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Effect of CdS precipitation on the partitioning of Cd isotopes: implications for Cd oceanic cycle

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The biogeochemical cycling of cadmium and its isotopes in the ocean is mainly ascribed to the assimilation-remineralization cycle occurring in phytoplankton [1, 2]. Recently, several studies reported an alternative Cd scavenging through CdS precipitation in Oxygen Minimum Zones (OMZ) based on the decrease of Cd/PO_4 ratio and of a concomitant positive Cd isotope excursion in dissolved seawater compared to sinking particles [3,4,5]. To identify if CdS precipitation effectively engenders a Cd isotope fractionation, we performed cadmium-sulphide precipitation experiments under controlled atmosphere at low (MilliQ-water) and high ionic strengths (synthetic seawater) by varying reaction time as well as cadmium/sulphide ratio.

Enrichment in light Cd isotopes is observed in the precipitated CdS phase, in agreement with *ab initio* simulations performed between the various speciation of Cd in aqueous solution [6]. The data follow a closed-system Rayleigh fractionation model with the fractionation factor ($\alpha_{Cdsol-CdS}$) decreasing with increasing salinity (from 1.00026 for Milli-Q to 1.00014 for a salinity twice that of modern seawater). We propose that this fractionation is directly controlled by an isotope equilibrium between the various Cd aqueous species with preferential involvement of Cd^{2+} in CdS formation.

The magnitude of the Cd isotope fractionation determined in our study is in excellent agreement with the Cd isotope shift observed in modern oceanic OMZ and attributed to CdS precipitation [3,4,5], witnessing the impact of this scavenging process. In restricted euxinic basins such as the Black Sea, Cd isotopes may be useful tracer of the near-quantitative sequestration of cadmium sulphides. Finally, CdS precipitation in OMZ can represent the main sink of oceanic Cd, witnessing the importance of these results, in the frame of a better understanding of Cd oceanic cycle.

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