A combined Eu/Ca and Ba/Ca based proxy to distinguish between fresh water and marine habitats

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Due to the deterioration of fossils through time, it is often difficult to constrain the paleohabitat of organisms using morphological clues alone. An important question is whether a fossilized organism lived in freshwater or in a marine environment. Sedimentological data can provide clues about the salinity conditions that prevailed during deposition, but with the possibility of post-mortem transport, there are chances of incorrectly labelling a freshwater species as marine and vice-versa.

We provide an alternate approach that involves elements which are, (1) not biologically essential and can be assumed to be entirely passive in the biochemistry that is involved in the production of skeletal tissues, and (2) are subject to the same biochemical pathways as Ca because the biochemistry of the organism is unable to discern between Ca^{2+} and the $Me^{(1+/2+/3+)}$ ions. In addition, these elements must be (3) enriched in the skeletal tissues relative to the ambient water, and (4) display several orders of magnitude change in Ca-normalized ratios in response to environmental salinity change. Barium concentration decreases by 2 orders of magnitude, Eu concentration decreases by 3-4 orders of magnitude while concentration of Ca increases by roughly 2 orders of magnitude from the fresh water to seawater leading to large changes in the Eu/Ca and Ba/Ca ratios. In addition, the concentrations of these elements are enriched in skeletal tissues relative to the water.

We have compiled Ca, Ba and Eu concentration data from published literature as well as analysed the concentrations of these elements in samples of high altitude himalayan and low altitude tropical rivers, seawater from rocky shores, mangroves, open ocean and estuaries, modern marine vertibrates, benthic molluscs, coastal gastropods, fresh water vegetation, as well as fossil vertibrates and fossil molluscs, using a quadrupole ICP-MS. Based on the above dataset involving 220 data points, we find that a plot of Ba/Ca versus Eu/Ca clearly distinguishes the freshwater and marine habitats. Fresh water species have Eu/Ca and Ba/Ca higher than 1e-7 and 1e-4, respectively, while marine species show much lower values.