

# Complex Ba isotope biogeochemistry across a sedimentary barite front in the Guaymas Basin, Gulf of California

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Fluxes of particulate barium (Ba) below the euphotic zone and barite (BaSO<sub>4</sub>) preserved in deep-sea sediments have long been linked to particulate organic matter export from the surface ocean[1]. Recent advances in marine Ba isotope studies, however, suggest that adsorption onto particle surfaces and large-scale ocean circulation may mask Ba isotope fractionation induced during biogenic barite formation. Conversely, little is known on how water column particulate Ba isotope signatures are preserved in sediments over time.

Here we present Ba isotope data on seawater, sinking particles, down-core sediments and porewater samples from the Guaymas Basin in the Gulf of California. Water column data show a systematic -0.5‰ offset between the particulate and dissolved phases, consistent with previously reported values. Ratios of particulate Ba/P and Ba/Al, and dissolved Ba-PO<sub>4</sub> correlation could not elucidate if adsorption onto sinking particles or biogenic barite formation plays a more dominant role in removing isotopically light Ba into the solid phase. Downcore bulk sediments display small variations in  $\delta^{138}\text{Ba}$  ranging from -0.05 to +0.08‰. Within the sediment, a distinct barite front is seen at 350 cm below the sea floor (bsl) where excess [Ba] increases by 50%. Below this barite front, pore water [Ba] increases sharply to > 35000 nmol/kg in the sulfate-methane transition zone at 350 cm bsf, while pore water  $\delta^{138}\text{Ba}$  shows strong variations below (+0.06 to +0.19‰), within (+0.02 to +0.19‰), and above (+0.13 to +0.45‰) the barite front. A Rayleigh fractionation model indicates that heavy Ba isotopes are preferentially incorporated into authigenic barite, with an isotope fractionation difference of  $\Delta^{138}\text{Ba}_{\text{barite-porewater}} = +0.05\text{‰}$ , a finding in complete contrast to laboratory barite precipitation experiment [2] but consistent with a recent sedimentary and pore water Ba isotope study from the Baltic Sea[3]. Bulk sediment  $\delta^{138}\text{Ba}$  across the barite front ( $-0.02 \pm 0.01\text{‰}$ , 2SD, n=4) is isotopically lighter than that above the front ( $+0.02 \pm 0.02\text{‰}$ , 2SD, n=4). This small but resolvable difference suggests that bulk sedimentary  $\delta^{138}\text{Ba}$  signature is vulnerable to post-depositional redox processes.

[1] Dehairs et al. (1980) *EPSL* 49(2):528-550

[2] von Allmen et al. (2010) *Chem. Geol.* 277(1):70-77

[3] Scholz et al. (2023) *Front. Mar. Sci.* 10: 1101095