Hydrogen isotopic signatures of algal biomarkers as a proxy of hydroclimatic variability in Lake Isabel, Mexico

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Based on the observed linear relationships between the isotopic composition of the source water and the δD values of aquatic and terrestrial lipid biomarkers, the analysis of the isotopic signature in these organic molecules preserved in sediments has become a new tool for paleohydrological reconstruction. However the influence of additional factors (i.e. growth rate, salinity, and temperature) on the δD values of algal lipids remains poorly understood. Therefore, sediments from a short core corresponding to the time period 1943-2003 A.D from a hypersaline crater lake located on Isla Isabel, 30km off the Pacific Coast of Mexico, were analysed for lipid biomarker δD values and compared to instrumental climate data. δD values of the 1,15C_{32} diol, a specific biomarker for algal populations, showed a significant relationship with the instrumental record of rainfall amount confirming its potential as a proxy of past hydroclimatic conditions. Unexpectedly, deuterium-enrichment in diols was observed during wetter conditions while these were significantly depleted during drier periods. We hypothesize that under this strongly seasonal climate regime algal growth conditions play an important role in determining algal lipid δD values. This calibration study between the isotopic signatures and the climatic record shows the complexity but also the potential of hydrogen isotope analyses of lipids as proxy to reconstruct the past climatic variability.

The role of inorganic additives in evaporitic carbonate precipitation

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Interactions between carbonate-bearing groundwaters and sulphate minerals in evaporitic settings lead to the formation of carbonate deposits [1]. However, our understanding of the reaction kinetics in these processes is still fragmented.

An experimental study following the formation of $CaCO_3$ phases from gypsum (GYP, $CaSO_4.2H_2O$) in the presence of 1 to 100 mM of Mg, Zn, Sr, or PO_4 was carried out at 25°C. GYP (Ø < 420 μm) was reacted with 50 mM Na_2CO_3 at a GYP/liquid ratio of ~ 0.007 in stirred closed reactors. The experiments were run at two different initial pH settings (***a***) pH ≈ 11.4, due to the Na_2CO_3 or (***b***) pH ≈ 6.8, where the solutions was also supersaturated with $CO_{2\ (g)}$. Solids were characterized over time by X-ray diffraction and high-resolution microcopy imaging while changes in aqueous contentrations were determined by ion chromatography.

The results of both sets showed that the dissolution of GYP (release of Ca^{2+}) lead to a relatively fast nucleation and growth of $CaCO_3$ polymorphs. As long as the solution had excess carbonate, the continuous dissolution of gypsum was mirrored by a simultaneous precipitation of $CaCO_3$. In all cases, the first phase nucleating on the gypsum surface was amorphous $CaCO_3$ (ACC). Depending on experimental approach or the presence of additives, ACC transformed gradually to various $CaCO_3$ polymorphs. At condition (***a***) the GYP completely dissolved in ~ 24 h and the initial ACC transformed into calcite within 2 days, while in approach (***b***) GYP took only ~ 5 h to fully dissolve and the carbonate that formed after 30 h was 'stable' vaterite [2]. The presence of additive ions strongly influenced both the reaction kinetics and the nature of the crystalline end products. For example, using approach (***b***) but adding 1 mM Zn produced calcite (instead of vaterite) with Zn becoming incorporated into the calcite structure; conversely, with 100 mM Mg present in the initial solution, ACC transformed to aragonite after 12 h and calcite was not observed. These results revealed that aqueous additives play a fundamental role in controlling the nature and formation pathway of the end product and this has major implications for biomineralization, industrial applications, and CO_2 sequestration.

[1] Sanz-Rubio *et al.* (2001) *Sedim. Geology* **140**, 123–142.
[2] Bots *et al.* (2011) *Geology* **39**, 331–334.