## 1 Ga old plume-derived peridotite xenoliths from Kauai, Hawaii

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We present the first comprehensive geochemical investigation (major - trace elements, and Hf-Os-Nd-Sr-Pb isotopes) of peridotite xenoliths from Kauai, Hawaii. The xenoliths were collected from six onland and one submarine locations (recovered south of Kauai by the ROV "Tiburon" of the MBARI) within the rejuvenated stage Koloa Volcanics lavas and represent ca. 50km of north-south area coverage.

The Kauai peridotite major and trace element compositions overlap those of abyssal peridotites (the melt residues of MORB), with most samples falling at the depleted end (e.g. cpx: Mg#= 0.906 - 0.93, Na<sub>2</sub>O= 1.5 -<0.03wt %, Ti= 2800 - 150 ppm,  $[Ce/Yb]_N = 7 - < 0.002$ ). Model calculations suggest >17% melt depletion of a MORB-source for the most depleted samples. In Sr-Nd isotope space the cpx extend to both more depleted (MORB-like) and more enriched (similar to Kauai and Mauna Kea tholeiites) compositions than the host lavas (cpx  ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7027 - 0.7037,  $\varepsilon_{Nd}$  = 6.5 - 10). The cpx Hf isotope data ( $\varepsilon_{\rm Hf}$  = 19.5 - 51) plot above the terrestrial array in Hf-Nd space with radiogenic Hf for a given Nd, similar to the Salt Lake Crater peridotites from Oahu [1]. Bulk rock <sup>187</sup>Os/<sup>188</sup>Os ratios range from 0.1195 to 0.1295. The peridotite with the highest <sup>187</sup>Os/<sup>188</sup>Os is the only Hawaiian peridotite analyzed thus far that overlaps Hawaiian shield stage lavas in Os-Sr-Nd-Pb space. This composition cannot be explained by metasomatism of the Pacific lithosphere by tholeiitic melts. The presence of both enriched and depleted (up to 1 Ga old Re-depletion age and 650Ma Lu/Hf model age) isotopic compositions in the Kauai peridotites is difficult to reconcile with an origin from the 100 Ma Pacific lithosphere. Instead, some of these peridotites could be fragments of the Hawaiian plume that are brought to shallower levels (ca. 60km) within the Pacific lithosphere and consistent with seismic observations [2] that argue for large-scale erosion and replacement of the Pacific lithosphere by the Hawaiian plume.

[1] Bizimis et al. (2007) EPSL 257, 259-273. [2] Li et al., (2004) Nature 427, 827-829.

## **Redox-related isotope fractionation**

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The importance of redox related isotope fractionations in Earth & planetary processes is well established [1], and yet the mechanisms by which these processes occur are not as well understood. Recent studies using a potentiostat as a laboratory proxy for environmental redox reactions have shown voltage-dependent isotope fractionations during electrodeposition of Fe [2] and Zn [3]. One hypothesis to explain this data suggests that the observed fractionations are rooted in equilibrium isotope partitioning between product and reactant, and are amplified by the thermodynamic driving force for the reaction [2, 3]. The goal of this study is to distinguish between this hypothesis and one where mass transport is used to explain the fractionation at an electrode.

## **Results and Discussion**

Iron was plated on glassy carbon electrodes as a function of overpotential (vs.  $E^0$  for  $Fe^{(II)}$ - $Fe_{(s)}$ ) and temperature (0, 25, 35°C) from a solution of 1M FeCl<sub>2</sub>. In each case, the amount of plated Fe was small compared with the amount in the reservoir. The plated Fe was collected for isotopic analysis of <sup>54,56,57</sup>Fe using a Termo-Finnigan Neptune MC-ICP-MS.



**Figure 1:**  $\Delta^{56}$ Fe plated iron vs. ferrous stock.

The electrochemical isotope effect yields mass-dependent fractionations from -2.3 to -0.9 permil (Fig. 1) as driving force is increased. Interestingly, we observe a temperature effect; however fractionation increases in the higher temperature case (Fig. 1), the opposite of what thermally-activated isotope fractionation processes predict.

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[1] Anbar (2007) Ann. Rev. EPS **35**, 717. [2] Kavner et al. (2005) GCA **69**, 2971. [3] Kavner et al. (2008, in press) GCA.