

Generation of HIMU and EM-1 reservoirs by CO₂-fluxed lower mantle melting: Implications for OIBs, kimberlites and carbonatites

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A New Paradigm

P/D isotope ratios of enriched mantle (EM) and high- μ (HIMU) reservoirs sampled by OIBs, CFBs, kimberlites and carbonatites are produced by CO₂-fluxed lower mantle (LM) melting [1]. Our model resolves the long-standing conjecture regarding the formation of HIMU and EM.

Modelling and Implications

Using measured or inferred partition coefficients, we show that U/Pb, Rb/Sr, Sm/Nd, Lu/Hf, and Re/Os ratios of EM are associated with C-rich melts while residues evolve to HIMU [1]. LM melting occurs in thermochemical upwellings by carbonate suppression of the liquidus. End-members originate in domains isolated from whole mantle convection. Melts with > 1% CO₂ and residues are variably buoyant allowing spatial separation of EM and HIMU. HIMU is a refractory residue with long LM residence time and thus it evolves to extreme isotopic compositions. EM is a melt that reacts with ambient mantle and does not produce such extreme isotope ratios. Entrainment in plumes transports EM and HIMU domains at different ascent rates to magmagenetic zones at the top of the LM and in the transition zone.

HIMU does not involve hydrothermally altered oceanic crust, and EM does not require entrainment of continent-derived sediment. Generating EM and HIMU by a single melting process from pristine mantle explains the presence of primitive rare gas end-member isotope ratios in mantle plume magmas as well as constraints of the Pb isotope paradoxes. Carbon in the deep mantle clearly plays an important role in Earth's geochemical evolution. Kimberlites, carbonatites and OIBs all preserve an isotopic record of their LM pedigree.

[1] Collerson *et al.*, (2010) *PEPI*, **181**, 112-131.

Ferric iron geometry and coordination during hydrolysis and ferrihydrite precipitation

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Definitive structural characterisation of ferrihydrite has challenged scientists primarily due to its nanosized particles and inherent long-range structural disorder which challenges analytical methodology (and modelling) typically employed to determine the structure of minerals. Here we report on the application of a synchrotron quick-scanning X-ray absorption spectroscopy (XAS) approach, which allows the collection of Extended X-ray Absorption Fine Structure (EXAFS) spectral data to $k = 15 \text{ \AA}^{-1}$ in < 1 minute, to obtain unparalleled iron K-edge data on the hydrolysis of Fe^{III}(H₂O)₆ and ferrihydrite precipitation.

Modelling of the pre-edge and EXAFS data: 1) supports theoretical studies which have suggested the existence of a monomeric penta-coordinated Fe^{III} hydrolysis species and; 2) corroborates recently proposed structural models of ferrihydrite that contain tetrahedral Fe^{III}. Modelling results indicate that ferrihydrite consists of 15 to 25 % tetrahedral Fe^{III} and suggest that this geometry must be included in any comprehensive structural model of ferrihydrite and, furthermore, should be considered when evaluating the reactivity, stability and other structure-property relationships of this mineral.