

## Hf isotope evidence for continental lithosphere pollution of the Asthenosphere near the Oceanographer Fracture Zone

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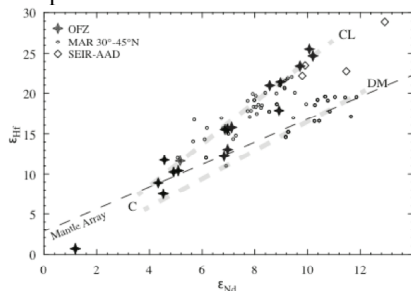
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Pb, Sr, and isotope data from a suite of basalts from ~35°, ~0-10 miles north of the Oceanographer Transform (OFZ) are interpreted as mixing between three chemically distinct mantle sources [1]. The transform offsets the ridge right-laterally by 130 km and lies within the geochemical gradient attributed to dispersion of the Azores plume and mixing with the depleted upper mantle MORB source [2]. The third mantle component's isotope and geochemical characteristics suggest that portions of the mantle in the region contain detached fragments of ancient sub-continental lithosphere. We have analyzed a subset of the the samples previously analyzed for Pb, Sr, and Nd [1] for Hf isotopes and high precision Pb isotopes.



**Figure 1:** New Hf isotope data for the OFZ region. Also shown are published data [3-5] for the MAR and ultra-depleted MORB from

the Southeast Indian Ridge-AAD Pacific-Indian mantle boundary.

Bifurcating trends bound the data and require at least 3 mantle components. An enriched C-like (low  $\epsilon_{Nd}$  and  $\epsilon_{Hf}$ ), common to both trends, and two depleted components, one DM like (high  $\epsilon_{Nd}$  and intermediate  $\epsilon_{Hf}$ ), the other (very high  $\epsilon_{Hf}$ ) similar to ultra-depleted MORB from the AAD, where the upper mantle is contaminated by continental material entrained during Gondwana rifting. The new OFZ Hf isotope data confirm the Pb and Nd isotope results [1] indicating pollution of the upper mantle MORB source by material derived from the continental lithosphere mantle, also advocated for the Azores plume [6]. This suggests that during plume-lithosphere interaction and rifting, accompanying the early opening of the Atlantic Ocean Basin, fragments of refractory continental lithosphere mantle were incorporated into the OFZ MORB source.

[1] Shirey *et al* (1987) *Nature***325** 217-223 [2] Schilling (1975) *EPSL***25** 103-115 [3] Agranier *et al* (2005) *EPSL***238** 96-109 [4] Debaille *et al* (2006) *EPSL***241** 844-862 [5] Hamelin *et al* (2013) *ChemGeol***341** 128-139 [6] Widom *et al* (1997) *ChemGeol***140** 49-68.

## Novel approaches to reconstructing sulfur cycling in methane seeps

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Methane ranks among the key greenhouse gases throughout Earth history, particularly under the generally more reducing conditions of the Precambrian. The mechanisms of methane cycling have been studied extensively, but a complete understanding of its role in the chemical and organismal evolution of the ocean through time, including its closely coupled relationship to the sulfur cycle, are still largely unresolved. Modern and ancient seeps provide outstanding natural labs for studying coupled methane-sulfur cycles and their geochemical fingerprints. Many seep studies examine sulfide in pyrite, but pyrite formation in these settings is typically limited by the availability of reactive iron and thus only captures the earliest diagenetic processes. In such cases, a better way to track sulfur and its role in modulating methane production and consumption is by following the pathways of dissolved sulfate, specifically using carbonate-associated sulfate or CAS. This study focuses on modern and ancient seep sites marked by complex carbonate paragenesis and traces sulfur, carbon and oxygen isotopes to unravel ancient methane cycling, its relationship to sulfur metabolic pathways and the preservational history of proxies during early to late burial. Our initial results suggest that coupled isotopic and concentration measurements of CAS may closely track spatiotemporal variation in rates of microbial sulphate reduction as coupled to anaerobic methane oxidation. These rates in ancient settings seem highly variable spatially and temporally, as they are in modern seeps. CAS isotopic relationships also reveal the relative patterns of sulfate reduction and sulfide oxidation, thus providing an essential backdrop for interpreting thiotrophic and methanotrophic symbiosis among the seep-dwelling macrofauna.