

## Past changes in riverine input and ocean circulation in the Gulf of Guinea

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Large river systems draining the West African Monsoon area deliver sediments and dissolved trace elements into the Gulf of Guinea (GoG) in the easternmost equatorial Atlantic. The different catchment areas of these river systems are characterized by different geological ages and rock types releasing distinct radiogenic neodymium isotope compositions during weathering which are supplied to the GoG. The main rivers discharging into the GoG are the Niger, the Sanaga, the Nyong and the Ntem with present day  $\epsilon\text{Nd}$  signatures of -10.5 [1], -12.3, -12.5 and -28.1 [2], respectively. These riverine inputs mix with the tropical Atlantic surface waters. At intermediate water depths Antarctic Intermediate Water (AAIW) prevails whereas the deep basin at this location is mainly filled with NADW.

We focus on a marine sediment core that was recovered off the Sanaga and Ntem Rivers and we reconstruct changes in riverine inputs and in mixing of surface and deep water masses over the past 140,000 years.

Changes in riverine inputs most likely reflecting latitudinal shifts of the rainfall zones across the different catchment areas were obtained from the Nd isotope signatures of the residual detrital fraction of the sediment. Sediment leachates of several GoG core top samples reflect the riverine input from nearby rivers indicating transport of particles coated in the rivers. Both the sediment leachates and the residual detrital fraction show similar patterns, with shifts towards radiogenic values during the interglacials and least radiogenic values during glacial periods. This shift in  $\epsilon\text{Nd}$  values may be attributed to the migration of the rainfall zones towards the north during interglacial times and thus implies the increased influence of the northern rivers, the Sanaga and Nyong.

The oxidatively-reductively cleaned planktonic foraminiferal calcite of the core top samples in the GoG reflects surface seawater signatures. Non-reductively cleaned planktonic foraminiferal tests and cleaned shallow endo-benthic and epi-benthic foraminiferal tests were used to acquire information about past bottom waters. Difficulties in cleaning down core foraminiferal samples were experienced and these samples appear to be contaminated by secondary manganese and iron bearing phases, even after cleaning. Those phases may have overprinted the original surface water Nd isotope composition in the planktonic foraminiferal tests. As the planktonic and benthic foraminiferal values are overall similar to the sediment leachates, the foraminiferal isotope signatures are most likely overprinted by isotopic signals originating from the rivers due to remobilization processes in the sediments and formation of secondary phases such as Mn-carbonates, which are attached to the foraminiferal calcites.

### References:

- [1] Goldstein et al. (1984) *Earth and Planetary Science Letter* **70**, 221-236.  
[2] Weldeab et al. (2011) *Geophysical Research Letter* **38**, pp. 5.

## Mg-dolomite nucleation in biofilm of sulfate-reducing bacteria at modern seawater salinity

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Sulfate-reducing bacteria (SRB) have been identified to facilitate present-day dolomite formation under hypersaline conditions. Our laboratory study demonstrates for the first time, to our knowledge, primary Mg-rich dolomite formation in biofilms of the marine sulfate-reducing strain *Desulfohalobus mediterraneus*, under modern seawater salinity and Mg/Ca ratio. Spatial distribution of crystals within the biofilm was investigated using confocal laser scanning microscopy. Crystal morphology and mineralogy were examined with scanning electron microscopy, X-ray diffraction, and electron microprobe. Values of  $\delta^{44/40}\text{Ca}$  of crystals, biofilm, and bulk fluid were analyzed by double spike thermal ionization mass spectrometry. Mg-dolomite crystals precipitated in association with extracellular polymeric substances (EPS) in the biofilm. Three days after inoculation, nucleation of single nano-spherulites (~50 nm) was observed, subsequently aggregating to spherulites of ~2–3  $\mu\text{m}$  in diameter after 14 days. Differences in Mg/Ca molar ratios and  $\delta^{44/40}\text{Ca}$  (‰) values between the biofilm material (including cells and EPS;  $0.87 \pm 0.01$  [2 SD] and  $0.48\text{‰} \pm 0.11$  [2 SE], respectively), the crystals ( $1.02 \pm 0.11$  [2 SD] and  $<0.08\text{‰} \pm 0.24$  [2 SE], respectively), and the liquid bulk medium were observed after mineral precipitation ( $4.53 \pm 0.04$  [2 SD] and  $1.10\text{‰} \pm 0.24$  [2 SE], respectively). These data indicate that the EPS bind relatively more  $\text{Ca}^{2+}$  than  $\text{Mg}^{2+}$ . We also propose a two-step fractionation process for Ca, shown by successive relative enrichment of  $^{40}\text{Ca}$  in the biofilm and the crystals, compared to the bulk medium. Our results demonstrate the capability of EPS to overcome kinetic inhibition for dolomite, also suggesting contribution of SRB to dolomite deposition during periods of low oxygen concentration in the Phanerozoic.