Evaluating Ba/Ca and $\delta^{137/134}$Ba of *Porites* corals as proxies for oceanic Ba cycle

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Barium in the skeletons of scleractinian shallow-water corals has been used as proxy for coastal and oceanic processes such as river discharge, oceanic upwelling and surface ocean productivity. However, the variation of Ba/Ca in aragonitic coral skeletons remains difficult to be interpreted as environmental proxy. This is mainly due to the disturbance by internal (biomineralization) and multiple external (environmental) processes on Ba incorporation into coral skeletons, and these processes are hard to be constrained with Ba/Ca alone. Here we use Multicollector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) with double spike correction to obtain the first annually-resolved records of the Ba isotopic composition ($\delta^{137/134}$Ba) in shallow-water corals (*Porites*) collected alive in the field, supplemented by the analysis of Ba/Ca ratios. Seven coral cores were recovered at different oceanic settings in the South China Sea, extending from the northern inner shelf to the central and southern deep basin. The $\delta^{137/134}$Ba values of six corals fall within a narrow range from 0.18 ± 0.03‰ to 0.31 ± 0.03‰, with a mean value of 0.25 ± 0.06‰ (N = 21). A single inner-shelf coral reveals anomalously light $\delta^{137/134}$Ba values (0.08 ± 0.03‰), which might reflect a terrestrial influence.

Our annual coral $\delta^{137/134}$Ba records from diverse oceanic settings display a relatively constant negative fractionation offset from surface seawater, and suggest that the coral Ba isotopic composition is largely independent from biomineralization processes and temperature. In contrast, the coral Ba/Ca ratios show a wide range of inter-colony differences, from 2 to 14 μmol/mol, which is too large to be ascribed to changes in Ba concentration of seawater or to be explained by other environmental parameters. Rayleigh fractionation of corals and seawater during biomineralization has been proposed to explain the large variation of Ba/Ca observed in coral skeletons. However, this cannot be supported by the new Ba isotopic data of the South China Sea corals. Our results suggest that Ba isotopes ($\delta^{137/134}$Ba) in shallow-water coral skeletons are better suited to document the chemical composition of seawater than Ba/Ca ratios, and might enable more reliable estimates of perturbations to upper ocean Ba cycling from river input, upwelling and marine productivity throughout the past.