

Isotope imaging via LA-MC-ICPMS: A $\delta^{11}\text{B}$ study in marine carbonates

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Besides accuracy and precision of isotope ratio data spatial information can be crucial to allow for interpretation of natural samples with complex structures. Tools providing this combination may open up a new field of applications in isotope geochemistry. *Laser Ablation-Multi Collector-ICPMS* offers the analytical preconditions to achieve this challenging task.

Using a recently published method we present the first $\delta^{11}\text{B}$ 2D-images in a sample of coralline red algae [1]. The *Clathromorphum nereostratum* specimen used in this study was collected alive in 2004 off the coast of Attu island (Alaska, USA). It had been growing for more than 120 years covering most of the period of anthropogenic CO_2 emission and resulting ocean acidification. Forming annual layers of high-Mg calcite it is a promising climate archive for the high latitudes. Conventional bulk techniques appear inadequate for the determination of $\delta^{11}\text{B}$ used as pH proxy when considering the annual growth rate of about $400\mu\text{m}$. Using LA-MC-ICPMS we were able to determine the long-term decline in pH ($\sim 0.08 \pm 0.01$ pH units in 100 years). Additionally, a seasonal signal (0.1 pH units) could be identified presumably originating from strong CO_2 consumption during phytoplankton blooms in spring.

Our results clearly show a heterogeneous but systematic distribution of $\delta^{11}\text{B}$ within this sample, being the result of different phases of calcite precipitation by the alga. The seasonal cycle and spatial distribution of $\delta^{11}\text{B}$ can only be evaluated using high-resolution methods like the one applied here. Bulk techniques only would have picked up the long-term pH trend, but such measurements may have been compromised by mixing sample material from distinct phases, differing in $\delta^{11}\text{B}$. Thus, we consider this a good example of the gain in information which can be obtained using high-resolution in-situ techniques in isotope analysis.

[1] Fietzke et al (2010) *J. Anal. At. Spectrom.* **25**, 1953-1957

Depositional controls on spatial heterogeneity in pyrite $\delta^{34}\text{S}$: comparing the modern and ancient

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The sulfur cycle plays a key role in regulating Earth's surface redox balance and provides a record of environmental and ecological change over Earth history. As new data are generated, we observe that (1) select records have more stratigraphic variability than expected; and (2) mean isotopic values differ from location to location for both sulfate and sulfide. Interpreting these ancient data is a challenge, in large part because we have only a limited understanding of sulfur isotope systematics in modern depositional environments.

Here we examine variability and mean values in pyrite sulfur isotopes from both modern and ancient strata. In the modern, we analyzed $\delta^{34}\text{S}_{\text{pyr}}$ from a series of cores taken across a gradient of water depths from the Gulf of Papua deltaic complex. In cores from physically undisturbed locations, $\delta^{34}\text{S}_{\text{pyr}}$ values were depleted ($\sim 20\text{‰}$ to 0‰) in the upper sediments, becoming progressively enriched with depth (approaching $\sim +10\text{‰}$ to $+20\text{‰}$). In general, these cores were characterized by smooth profiles with little sample-to-sample scatter ($< 5\text{--}10\text{‰}$). In contrast, cores overlain by remobilized muds had very enriched $\delta^{34}\text{S}_{\text{pyr}}$ values (up to $+35\text{‰}$, often within the remobilized near-surface samples) and large scatter in the profiles (variability between adjacent samples up to 35‰). Such drastically different isotopic signatures could easily result in divergent environmental reconstructions without knowing the depositional context of these samples. The magnitude of local, microbially driven variations in S isotopes in modern sediments is sufficiently large that uneven incorporation of these signatures during deposition and lithification can explain much of the observed discordance in chemostratigraphic reconstructions of sulfur cycling over Earth history. To illustrate the impact of depositional conditions in the ancient record, we compare coeval sedimentary strata from two late Ediacaran sedimentary basins: the Nama Group of Namibia and the Ara Group of Oman, where different depositional environments yield strongly divergent $\delta^{34}\text{S}$ data. A detailed understanding of depositional context and its impacts on $\delta^{34}\text{S}$ signals is essential for robust interpretations of geochemical data.