Stable barium isotope geochemistry of large river estuaries

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Barium (Ba) is a proxy used for past surface ocean salinity given that its concentrations reflect the fraction of highly Ba-enriched river waters in surface seawater. This is based on the conservative behavior of dissolved Ba (DBa) during estuarine mixing after a DBa concentration maximum at low salinities, which allows the reconstruction of precipitation and climatic changes on the nearby continents. The recently developed measurement of stable Ba isotopic compositions in seawater and river waters offers a potential new tracer for land-ocean interactions given the systematically light Ba isotope signatures of river waters. However, Ba isotope geochemistry in river estuaries has not yet been systematically examined. Here we present dissolved Ba isotope ($\delta^{137}Ba_{DBa}$) distributions along salinity gradients in the estuaries of three of the world's largest rivers, the Amazon (1st), Yangtze (4th) and Pearl (13th) River. We find that $\delta^{137}Ba_{DBa}$ gradually increases seawards from 0.0-0.2‰ marking the lithogenically dominated riverine input to 0.7-0.9‰ in marine surface waters. Combined with DBa concentrations, Ba isotope distributions are consistent with two-endmember mixing of fresh and marine waters in the Amazon and Yangtze River estuaries. In contrast, $\delta^{137}Ba_{DBa}$ signatures heavier by 0.2-0.3‰ than expected for strict conservative mixing are observed at mid-salinities between 11.8 and 27.7 in the Pearl River estuary despite apparent conservative behavior of DBa concentrations. We suggest that repetitive adsorption and desorption of Ba likely induce significant Ba isotope fractionation in some estuarine environments, which are not mirrored by DBa concentrations. These hidden processes have to be taken into account when using Ba and its stable isotopes as proxies for past salinity and are essential to better constrain the globally major source of oceanic Ba, the riverine input.