

## Controls on upper ocean Cd isotope fractionation

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Oceanic dissolved Cd profiles [1, 2] and culture experiments [3, 4] have provided strong support for a biologically-induced Cd isotope fractionation in surface waters relative to deep waters. With the increasing body of oceanic Cd isotope data, the mechanisms governing Cd isotope fractionation in shallow waters appear to differ regionally with the local biogeochemical conditions.

Here, we present coupled dissolved Cd concentrations ([Cd]) and isotope ratios ( $\epsilon^{112/110}\text{Cd}$ ) of the upper South Atlantic (GA02) and subarctic northeast Pacific (Line P). Our results show that Rayleigh fractionation closely reproduces the subsurface Cd isotope distribution, but that there is a clear deviation and breakdown of the Rayleigh model at a nominal [Cd] of 0.1 nmol kg<sup>-1</sup>. Below this [Cd] threshold,  $\epsilon^{112/110}\text{Cd}$  is relatively uniform at  $\sim +3.4$ , in line with the global ocean average of  $+3.8 \pm 3.3$  (2SD, n = 173). While a large subset of the data at hand is compatible with the Rayleigh model, our new data indicate that other processes control the cycling of Cd in nutrient-deficient oceanic regions. The role of organically-bound Cd in these waters, and an open-system, steady-state model provide two possible alternative solutions for explaining the global surface  $\epsilon^{112/110}\text{Cd}$  dataset in the tropical, subtropical and subpolar ocean.

[1] Abouchami et al. (2014) GCA 127, 348-367; [2] Ripperger et al. (2007) EPSL 261, 670-684; [3] Lacan et al. (2006) GCA 70, 5104-5118; [4] John and Conway (2014) EPSL 394, 159-167.