth's core and reactions at the core-mantle boundary

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The density deficit of the Earth's core indicates that one or more light elements must have partitioned into the core during its formation. We have studied the partitioning of the light elements O, S and Si between liquid Fe metal and mantle phases as a function of pressure and temperature in multianvil and diamond anvil cell devices. We use experimental observations of liquid immiscibility in various Fe-light element systems to derive excess mixing properties for light elements in Fe metals. Knowledge of these properties strengthens models for the partitioning of these elements when extrapolated to core-mantle boundary conditions. Our results indicate that Si has a strong ternary interaction in Fe-metal liquids, which decreases the proportions of other light elements that partition into Fe. Modelling core formation thus indicates that Si is likely to be the major light element in the core. Our results indicate that the core is undersaturated in both Si and O with respect to the bulk of the mantle, implying that both O and Si will be extracted from the mantle at the present day core-mantle boundary. This will leave a layer at the base of the mantle that is strongly depleted in  $\text{SiO}_2$  and FeO, which will be composed essentially of MgO. The high melting temperature of MgO ensures that the mantle remains solid at the boundary. Formation of a refractory MgO-rich layer may have also limited reactions between the core and a basal magma ocean towards the final stages of accretion or caused the basal magma ocean to rapidly crystallise as an MgO-rich layer. Alternatively, or in addition, reactions at the CMB may result in the core developing a thin buoyant outer layer that is strongly enriched in the light elements Si and O.

## SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model

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Based on a review of the current state of knowledge concerning the aqueous alteration of SON68 nuclear glass GRAAL (Glass Reactivity with Allowance for the Alteration Layer) mechanistic model has been proposed [1] : An amorphous layer at the glass/solution interface gradually reorganized by hydrolysis and condensation mechanisms constitutes a barrier against the transport of water toward the glass and of solvated glass ions into solution [2]. The existence of this transport-inhibiting effect rapidly causes this layer to control glass alteration. The reaction affinity responsible for the glass alteration rate drop is expressed with respect to this passivating reactive interphase (PRI). Some glass constituent elements precipitate as crystallized secondary phases on the external surface and can sustain glass alteration. Correctly modeling the seat of recondensation (PRI or secondary crystallized phases) of elements is a key point for understanding their effect on glass alteration. Describing not only (1) solution chemistry but also ion transport (2) in solution by at a macroscopic scale and (3) by reactive interdiffusion in the PRI at a nanometer scale by means of a single model at each point in space and time is a complex task. Most existing models describe only one or two of these aspects. GRAAL describes a simple and still effective manner of coupling these three phenomena using a calculation code coupling chemistry and transport HYTEC [3]. The model results are compared with experimental data for SON68 glass leached in initially pure water both in a closed system and in renewed media. The comparison shows the model very satisfactorily accounts for variations in the pH and the element concentrations in solution as a function of time, glass surface area in contact with solution, and solution renewal rate. Interdiffusion through the PRI cannot be disregarded under most experimental conditions — if only to predict the solution pH — and is therefore an integral part of the geochemical model.

- [1] Frugier *et al.* (2008) *Journal of Nuclear Materials* **380**, 8-21. [2] Cailleteau *et al.* (2008) *Nature Materials* **7**, 978-983. [3] Van der Lee *et al.*, (2003) *Computers & Geosciences* **29**, 265-275.