

## The rheological properties of post-perovskite and implications for D''

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We have used first principles methods to calculate *absolute* diffusion rates in MgSiO<sub>3</sub> perovskite and post-perovskite. The nudged elastic band method was used to find the minimum energy diffusional pathways and harmonic transition state Vineyard theory for the attempt frequency and entropy. Our calculated diffusion rates for perovskite are in excellent agreement with available experimental data, and provide confidence for our results on post-perovskite where no experimental data exist. We find that post-perovskite has exceptionally anisotropic diffusion rates. As might be expected, Si and Mg are slowest in the [010] direction – which is perpendicular to the layers of silica octahedra – and is several orders of magnitude slower than within the layers. Even within the layers diffusion is very anisotropic, with Si and Mg diffusing as much as four orders of magnitude faster in the [100] direction than [001]. On average diffusion in post-perovskite is significantly faster than in perovskite. This is supported by deformation experiments in the CaIrO<sub>3</sub> analogues. This could explain the requirement of recent long-period geoid models for a laterally varying viscosity in the lowermost mantle.

How a strongly anisotropic material deforms under low stresses is not clear. Although it is generally believed that diffusion creep does not produce a lattice preferred orientation (LPO), this may not be true for a diffusionaly very anisotropic material. Moreover, we would expect a significant history-dependent rheology in D'', with the development of fast diffusion creep as grains become increasingly oriented. This may lead to localised shear-zones that separate large regions undergoing little deformation. One could envisage a scenario where a large-scale LPO was developed during an initial period of dislocation creep, with later deformation occurring along shear-zones. The original LPO would be preserved, but it would not necessarily represent the current strain regime. Attempts to correlate observed anisotropy within D'' with current flow would, therefore, be incorrect. The development of shear-zones may also permit regions of different anisotropy to become adjacent; this may be an alternative explanation for rapid changes in seismic properties seen in some parts of D'' that are currently explained as being due to a combination of varying composition and temperatures.

## REE-SiO<sub>2</sub> systematics and the origin of intra-oceanic arc felsic magmas

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Two very different processes are commonly invoked to explain the origin of intra-oceanic arc felsic (> 63 % SiO<sub>2</sub>) magmas. These include fractional crystallization of basaltic magma and partial melting of lower crustal amphibolite. A commonly under-appreciated aspect of Rare Earth Element (REE) solid-liquid partitioning behavior is that  $D_{\text{REE}}$  for most common igneous minerals increase significantly with increasing liquid SiO<sub>2</sub> contents. For some minerals (e.g., hornblende and augite), REE partitioning can change from incompatible ( $D < 1$ ) at low liquid SiO<sub>2</sub> to compatible ( $D > 1$ ) at high liquid SiO<sub>2</sub>. Incorporation of this partitioning behaviour into mass-balance models for both amphibolites melting and basalt fractionation yields the following general predictions for felsic magmas. Partial melting of amphibolite yields REE abundances that remain essentially constant and then decrease, or steadily decrease with increasing liquid SiO<sub>2</sub> content. At high liquid SiO<sub>2</sub> contents LREE abundances should be slightly-enriched to slightly depleted (i.e.,  $C_1/C_0 \sim 2 - 0.2$ ) while HREE abundances should be slightly depleted ( $C_1/C_0 \sim 1 - 0.2$ ). Lower crustal hornblende-bearing basalt fractionation should yield roughly constant REE abundances with increasing liquid SiO<sub>2</sub> and exhibit only slight enrichment ( $C_1/C_0 \sim 1.2$ ). Mid to upper crustal hornblende-bearing basalt fractionation should yield steadily increasing LREE abundances but constant and then decreasing HREE abundances. At high liquid SiO<sub>2</sub> contents LREE abundances may range from non-enriched to highly enriched ( $C_1/C_0 \sim 1-5$ ) while HREE abundances are generally non-enriched to only slightly enriched ( $C_1/C_0 \sim 1-2$ ). Hornblende-absent basalt fractionation should yield steadily increasing REE abundances with increasing liquid SiO<sub>2</sub> contents. At high SiO<sub>2</sub> contents both LREE and HREE are highly enriched ( $C_1/C_0 \sim 3-4$ ). It is proposed that these model predictions constitute a viable test for determining a fractionation or amphibolite melting origin for felsic magmas in intra-oceanic arc environments where continental crust is absent.