

Interpreting Molybdenum isotopes as a proxy for the spatial distribution and intensity of ocean de-oxygenation events in an Earth System Model

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Molybdenum (Mo), and its isotopes, are used as a proxy for global ocean redox states. This proxy has already been applied to investigate the degree of euxinia in the Proterozoic ocean [1] and the spatial extent of de-oxygenation during the Mesozoic [2]. However, at intermediate oxygen states the interpretation of $\delta^{98/95}\text{Mo}$ is difficult because of the complex non-linear system controlling the spatial and temporal pattern of Mo sequestration into the sediments. We aim to investigate this complexity in the Earth System Model GENIE. The model will be enabled with a relatively complete description of redox-dependent dynamics of marine iron and sulphur cycling and so providing us with a powerful tool to describe the water column dynamics of Mo (plus its sources and sinks). In particular the model will allow us to examine the role of iron-sulphide minerals in the scavenging of Mo, which is a key process in its removal from the global oceans.

Here we present preliminary results of the evaluation of the model for the present-day ocean and an outline for its application to past climatic states where ocean euxinia is present, taking OAE2 as a test study.

[1] Arnold, G.L. *et al.* (2004) *Science* 304, 87-89 [2] Pearce, C.R. *et al.* (2008) *Geology* 36, 231-234

Interactions of dissolved CO₂ with Cadmium Isotopes in the Southern Ocean

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Cadmium has a biochemical function in the carbonic anhydrase (CA) class of enzymes for CO₂ metabolism in photosynthesis by algae [1,2]. This occurs either by substitution for Zn in the common Zn-CA, or as a genuine Cd-CA as found in certain marine diatoms [2]. The CA enzyme class is pivotal for conversion of bicarbonate [HCO₃⁻] to CO₂. This CA also appears responsible for high Cd/P uptake ratio by plankton at low ambient aqueous CO₂ [1]. The uptake of Cd has been related to ambient Cd, Zn, Mn and Fe [3, 4]. Also the Mn/P uptake ratio of plankton has been shown to be dependent [5] on ambient dissolved Fe [6] in the Southern Ocean.

Here we report the first ever observations of strong correlations in ocean surface waters of dissolved aqueous CO₂ with dissolved Cd and with the stable isotope ratio ¹¹⁴Cd/¹¹⁰Cd [7,8]. This is observed along the 0°W meridian in both the Antarctic Circumpolar Current and the Weddell Gyre, as well as in the Weddell Sea proper and also in Drake Passage. This uniform trend in several surface water masses hints at a uniform biochemical mechanism. The relationships in the Southern Ocean between the relative uptake of aqueous [CO₂] versus [HCO₃⁻] by algae [9] and the biological Cd isotope fractionation [7,8] will be discussed. Parallel trends of apparent Cd/PO₄ uptake ratio and interactions with Mn, Zn and Fe will be presented. Conceivable implications for paleoceanography will be mentioned.

[1] Cullen and Sherrell (2005) *Limnol. Oceanogr.*, 50: 1193.

[2] Xu *et al.* (2008) *Nature*, 452: 56. [3] Sunda and Huntsman (2000) *Limnol. Oceanogr.*, 45:1501. [4] Cullen (2006) *Limnol. Oceanogr.*, 51: 1369. [5] Middag *et al.* (2013) *Limnol. Oceanogr.*, 58: 287. [6] Klunder *et al.* (2011) *Deep-Sea Res. II*, 58: 2678. [7] Abouchami *et al.* (2011) *Earth Planet. Sci. Lett.* 305: 83. [8] Xue *et al.* (2013) *Earth Planet. Sci. Lett.* [9] Neven *et al.* (2011) *Deep-Sea Res. II*, 58: 2636.