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Barium isotope fractionation during ion exchange at the barite-fluid interface: Implications for barium cycling in seawater

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The occurrence and chemistry of barite offers a window into the productivity and chemistry of the ancient oceans, respectively. Recent methodological developments indicate that the isotope composition of barium in barite, $\delta^{138}BaSO_4$, may likewise offer a window into the ancient barium cycle. However, successful application of this emerging proxy is predicated on the assumption that barites faithfully preserve primary $\delta^{138}BaSO_4$ over geological timescales. It is widely accepted that suboxic sedimentary conditions will result in poor barite preservation that may also corrupt records of $\delta^{138}BaSO_4$. However, the effect of morphology-preserving alteration, such as barium ion exchange between barite and dissolved barium while at chemical equilibrium, on $\delta^{138}BaSO_4$ has yet to be constrained under conditions relevant to the marine environment. Here we investigated how ion exchange affects $\delta^{138}BaSO_4$ by studying seawater, sediments, and co-located pore fluids from the Equatorial Pacific, where sedimented $BaSO_4$ remain in contact with barite-saturated pore fluids for millennia. We constrain these effects in three ways. First, we confirm that ion exchange occurs between sedimented $BaSO_4$ and seawater using a stable barium isotope tracer. Second, we constrain the rate of exchange by modeling barite–pore fluid interactions, which agree well with prior literature. Third, we combine these rate estimates with measurements of $\delta^{138}Ba$ in barites and co-located pore fluids to constrain the barium-isotopic signature associated with the ion exchange process. Our results demonstrate that morphology-preserving diagenetic reactions are an important process that may affect sedimentary $\delta^{138}BaSO_4$, which we discuss in the context of the use of barium isotopes to reconstruct ancient biogeochemistry.