

What the flux? Isotopic constraints on the marine barium budget

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The oceans internal cycle of Ba (barium) is controlled by a fundamentally different boundary condition to marine macronutrients: the major dissolved-particulate Ba transformation, precipitation of microcrystalline barite, is not driven by the production of organic matter but rather by its remineralization. The abundance and isotopic composition of Ba in seawater are thus connected to global carbon and nutrient cycling via processes occurring at the 'dark end' of the biological pump. However, the relatively short residence time of Ba in seawater (≤ 10 kyr; [1]) suggests that the marine Ba inventory may be sensitive to short-term changes in Ba inputs that are not necessarily related to marine biogeochemical processes. To understand the response of the marine Ba inventory to changes in Ba fluxes we obtained Ba-isotopic data for various Ba inputs and major output fluxes, such as barite. (The possibility for Ba-isotopic exchange during low-temperature hydrothermal alteration is also examined, though is not a significant net Ba flux *per se*.) We model these data in the context of existing Ba-isotopic measurements of other input terms such as rivers [2], submarine groundwater discharge [3], as well as emerging datasets for relatively minor outputs (e.g. biogenic carbonates [4]). Overall, our data indicate that the marine Ba cycle is close to steady state, with the Ba-isotopic composition of known inputs matching outputs (within uncertainty). Given that seawater is considerably 'heavier' [5] than any known Ba input or output, our results suggest that the major Ba fluxes possess considerable isotopic 'leverage': even relatively minor flux imbalances may render significant changes in the Ba-isotopic composition of seawater. We explore possible geological scenarios that may have led to such flux imbalances and discuss their impact on interpretation of the Ba-isotopic evolution of the oceans through time.

[1] Dickens et al. (2003) *Geol. Soc. Am. Spec. Pap.*, **369**.

[2] Cao et al. (2016) *Earth Planet. Sci. Lett.*, **434**.

[3] Bitterwolf et al. (2017) *Goldschmidt Abstr.*

[4] Pretet et al. (2016) *Depositional Rec.* **1**.

[5] Horner et al. (2015) *Earth Planet. Sci. Lett.*, **430**.