Quantifying the $[Ba^{2+}]$: $\delta^{18}O_{SEAWATER}$: surface salinity relationship in the Eastern Equatorial Pacific

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Fluvial inputs to the world's oceans serve as the main source for dissolved barium in seawater. Barium desorbs from suspended clays in freshwater, making riverine water enriched in $[Ba^{2+}]$ [1, 2]. The suspended clays flocculate when riverine water mixes with seawater in estuaries, resulting in a conservative linear mixing between high $[Ba^{2+}]$, low sea surface salinity (SSS) in estuaries and low $[Ba^{2+}]$, high SSS in open ocean waters. Therefore, SSS can be estimated from dissolved barium concentrations in regions influenced by high riverine input. Furthermore, planktonic foraminifera incorporate barium into their calcium carbonate tests in proportion to seawater Ba/Ca ratios [3, 4]. Thus, foraminiferal Ba/Ca ratios from ocean sediment cores can be employed as a proxy for paleosalinity reconstructions. However, integral to the use of this proxy is the quantification of the regional seawater Ba/Ca:SSS relationship. Here, we quantify this relationship for the eastern equatorial Pacific Ocean, a location where intense seasonal rainfall and high riverine input from Central and northern South America creates the sharpest SSS gradient in the modern tropics. In October and November of 2010, surface seawater samples were collected along 85°W in a latitudinal transect from 10°N to 8°S during the RV *Melville* cruise MV1014, and analyzed for SSS, Ba/Ca ratios, and $\delta^{18}O$. For salinities < 31.4, we find a large change in Ba/Ca of 8.02 µmol/mol per salinity unit, while for salinities > 31.4 the relationship levels off at a Ba/Ca ratio of 4.5 µmol/mol. Based on the $\delta^{18}O$:SSS relationship in our samples, we also find two distinct end members of freshwater input to the region, one with a Costa Rican riverine $\delta^{18}O$ end member of -10.0‰ for salinities up to 31.4 and one with a freshwater end member of -7.2‰ dominated by freshwater precipitation for salinities > 31.4. This indicates that the Ba/Ca:SSS relationship for salinities < 31.4 is indeed driven by regional fluvial inputs. We will also present new reconstructions of regional SST and SSS based on a new set of multicores collected from the Cocos and Carnegie Ridges.

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REE in fossil biogenic apatite

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Rare earth elements (REE) in fossil biogenic apatites are frequently used as palaeonevironmental proxies, because the in-vivo REE concentrations (lower ppb range) are efficiently overprinted by diagenetic post-mortem REE uptake (in the ppm range) especially in fossil bone and dentin. The post-mortem REE uptake was long assumed to be limited to the fossilisation process, were carbonate hydroxyl-apatite is transformed into a more stable fluor-apatite, organic components are degraded and the porosity is filled by secondary minerals. However, recent studies reveal that REE uptake takes place over prolonged timescales in the order of millions of years, rather than thousands of years [1,2]. Furthermore, substantial intra-bone fractionation of the REE is observed, even exceeding two orders of magnitude in $(La/Sm)_N$ and $(La/Yb)_N$ within single bone specimens [2]. These observations necessiate a deeper understanding of REE with respect to fossil bones, if this group of elements is to be used as a palaeoenvironmental proxy in the future.

We will present REE profiles measured by LA-ICPMS over individual fossil bone samples from a wide range of diagenetic settings, ranging from Lower Triassic to Holocene age. Key observations are (1) MREE are efficiently scavenged at the outer bone rim and are increasingly depleted towards the central bone; (2) negative Ce-anomalies develop with increasing distance from the outer bone rim, which have no environmental significance; and (3) positive La and superchondritic Y/Ho anomalies evolve with increasing distance from the bone rim and decrease again towards the marrow cavity. A comparison with literature data indicates that (1) fossil bones derive their REE budget from the ambient pore fluid, rather than surface waters; and (2) that individual fossil bones may have intra-bone $(La/Sm)_N$ and $(La/Yb)_N$ variability covering more than half of the range previously found in literature compilations [n = 1691; 3]. Our data implies, that HREE are generally more mobile in diagentic fluids, which is likely due to stronger complexation of HREE with carbonate ions, when compared to the LREE.

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