

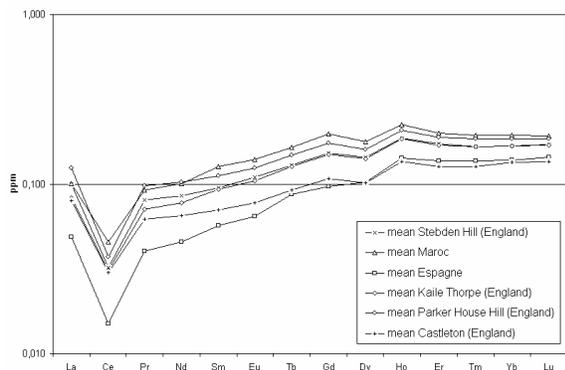
## Mississippian microbial carbonates: Test for the validation as proxy for marine REE geochemistry

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First results suggested that recent microbial carbonates are so far the best proxy material for the record of marine REE-patterns (Webb & Kamber 2000). The results were confirmed by further tests on Archean (Kamber & Webb, 2001, Kamber *et al.*, 2004) and Devonian (Northdurft *et al.*, 2003) microbial carbonates.

To further validate this proxy, REE and some additional trace elements of microbial carbonates were analysed from several locations from the upper Viséan (Carboniferous) of England, Morocco, and Spain. Very clean microbial material was chosen by thin-section studies and analysed by ICP-MS. All samples show very smooth REE-patterns that perfectly display the REE-geochemistry characteristics of modern seawater as e.g. LREE depletion, positive La- and Gd- and negative Ce-anomalies. The nearly marine Y/Ho-Ratio as well as the contents of Zr, Sc, Hf and Th suggest very low terrigenous contamination.



While accompanying non-microbial carbonates show the same REE-pattern as the microbial ones, they have a significantly lower absolute REE content and are therefore less readily accessible for analysis.

Slight differences exist in REE content of the different locations. Potential interrelation with the local paleogeographic situation, e.g. by incorporation of variable degrees of terrigenous input requires further examination.

Our data confirm the results by Webb & Kamber (2000) that microbial carbonates are so far the most reliable and additionally easiest accessible proxy for fossil marine REE-geochemistry. They do not show the fractionation problems of skeletal carbonates, incorporate high REE content and are overall relatively resistive to diagenetic overprint.

Further investigations to elucidate the possibilities of application to paleogeographic and paleoceanographic reconstructions are necessary.

## Carbonate and anhydrite veins from altered gabbroic oceanic crust (Atlantis Massif, MAR 30°N)

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Atlantis Massif is an Oceanic Core Complex (OCC) that formed in the past 1.5-2.0 Myr at the intersection of the Mid-Atlantic Ridge and the Atlantis fracture zone. IODP Hole U1309D, drilled in the central part of the Atlantis Massif OCC, is the third-deepest hole in oceanic lithosphere with a core recovery of 75%. Gabbros and troctolites are the dominant rock types (92%), followed by ultramafic (~5%) and basaltic (~3%) rocks. The magmatic sequence is metamorphosed and fractured, and fluid flow during uplift resulted in the formation of several generations of late-stage veins that record sub-seafloor water-rock interactions. Below the diabase-dominated top section of U1309D carbonate veins are the most abundant late-stage vein type. Macroscopic anhydrite veins occur only at about 740 mbsf.

Carbon, O and Sr isotope compositions of the calcites do not vary systematically down-hole. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios are relatively unradiogenic and span a limited range between 0.7043 and 0.7051. Oxygen and C isotope ratios are both isotopically light displaying δ<sup>18</sup>O (VSMOW) values of about 10‰ and δ<sup>13</sup>C (VPDB) values of about -4‰. Oxygen isotope compositions of calcites yield minimum precipitation temperatures between 150° and 220°C (assuming seawater δ<sup>18</sup>O for the fluid). The temperature could have been significantly higher, if the fluid had exchanged oxygen with basement. For instance, if the δ<sup>18</sup>O value of the precipitating fluid was 2‰, like in the Rainbow hydrothermal fluids, calculated formation temperatures would be 30° to 50°C higher. In fact, Sr isotope ratios of the carbonate veins approach values for high-temperature hydrothermal systems such as Rainbow or Logatchev. Unlike in the calcites from detachment fault rocks from the 15°20'N Fracture Zone area, however, the calcites from Site U1309D lack carbon isotope signatures for thermal methanogenesis. Hence, temperatures were likely not higher than 300°-350°C.

Two massive cm-wide single anhydrite veins were recovered at about 740 mbsf at Site U1309D. For the anhydrite veins we obtained <sup>87</sup>Sr/<sup>86</sup>Sr ratios of 0.70774 for core 150R3 and 0.70631 for core 153R3. As the Sr isotope composition of anhydrites from 1309D and 504B are similar we infer that 1309D anhydrites may also have formed in the down-flow limb of a hydrothermal convection cell, from seawater that has been heated to about 150°C and has had limited opportunity to exchange Sr with the basement.