Importance of Cadmium Sulphides for Cd Cycling in the Oxygen Deficient Zone of the Angola Basin

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The biogeochemical cycling of cadmium (Cd) and its isotopes in the ocean is dominated by biological uptake of Cd into phytoplankton in the surface ocean, while regeneration of the sinking particulates mainly governs the shapes of Cd profiles in the deeper ocean [1,2,3]. Superimposed on this nutrient-like consumption-regeneration cycle, it has recently been argued that Cd scavenging as cadmium-sulphide (CdS) can occur in oceanic Oxygen Deficient Zones (ODZ) [4,5,6]. To assess the magnitude of this Cd sequestrating process, Cd isotope and concentration data were obtained on seven vertical seawater profiles during GEOTRACES cruise GA08 (M121) in the Angola Basin where a significant ODZ prevails between 200 and 1000 m depth.

Deep waters show a narrow range in Cd concentrations (0.30-0.55 nmol kg^{-1}) and $\varepsilon^{112/110}$Cd (1.1 to 2.7), entirely consistent with mixing of northern (NADW) and southern waters (AAIW and AABW). Surface waters show a strong Cd depletion, to picomolar level, with $\varepsilon^{112/110}$Cd ranging from heavier (2.0-3.0) to lighter values (near 1.0), which contrast with the extremely heavy surface values seen elsewhere and linked to biologically-induced fractionation [3,5]. The $\varepsilon^{112/110}$Cd in these surface waters can be explained by the buffering effect of Cd complexation by organic ligands [7].

In the ODZ, the stronger Cd depletion relative to that of PO_4^{3-} is associated to a shift of $\varepsilon^{112/110}$Cd towards heavier values, indicative of CdS precipitation as previously shown in the North Atlantic ODZ [4,5]. The extent of Cd isotope fractionation in our samples agrees well with the fractionation factor, $\alpha_{Cdsol\text{-}CdS}$ of 1.00016 that we determined experimentally in a seawater-like matrix [8]. Altogether, our new results demonstrate that CdS precipitation in ODZ represents an efficient pathway for sequestering and exporting oceanic Cd to bottom sediments and can thus significantly impact the global oceanic Cd mass balance.

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