

## Displaced helium in tilted mantle plumes

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Primordial <sup>3</sup>He is widely thought to be a diagnostic tracer distinguishing mantle plume-related magmas from MORB-type magmas, under the assumption that the deep mantle serves as storage reservoir of primordial <sup>3</sup>He and also as source of mantle plumes. Yet on several high-<sup>3</sup>He/<sup>4</sup>He-hotspots, e.g. Hawaii, Galapagos, and Iceland, the maximum <sup>3</sup>He/<sup>4</sup>He ratio appears to be displaced from the plume center in the direction opposite to that of inferred asthenospheric flow and/or plate motion. We model this process using the assumption that helium initially located in the center of a plume conduit is sequestered into a carbonatite melt forming in the rising plume at a depth of 400 to 600 km. The model predicts that such a carbonatite liquid will ascend rapidly and subvertically through the plume with separation velocities up to a meter per year or more. As the plume is tilted by upper-mantle flow, the carbonatite carrier of the plume helium is displaced in the upwind direction. This can explain the helium maximum at Loihi Volcano for Hawaii, at Fernandina (Galapagos), and possibly the high <sup>3</sup>He/<sup>4</sup>He values on the Reykjanes Ridge. The model also predicts the declining <sup>3</sup>He/<sup>4</sup>He ratios on Mauna Loa, Mauna Kea, and Haleakala, as these volcanoes age, as well as the uniformly MORB-like helium in all post-shield and rejuvenated Hawaiian lavas.

Our model is consistent with the model of Tolstikhin and Hofmann (2005), in which the storage reservoir for primordial solar helium is located in the D'' layer at the base of the mantle, from where it diffuses into the overlying actual source of the mantle plume. The base of this source layer, which subsequently forms the center of the conduit, therefore contains the highest <sup>3</sup>He/<sup>4</sup>He ratio. This plume source consists of a mixture of recycled (oceanic) crustal-lithospheric material and normal depleted mantle peridotite; the radiogenic <sup>4</sup>He derived from its local Th-U content strongly affects the ultimate <sup>3</sup>He/<sup>4</sup>He ratio of a given plume.

## Ion desolvation as a mechanism for kinetic isotope fractionation

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Kinetic processes, including mass-dependent diffusivity differences and boundary-layer reactions, have been invoked to explain non-equilibrium Ca isotopic fractionations observed in calcite precipitation from aqueous solutions [1,2]. Current available data suggest that a 1.6 ‰ kinetic fractionation between <sup>44</sup>Ca and <sup>40</sup>Ca occurs during non-biogenic calcite precipitation [2]. This fractionation cannot be attributed to isotopic diffusion in bulk liquid water, which causes a much smaller fractionation of 0.6‰ [3]. Ion desolvation—both of the crystal surface and of the cations in solution—has been implicated as a rate-limiting step in crystal growth [4,5,6,7], but, to the best of our knowledge, it has not previously been proposed as a mechanism for isotopic fractionation. Here, we carry out the first study of the isotopic mass dependence of metal cation desolvation rates.

To investigate the effect of isotopic mass on desolvation rate, we performed a series of classical molecular dynamics simulations involving one cation (Li<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, or Ba<sup>2+</sup>) and 550 water molecules in a periodically replicated cell. Simulations were performed with two prominent water models (SPC/E and TIP4P) at 278, 298, and 323K for a range of real and hypothetical masses (2-200 Da).

Our results indicate that the desolvation rates  $k_w$  of the alkali metals and at least some of the alkali earths follow an inverse power-law dependence on isotopic mass  $m$  ( $k_w \propto m^{-\gamma}$ ). In other words, lighter isotopes exchange water molecules between their first hydration shell and the bulk liquid more quickly than heavier isotopes of the same species. Preliminary results show that the power-law exponent  $\gamma \sim 0.05 \pm 0.02$  for Ca<sup>2+</sup>, Ba<sup>2+</sup>, Li<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup> at 298 K, with no clear dependence on temperature, water model, or the identity of the cation. Thus, if ion desolvation is the rate-limiting step for calcite precipitation, our preliminary results are consistent with a fractionation between <sup>44</sup>Ca and <sup>40</sup>Ca of ca.  $5 \pm 3$  ‰.

[1] Gussone *et al.* (2003) *GCA* **67**, 1375-1382. [2] DePaolo (2011) *GCA* **75**, 1039-1056. [3] Bourg *et al.* (2010) *GCA* **74**, 2249-2256. [4] Nielsen (1984) *J. Cryst. Growth* **67**, 289-310. [5] Dove & Czank (1995) *GCA* **59**, 1907-1915. [6] Kerisit & Parker (2004) *JACS* **126**, 10152-10161. [7] Piana, Jones, & Gale (2006) *JACS* **128**, 13568-13574.