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Isotopic evidence for methane seep origin of barite in Neoproterozoic cap carbonates of NW Africa

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Barite has been reported from post-Marinoan cap carbonates throughout NW Africa and from correlative successions in Australia, Canada, Norway and China. Much of this barite has been replaced by carbonate but in NW Africa, the original barite has been preserved. Samples of barite were collected from two geographically distant locations within the Taoudéni Basin in Mauritania and Mali. The $\delta^{34}S$ compositions of these deposits range between 20‰ and 45‰ CDT, which indicates that microbially mediated sulphate reduction was active in the fluids that eventually precipitated barite. $^{87}Sr/^{86}Sr$ ratios of the barites range in both locations between 0.7077 and 0.7082, which is close to the earliest Ediacaran seawater value. In today's oceans barite can precipitate in one of three ways: directly from seawater as biogenic barite, or from modified seawater issuing out of hydrothermal vents or cold methane seeps. These three origins can be cleanly distinguished using a combination of S and Sr isotopes [1]. Our data suggest that barite from cap carbonates of the Taoudéni Basin precipitated from methane seeps, which agrees with carbon isotopic evidence for methanogenesis in barite-bearing cap carbonates from South China [2]. Our study lends strong support to the notion that cap carbonates and their characteristically deformed nature resulted from methane gas escape following the thermal destabilisation of methane hydrate [2].

References

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4.1.21

Role of iron in marine biogeochemistry

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This paper discusses the marine biogeochemistry of iron and its role in climate change. Iron is an essential micronutrient for organisms and plays a critical role in oceanic primary production. Iron limitation of phytoplankton growth has been observed in a number of High Nutrient Low Chlorophyll regions (e.g. Southern Ocean, Equatorial and Subarctic Pacific) and coastal upwelling systems. Furthermore, co-limitation of iron and phosphate has recently been observed for diazotrophs in the North Atlantic. Iron limitations result from low input. The atmosphere forms the main source for open ocean environments, whereas benthic and riverine sources dominate in continental shelf waters. The biogeochemical processes that control the chemical speciation and uptake of iron are poorly constrained.

Marine bacteria, as their terrestrial counterparts, secrete Fe(III)-chelating siderophores and take up these complexes via high affinity membrane transporters. The Fe(III) in siderophore complexes is subject to photochemical reduction to Fe(II) upon cleavage of both the hydrophobic tail and α-hydroxy acid group by UV light. An alternative uptake mechanism for phytoplankton involves the direct reduction of Fe(III) complexes by membrane-bound NAD(P)H oxidase enzymes, thereby increasing levels of free Fe(II), and subsequent Fe(II) or Fe(III) (following oxidation) uptake via metal transport proteins. The biogeochemistry of Fe(II) is intriguing, with photochemical and biological production routes. Moreover, wet and dry atmospheric deposition form a source of Fe(II) for surface waters, and sediments for deeper waters. Despite its high solubility, Fe(II) concentrations in oxygenated seawater are estimated to be negligible ($<10^{-18}$ M at pH 7) due to its rapid oxidation rate (half-life < 5 min at 25°C). However, recent work in shelf and open Atlantic Ocean waters has shown that ca. 3-8% of total dissolved iron occurs in the Fe(II) form, indicating that there is a mechanism for buffering iron(II) in seawater. Typical iron(II) concentrations were between 15 and 150 pM, and higher concentrations (ca. 100 pM) were generally found in the shallow Atlantic shelf waters.