Barite control on the Southern Ocean barium isotopic signature

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Barium is a bio-intermediate element, used as a proxy for present and paleo-biological productivity. In order to understand better Ba cycling in the oceans, we have measured Ba stable isotopic compositions in seawater alongside dissolved [Ba]. The data were obtained by TIMS using a ^{134}Ba-^{135}Ba double spike and reported as $\delta^{138/136}$Ba (‰) relative to NIST SRM-3104a. The sixty Southern Ocean samples from cruise ANT XXIV/3 (GIPY5, spring 2008) along the Zero Meridian consist of a continuous surface water transect (47°-67°S) and four depth profiles within the ACC and Weddell Gyre. In addition, seawater reference standards from the Atlantic and Pacific were analyzed to assess inter-ocean Ba isotope variability.

Dissolved Ba concentrations are consistent with those found previously in the Southern Ocean [1]. Surface water [Ba] along the transect increases from N to S until ~60°S, then gently decreases; $\delta^{138/136}$Ba behaves antithetically to [Ba], decreasing from ~0.25 to 0.15‰. These trends suggest increasing Ba removal northwards into barite in organic-rich microenvironments [1]. Mass balance dictates a $\delta^{138/136}$Ba of ~0‰ for barite, implying a barite-seawater fractionation factor of around -0.2‰, consistent with mixing and Rayleigh fractionation, as well as barite precipitation experiments [2]. Similar trends, associated with the polar fronts, are seen in Cd isotopes [3, 4]. Dissolved [Ba] and $\delta^{138/136}$Ba are anti-correlated in the different ocean basins, in agreement with recent studies [5, 6], and in accord with precipitation of barite in surface waters and its re-dissolution deeper in the water column. $\delta^{138/136}$Ba in barite preserved in bottom sediments is therefore potentially a promising new proxy of ocean biological paleo-productivity, but its utility is likely to be limited by variability in barite saturation in the oceans [7].

[1] Hoppema et al. (2010) *Mar. Chem.* **122,** 118-129; [2] von Allmen et al. (2010) *Chem. Geol.* **277,** 70-77; [3] Abouchami et al. (2011) *EPSL* **305,** 83-91; [4] Abouchami et al. (2014) *GCA* **127,** 348-367; [5] Horner et al. (2015) *EPSL* **430,** 511-522; [6] Cao et al. (2016) *EPSL* **434,** 1-9; [7] Monnin and Cividini (2006) *GCA* **70,** 3290-3298.