

Nature of mantle heterogeneities

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Seismic studies have revealed discontinuous changes and lateral variations in velocities at different depths in the mantle. While temperature variation is an important factor, the interpretation of some large-scale mantle structures requires compositional variation. However, the composition of the heterogeneities remains unclear (e.g. primordial or recycled).

Our high-resolution seismic GRT imaging revealed discontinuities at 300, 540, 800 km depths beneath Hawaii [1]. The silica phase transitions can explain the shallower discontinuities. The post-stishovite transition in an Al-rich rock or the post-garnet transition in a Si-rich rock can explain the deeper discontinuity. We also found splitting of the 520 discontinuity (to 520 and 540), which can be related to the exsolution of CaSiO_3 perovskite in a Ca-rich rock. These suggest a significant amount of recycled materials (e.g. basalt) in the upper mantle beneath Hawaii.

In the mid-mantle, Fe^{3+} in perovskite [2] and Fe^{2+} in ferropericlasite [3] undergo high spin to low spin transitions. Although these transitions are unlikely to cause seismic discontinuities, the spin transition of Fe^{3+} in perovskite may change the bulk sound speed of Al-rich heterogeneities (such as basalt) at 1700-2000 km depth, where lateral variations in bulk sound speed have been documented seismically [4].

The effects of Al in the lowermost mantle would make the perovskite-to-postperovskite boundary seismologically undetectable in pyrolite [5, 6]. Our new experiments reveal that the boundary is seismically detectable in harzburgite and basalt due to element partitioning with ferropericlasite and silica, implying that the observation of the D'' discontinuity is related to a significant presence of recycled materials in the lowermost mantle [6].

This series of studies implies that differentiated rocks (e.g. basalt) injected into the mantle by subducting slabs may exist over the entire depth range of the mantle and survive over geologic time scales.

[1] Cao *et al.* (2011) in review. [2] Catalli *et al.* (2010) *EPSL*. [3] Badro *et al.* (2003) *Science*. [4] Trampert *et al.* (2004) *Science*. [5] Catalli *et al.* (2009) *Nature*. [6] Grocholski *et al.* (2011) in review.

Electrolyte ion adsorption at the hematite/water interface: A cryogenic X-ray photoelectron spectroscopy study

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Cryogenic X-ray photoelectron spectroscopy was used to probe monovalent ions (Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , F^- , Cl^- , Br^- , I^-) associated to the hematite/water interface. Our findings revealed coexisting cations and anions both below and above the isoelectric point of hematite. Surface loadings tend to follow the trend in the ionic radii of both alkali metal and halide ions. Chloride loadings are largely unaffected by the identity of the associated alkali metal ion. Sodium loadings are, on the other hand, considerably affected along the halide series (Fig. 1). Sorption of ammonium ion occurs by hydrogen bonding to surface hydroxyl groups, a mechanism shifting the pK_a of NH_4^+ from 9.3 in water to 8.4 at the interface.

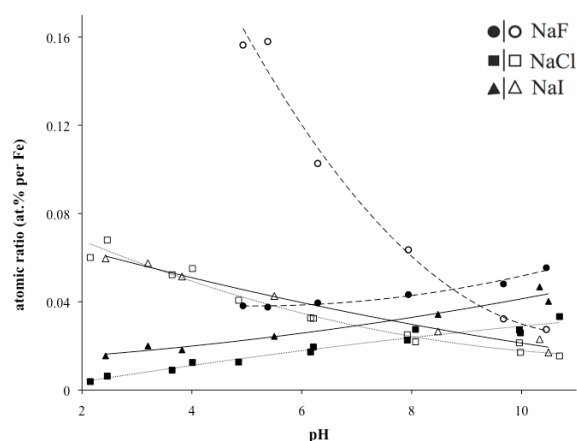


Figure 1: Surface loadings of electrolytes sodium (closed symbols) and halide (open symbols) ions ($I=50$ mM).