Redox controls on diagenetic incorporation of rare earth elements in fossil fish teeth

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Fossil fish teeth and skeletal debris are considered one of the most robust archives for reconstructing Nd isotope ratios of seawater in the geological past, and have been widely used to fingerprint individual water masses and trace their distribution through time. Little systematic work, however, has been done to verify the robustness of this proxy in marginal settings and under varying bottom-water and sedimentary redox conditions.

IODP Expedition 318 recovered Paleogene drillcores from offshore of the East Antarctic margin (Site U1356; 63°18.61′S, 135°59.94′E). Strata of early Eocene age (~48 to ~49 Ma) deposited in a shelf environment during the warmest period of the Cenozoic - the Early Eocene Climatic Optimum (EECO) - show striking cyclical variations between oxidised and reduced conditions. Since Site U1356 is located proximal to the Tasman Gateway and the EECO is of particular interest for palaeoceanographic reconstructions during the early Paleogene greenhouse, we investigated the robustness of the Nd isotope signal in fish debris deposited during the early Eocene at this site.

Individual fish teeth were picked from the >125μm fraction of washed bulk sediments. Comparison between fully reductively cleaned samples and samples only cleaned with water and methanol yielded the same Nd isotopic composition, and hence the latter cleaning procedure was used for the majority of the samples. All samples were dissolved in HCl, aliquoted for major and trace element analyses, and subjected to a standard two stage ion chromatography. Neodymium isotope ratios were determined using a Nu Plasma MC-ICP-MS and major and trace element data, including rare earth element patterns, were obtained on an Agilent 7500a quadrupole ICP-MS.

Preliminary data show systematic variation in the Nd isotopic composition of fish teeth extracted from reduced and oxidised sediments. We will evaluate these findings in the context of a more comprehensive data set, including main and trace element data, and discuss the implications of varying redox conditions at the sea floor on the incorporation and preservation of seawater Nd isotopes in fossil fish teeth.

Melt-inclusion evidence for a CO_2-rich mantle beneath the western branch of the East African Rift

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CO_2 in the mantle may moderate the generation of low silica magmas. Here, we present data from olivine-hosted melt inclusions that are consistent with a carbonated mantle source beneath the western branch of the East African Rift.

Twenty-four samples were collected from the Virunga province of the East African Rift. These rocks are silica-understaturated potassic lavas (kamafugites) with 38-45 wt% SiO_2 and K_2O/Na_2O>1. We quantified the abundances of major, minor, and trace elements, as well as the volatiles H_2O, CO_2, F, S, and Cl in olivine-hosted melt inclusions from five whole-rock samples. The H_2O and CO_2 concentrations range from ~0.3 to 2.5 wt% and ~30 to 9,950 ppm, respectively. The CO_2 values are consistent with molecular dynamics simulations for the solubility of CO_2 in MORB and may represent less degassed melt[1]. The melt inclusions have elevated Li concentrations (up to 117 ppm) and B/Be ratios (>10) relative to MORB (Li ~3 to 4 ppm, B/Be ~2 to 4).

Two plausible sources of the volatiles are fluids evolved during paleo-subduction, and fluid exsolved from the melting of a mantle plume. Published Nd, Hf, Sr, and Os data for rocks across the EAR western branch suggest mixing of two metasomatized mantle sources as the source of these magmas, requiring previous fluid-mantle interaction[2]. Elevated Li and B concentrations measured in arc magmas have been used as a fluid tracer to investigate the role of fluid additions to the mantle wedge. As such, volatiles subducted by the closure of the Mozambique Ocean during the Pan-African orogeny are a plausible source for the elevated CO_2 and H_2O. This scenario is consistent with evidence for long-term storage of volatiles in the mantle[3]. Other potential sources include ancient subducted slabs pooled in the lower mantle and fluids released from a partially melting mantle plume. Radiogenic and noble gas isotope studies may be required to fully distinguish the sources of the mantle metasomatism.

[1] Guillot and Sator (2011) *GCA* **75**, 1829-1857. [2] Rosenthal *et al*, (2009) *EPSL* **284**, 236-248. [3] Pettke *et al*, (2010) *EPSL* **296**, 267-277.

DOI:10.1180/minmag.2013.077.5.8