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Induced and catalysed mineral precipitation in the deep biosphere

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Authigenic and early diagenetic minerals provide archives of past (bio)geochemical processes. In particular, isotopic signatures preserved in the diagenetic phases have been shown to document drastic changes of subsurface microbial activity (the deep biosphere) over geological time periods (Contreras et al., 2013; Meister, 2015). Geochemical and isotopic signatures in authigenic minerals may also document surface conditions and past climate. Nevertheless, such use of authigenic mineral phases as (bio)geochemical archives is often hampered by the insufficient understanding of mineral precipitation mechanisms. Accordingly the time, place and rate of mineral precipitation are often not well constrained. Also, element partitioning and isotopic fractionation may be modified as a result of the precipitation mechanism.

Early diagenetic dolomite and quartz from drilled sequences in the Pacific were compared with adjacent porewater compositions and isotope signatures to gain fundamental insight into the factors controlling mineral precipitation. The formation of dolomite in carbonate-free organic carbon-rich ocean margin sediments (e.g. Peru Margin; Ocean Drilling Program, ODP, Site 1229; Meister et al., 2007) relies on the alkalinity-increase driven by anaerobic oxidation of methane and, perhaps, by alteration of clay minerals.

In contrast, quartz is often significantly oversaturated in marine porewaters as the dissolved silica concentration is buffered by more soluble opal-A. For example, quartz does not form throughout a 400 metre thick sedimentary sequence in the Eastern Equatorial Pacific (ODP Site 1226; Meister et al., 2014) because it is kinetically inhibited. This behaviour can be explained by Ostwald's step rule, which suggests that the metastable phase forms faster. However, hard-lithified quartz readily forms where silica concentration drops sharply below opal-saturation. This violation of Ostwald's step rule must be driven by an auxiliary process, such as the adsorption of silica to freshly precipitated iron oxides along a deep iron oxidation front.

In conclusion, two different modes of precipitation can be observed in modern sub-seafloor porewater systems. Dolomite precipitation is thermodynamically controlled through microbially induced supersaturation. Quartz formation is controlled through an auxiliary process that helps it to overcome a kinetic barrier. These observations exemplify the importance to distinguish between kinetic and thermodynamic effects on mineral formation under Earth surface conditions. To evaluate geochemical signatures, these modes of precipitation need to be taken into account.

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