## A clumped isotopes perspective on sea surface temperatures in the Eocene southern high latitudes

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Recent studies of high southern latitude sea surface temperatures during the Eocene Epoch have suggested that very warm temperatures, possibly exceeding 30° C, extended to the Antarctic margin<sup>1,2</sup>. These results could have profound implications for understanding polar amplification of greenhouse warming. However, there are large uncertainties associated with the temperature proxies applied in these studies, due either to unconstrained seawater chemistry (in  $\delta^{18}$ O or Mg/Ca) or ambiguity in selecting the appropriate TEX<sub>86</sub> calibration. Clumped isotopes paleothermomtery is a thermodynamically controlled temperature proxy that does not depend on the isotopic compositions of seawater, and presents a novel opportunity to reduce uncertainties in Eocene SST estimates.

We measured clumped isotopes in Eocene bivalves from two southern high latitude localities: Seymour Island, Antarctica (~65° S paleolatitude) and the South Island of New Zealand (~55° S). Middle to late Eocene (45 to 35 Ma) paleotemperatures at Seymour Island range from 18 to 11°C. Analyses of New Zealand bivalves indicate a temperature decrease from ~26°C to ~20°C between the early and middle Eocene (49 to 40 Ma). These temperature estimates are most consistent with TEX<sub>86</sub> paleotemperatures from New Zealand and the East Tasman Plateau calculated using the TEX<sub>86</sub>L calibration<sup>3</sup>, supporting the use of this calibration in the Eocene southwest Pacific and possibly other high latitude regions.

Clumped isotope paleotemperatures suggest that New Zealand was approximately 7°C warmer than Seymour Island during the middle Eocene. This difference points either to a sharp meridional temperature gradient or to zonal heterogeneity in southern high latitude SSTs related to different paleocurrent systems influencing the southwest Pacific and southern Atlantic. Paleotemperatures from the East Tasman Plateau suggest that this temperature difference persisted into the late Eocene.<sup>1</sup>

Coupled clumped isotope and  $\delta^{18}O$  measurements in bivalves also provide an estimate of the oxygen isotope composition of coastal seawater. At Seymour Island  $\delta^{18}O_w$  values are generally within error of the ice free latitude-corrected value of  $-1.2\%^4$ . However a marked decrease to values less than -3% around 41 Ma suggests a pronounced hydrologic change. In New Zealand, mean  $\delta^{18}O_w$ estimates increase from -1.4% in the early Eocene to -0.8% in the late Eocene. This shift could suggest an increase in coastal salinity to normal marine conditions, either due to decreased continental runoff or a change in surface paleocurrents.

- [1] Bijl et al., (2009) Nature 461, 776-779.
- [2] Hollis et al., (submitted) Earth and Planet. Sci. Lett.
- [3] Kim et al., (2010) Geochim. Cosmochim. Acta 74, 4639-4674.
- [4] Zachos et al., (1994) Paleooceanography 9, 353-387

## Refertilisation of the Hawaiian oceanic lithospheric mantle

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A suite of fresh spinel peridotite xenoliths from the Island of Kaula, Hawaii erupted ~3 Ma ago and offer the opportunity to characterise the composition of the oceanic lithosphere and its metasomatic history. Peridotite xenoliths from continental and oceanic lithosphere often indicate early partial melting in which "basaltic" components were removed from the system, followed by varying degrees of metasomatic enrichment in incompatible trace elements.

Depletion of basaltic components in the Kaula samples is well demonstrated by the whole rock major element chemistry. Whole rock MgO wt% ranges from 40.52-45.24 and has strong negative correlations with basaltic components such as Na<sub>2</sub>O (0.10-0.33 wt%), CaO (0.69 – 2.41 wt%) and Al<sub>2</sub>O<sub>3</sub> (0.78-2.46 wt%) and a positive correlation with Ni (2129-2454 ppm). In particular, the low CaO and Al<sub>2</sub>O<sub>3</sub> (<2.5 wt%) indicate relatively refractory compositions, compared with fertile peridotite.

In contrast, trace elements in clinopyroxenes show strong positive correlations between HFSE such as Ti and the HREE. Samples that depart from this trend have elevated LILE contents, in particular Ba (>1 ppm vs. an average of 180 ppb) and Pb (>1 ppm vs an average of 300 ppb).

The enrichment in trace elements and the relationships between them suggest two distinct types of mantle metasomatism that are possibly related to localised refertilisation of the lithosphere by low degree partial melts of crustal components, within a broader scale metasomatic overprint linked with plume magmatism.