



New approach to global barium cycle understanding: barium isotopic composition of marine carbonates and seawater.

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In this communication we present the Ba isotope fractionation ($\delta^{137/134}\text{Ba}$) study on marine carbonates and seawater, initiated to gain a first order view of the marine Ba isotope cycle. A special focus is the question whether the nutrient type distribution of Ba in the water column, as well as different Ba sources, are reflected in Ba isotope ratios of carbonate archives. The approach ultimately aims to provide an improved Ba based paleonutrient proxy.

The data set is composed of carbonates (micrites and limestone standard), coral skeleton and seawater (IAPSO standard and Mediterranean seawater). Part of the corals were cultured in monitored environments (CSM, Monaco) others originate from natural environments (shallow and warm water corals from the Bahamas/Florida and cold water corals from the Norwegian shelf). The analytical procedure includes the application of a $^{130}\text{Ba}/^{135}\text{Ba}$ double spike, a cation exchange column followed by isotope measurements on a Nu Instruments Multicollector ICP-MS. The Ba fractionation of the samples is compared to a Ba nitrate standard solution and a standard natural limestone BSC-CRM 393 ($0.05 \pm 0.04 \text{ ‰}$ 2SEM).

No isotopic fractionation has been observed in the limestone standard and micrites ($N=8$) ($-0.01 \pm 0.04 \text{ ‰}$ 2SEM) compared to the Ba nitrate standard. On the contrary, coral skeletons show a significant positive fractionation (mean = $0.4 \pm 0.05 \text{ ‰}$ 2 SEM). No significant difference was found between different cultured coral species. Thus no species-specific fractionation is identified within the same environmental conditions. Diagenetic influence on Ba isotopic composition was further tested on 5 natural samples with varying calcite to aragonite ratios (0 to 0.3). No significant effect was observed. Moreover, the Ba isotope composition seems independent from the Ba concentration in the studied coral skeleton, within our measurement resolution. Seawater isotopic composition ($-0.05 \pm 0.07 \text{ ‰}$ 2SD) is lighter than coral skeleton, indicating a fractionation process opposite to those reported for Ca and Mg isotopes, and previous results from experimental Ba isotope fractionation into Ba-bearing carbonates.

These results clearly encourage a further investigation to evaluate the Ba cycle and associated Ba isotope fractionation on marine carbonate material in other locations, e.g. upwelling regions or ocean gyres.