Barium stable isotopes in the Ganga (Hooghly) River estuary, India

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Barium (Ba) mass balance of rivers and estuaries is strongly influenced by solute–particle interactions [1]. These interactions, principally estuarine desorption of Ba from suspended particulate matter (SPM), can enhance Ba fluxes to coastal seawater by orders of magnitude. However, these processes have hitherto escaped Ba-isotopic characterization, rendering mass balances incomplete. Here, we constrain this important term by investigating the Ba-isotopic systematics of the Ganga (Hooghly) River estuary. The Ganga constitutes the largest river system in India and is characterized by a high SPM load. Previous studies showed solute–particle interactions in this estuary can increase riverine Ba fluxes by >300 % [2]. Barium-isotopic data were obtained for both dissolved and SPM phases (bulk and exchangeable) across periods of contrasting water discharge. We find that dissolved $\delta^{138/134}$Ba varies between ~+0.1 to +0.2 ‰ (relative to NIST SRM 3104a), and, outside of the lowermost estuary, is broadly negatively correlated with salinity. Dissolved δ^{138}Ba values are consistently lower-than-expected from conservative mixing of sea- and river water. Bulk SPM exhibits a narrow Ba-isotopic range centred on ~0 ‰, with no salinity dependence. In contrast, exchangeable SPM exhibits a decrease in δ^{138}Ba with salinity, which correlates with the fraction of Ba lost via desorption. Together, these observations indicate that desorbed Ba is isotopically heavier than either bulk particulate or exchangeable Ba in freshwater, but is lighter than riverine Ba. An increase in dissolved δ^{138}Ba in the lowermost estuary is presumed to reflect removal of light Ba, which could occur through either (re)adsorption or barite precipitation. Overall, this study indicates that the solute–particle interactions that increase Ba fluxes from estuaries also work to lower δ^{138}Ba toward more crustal compositions (i.e., ~0 ‰ [3]). If true elsewhere, the net Ba flux from land to coastal seawater is likely isotopically lighter than river water. The isotopic make-up of continental Ba flux thus critically depends on the amount of riverine SPM and the loci of interaction with saltwater, both of which will reflect the prevailing tectonics and climate.

[1] Stecher & Kogut (1999) *Geochim. Cosmochim. Acta* **63**, 1003–1012. [2] Samanta & Dalai (2016) *Geochim. Cosmochim. Acta* **195**, 1–28. [3] Nan et al. (2018), *Geochim. Cosmochim. Acta* **233**, 33–49.