

$\epsilon^{182}\text{W}$ in ocean island basalts and the role of core-mantle interaction

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Combined radiogenic $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ ratios in some plume-related ocean island basalts have been interpreted in terms of chemical interaction between the Earth's core and mantle or recycling of Fe-Mn crusts [1, 2, 3]. Owing to the short half live of the ^{182}Hf - ^{182}W decay system ($t_{1/2} = 9$ Ma) and the contrasting geochemical behaviour of Hf (lithophile) and W (moderately siderophile), early core formation lead to the development of complementary $^{182}\text{W}/^{184}\text{W}$ isotope signatures (expressed as $\epsilon^{182}\text{W}$) in the Earth's core ($\epsilon^{182}\text{W} = -2.1$) and bulk silicate Earth ($\epsilon^{182}\text{W} = 0$) [3]. Previous $\epsilon^{182}\text{W}$ data for samples with radiogenic $^{186}\text{Os}/^{188}\text{Os}$ ratios from Hawaii could not support the presence of core material in the Hawaiian mantle source [3]. In this study, we improved our analytical techniques to further explore this unresolved debate using $\epsilon^{182}\text{W}$ data for a much wider range of samples of ocean island basalts. The dataset also includes samples from large igneous provinces as they may represent prime contenders for mantle material that originated at the core-mantle boundary.

In keeping with measurements from Hawaii, $\epsilon^{182}\text{W}$ values for samples from the Azores, Canary Islands, Cape Verdes and the Ontong-Java plateau are indistinguishable from that of the bulk silicate Earth value ($\epsilon^{182}\text{W} = -0.02 \pm 0.11$; 2σ) suggesting that their sources do not contain a contribution of core material. Our technique also allows the determination of stable $^{98}\text{Mo}/^{95}\text{Mo}$ isotope ratios (expressed as $\delta^{98}\text{Mo}$) from the same sample aliquot. Because Mo isotopes are only fractionated by low-temperature processes at the Earth's surface [4], negative $\delta^{98}\text{Mo}$ values are a highly diagnostic tracer of altered oceanic crust. Samples with radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios from La Palma (Canary Islands) also have negative $\delta^{98}\text{Mo}$ values. This suggests that radiogenic Os isotopes in ocean island basalts may be caused by recycled altered oceanic crust rather than by addition of outer core material.

[1] Walker *et al.* (1997) *GCA* **61**, 4799-4807. [2] Brandon (1998) *Science* **280**, 1570-1573. [3] Scherstén *et al.* (2004) *Nature* **427**, 234-237. [4] Anbar (2004) *Reviews in Mineralogy and Geochemistry* **55**, 429-454.

Silicon isotopic fractionation in marine sponges: A new paradigm and model for understanding silicon isotopic variations in sponges and diatoms

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The modern Southern Ocean plays a pivotal role in determine the air-sea balance of CO_2 and global biological production. However, there is debate regarding nutrient utilisation in Southern Ocean surface waters and how this transfers through to the deeper Southern Ocean, especially during the past. To fill this gap we have determined the silicon isotope composition of deep-sea sponges collected from near Antarctica, subantarctic waters (Tasmania Seamounts) and subtropical waters north of New Zealand with the aim of developing a new paleo-nutrient proxy. For deep-sea sponges, $\delta^{30}\text{Si}$ values widely between 0.87 ‰ and -3.40 ‰ (vs NBS). Depth profiles show that sponge $\delta^{30}\text{Si}$ compositions trend to lighter values with increasing depth. This is exemplified by sponges from the Tasmanian Seamounts which vary from 0.87 ‰ to -3.13 ‰ over a depth range from 100 to 1200 m. We find that silicon isotope fractionation ($\delta^{30}\text{Si}$ sponge - $\delta^{30}\text{Si}$ seawater) varies with seawater silicon concentration with more fractionated (lighter) isotope values being associated with specimens collected from water high in silicon. A mass-balance based model for silicon isotope fractionation is consistent with $\delta^{30}\text{Si}$ fractionation driven by changes in the difference between the silicon influx and efflux from the sponge. At higher seawater silicon concentrations efflux is correspondingly higher, and with $\delta^{30}\text{Si}$ having an apparent greater internal fractionation, this results in lighter $\delta^{30}\text{Si}$ spicule values. This model can also explain $\delta^{30}\text{Si}$ fractionation in diatoms and be used to reconstruct past seawater silicon concentrations from the $\delta^{30}\text{Si}$ signature of fossil sponges and diatoms.