

## Carbon isotope biosignatures: A surface-deep Earth abiotic connection

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Our quest for identifying the beginning of life in terrestrial (and possibly extraterrestrial) environments has been hampered by the lack of unequivocal biosignatures in the absence of many other lines of evidence. The claim for finding early life in the  $\geq 3.85$  Ga Istaq Gneiss Complex at Akilia Island [1] reignited the half-century old debate on the use of low  $\delta^{13}\text{C}$  values ( $< -20\text{‰}$ ) of ancient carbonaceous materials as an isotope biosignature. It is now well demonstrated that a number of possible abiotic pathways exist near Earth-surface that lead to the synthesis of various organic and reduced carbon compounds depleted in  $^{13}\text{C}$  due to large kinetic isotope effects [2]. Mantle carbons (graphite, diamond, dissolved carbons, carbide) with low  $\delta^{13}\text{C}$  values ( $< -20\text{‰}$ ) have previously been considered recycled sedimentary organic carbons or surface contamination. Other possible origins of these low  $\delta^{13}\text{C}$  values have been suggested, including (a) possible mantle heterogeneity since the accretion from the solar nebula and the core–mantle segregation and (b) unidentified mechanisms and processes for large carbon isotopic fractionation at high temperatures and pressures.

Our recent theoretical calculations, along with some experimental studies [3], show that Si/Fe-carbide is very depleted in  $^{13}\text{C}$  relative to other mantle compounds (diamond and calcite) even under deep-Earth conditions ( $> 1000^\circ\text{C}$ ). Our modelling shows that redox-controlled C-cycle in the mantle between diamond and Fe-carbide can produce low  $\delta^{13}\text{C}$  values ( $< -20\text{‰}$ ) in addition to a primary mantle value ( $-5 \pm 2\text{‰}$ ), a pattern similar to that observed from a global  $\delta^{13}\text{C}$  distribution of diamond. These mantle-derived diamond and carbide with low  $\delta^{13}\text{C}$  values can be brought up to near surface by mantle upwelling over geologic time. Thus, now a viable mechanism exists that can produce low  $\delta^{13}\text{C}$  values of diamond and other carbonaceous materials that could have originated from the deep-Earth. Abiogenic processes that can produce carbonaceous materials with low  $\delta^{13}\text{C}$  values, both near-surface and in deep-Earth, further challenge our notion of carbon isotope biosignatures for early life.

[1] Mojzsis *et al* (1996) *Nature* **384** 55-59. [2] Horita (2005) *Chemical Geology* **218**, 171-186. [3] Satish-Kumar *et al* (2011) *EPSL* **310** 340-348

## Suboxic sediments as an oceanic sink of isotopically-light cadmium

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Riverine and dust fluxes are thought to be the only two quantitatively significant sources of dissolved cadmium to the ocean. These inputs are balanced, within uncertainty, by burial of Cd into suboxic continental margin sediments [1]. Recent studies have characterized the Cd isotopic composition of the source terms [2, 3], indicating that the overall Cd isotopic composition of the inputs is isotopically lighter than average deep-ocean seawater by  $\delta^{114/110}\text{Cd} \approx -0.2 \text{‰}$  [4]. The offset between seawater and the inputs implies that either the system is not in steady state, or that suboxic sediments should also be characterized by a Cd isotopic composition that is close to the input value, and therefore also fractionated toward a lighter composition than seawater.

Here, we present Cd isotopic and multi-element geochemical data for suboxic sediments that were sampled from the Cape Margin, South Africa, during the UK GEOTRACES 40 °S cruise in 2011 (D357; GA10E). Our Cd isotopic data suggest that suboxic sediments are indeed fractionated from seawater by  $\delta^{114/110}\text{Cd} \approx -0.2 \text{‰}$ , and represent a significant sink of isotopically light Cd in the modern oceans. Our isotopic mass balance – the first of its kind for Cd – demonstrates that the isotopic composition of suboxic sediments balances the inputs, and therefore the isotopic budget of Cd in the oceans.

We explore possible mechanisms for the immobilization of isotopically light Cd in suboxic sediments using multi-element geochemical data from both the solid phase and sediment porewaters. The temporal sensitivity of the Cd isotopic composition of deep-ocean seawater is also investigated using a simple numerical model, as well as implications for the use of Cd isotopes in paleoceanography.

[1] Morford & Emerson (1999) *GCA*, **63**(11), 1735-1750. [2] Schmitt *et al* (2009) *EPSL*, **277**(1), 262-272. [3] Lambelet *et al* (2013) *EPSL*, **361**, 64-73. [4] Ripperger *et al* (2007) *EPSL*, **261**(3), 670-684.