

Deep Time: How did the early Earth become our modern world?

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One of the salient challenges in Deep Time studies is understanding how the Earth made the transition from early violent events –accretion, core formation, and impacts– to the rather normal equable conditions recorded in the Hadean Jack Hills zircons, with oceans, granitic crust derived in large part from partial melting of mature sediments, and perhaps even dynamical behavior similar to plate tectonics¹. An unresolved question is how the Earth's deep volatile cycles evolved through this time. One interpretation is that the combination of core formation, magma ocean degassing, and atmospheric loss produced an early mantle largely devoid of volatiles, which were then added chiefly in a late veneer. But if the late veneer was mixed in to the mantle only gradually over time scales of $> 1 \text{ Ga}^2$, then the Hadean near surface environment would have been dominated by super-oceans, flooding protocontinents and massive supracrustal storage of C, presumably as carbonate. Similarly, the consequences of a nearly volatile-free mantle on mantle dynamics and tectonics are poorly understood. However, there is reason to believe that a significant portion of Earth's present-day volatiles were delivered to the mantle prior to the late veneer. At a minimum, the distinct noble gas compositions of the mantle and atmosphere require retention of some early (including nebular) volatiles in the mantle. But more importantly, H/C³ and N/C⁴ ratios of the bulk silicate Earth demonstrate that Earth's major volatile inventories remember the processing associated with magma ocean and core formation stages, suggesting that significant fraction of Earth's early volatiles avoided catastrophic escape or core sequestration. The mechanisms of this retention are poorly understood, but may have been critical to the early approach to dynamical and climatic stability.

[1] Hopkins *et al* (2008) *Nature* **456** 493-456. [2] Maier *et al* (2009) *Nature* **460** 620-623. [3] Hirschmann&Dasgupta (2009) *Chem. Geol.* **262** 4-16. [4] Marty (2012) *EPSL* **313** 56-66.

Chemical diffusion in the deep Earth: Is it all about grain boundaries?

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Diffusion of chemical species in Earth's interior plays a controlling role in many of the large-scale processes which first formed and continue to reform the Earth through time. Traditionally, diffusivity of species has been considered to occur under subsolidus conditions mainly via lattice diffusion; i.e. the movement of species through bulk crystal structures. Recently however, researchers have started to attempt to constrain the importance of grain boundary diffusion (GBD) in the deep Earth: i.e. the mobility of species along grain boundaries. Grain boundaries provide alternative, fast pathways for mobile species which may be chemically and structurally very distinct from the bulk crystalline structure of polymineralic materials. It has recently been suggested that GBD provides a mechanism for transporting highly incompatible elements from the core into regions of lower mantle melting, and is an important component of H mobility in the upper mantle. Here we present results from an experimental study aimed at constraining the importance of GBD in 3 geochemically important but contrasting systems: H mobility in olivine, Li diffusion in olivine and Ti diffusion in quartz.

Experimental data demonstrate similar diffusivities for GBD and lattice diffusion of H under mantle conditions. When scaled to mantle grain sizes, results suggest that GBD of H is of minor importance, except at marked discontinuities in the mantle where there are abrupt changes in H solubility. In contrast, data suggest that GBD of Li is between 2 and 4 orders of magnitude faster than lattice diffusion. Differences in the behaviour of H and Li can be understood in terms of incorporation mechanisms and the contrasting nature of crystalline material vs relatively amorphous grain boundaries. Critically, these differences result in contrasting temperature dependences for GB vs lattice diffusion which imply that GBD always dominates at low temperatures. Similarly, we find that GBD of Ti in polycrystalline quartz is orders of magnitude faster than lattice diffusion, as result which has immediate implications for the applicability of the Ti in quartz geothermometer. Based on these results, we present a predictive model for determining the relative importance of GBD in the deep Earth.