Diagenesis in deep-seated Cretaceous black shales: Inverse modeling and transient model simulations

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A transport-reaction model was designed to identify the importance and specific rates of diagenetic processes operating in four sites drilled during ODP Leg 207 (Demerara Rise, Equatorial Atlantic). Model results reveal that almost 100 Ma after their deposition, deeply buried (200-500 mbsf) Cretaceous black shales still act as active bioreactors at great sediment depths. Methanogenesis in the black shales is identified as a key process, which dominates not only organic matter degradation but also the sulfate availability through the anaerobic oxidation of methane above the black shale sequences. The complete depletion of sulfate in the methane-rich black shale sequences promotes the dissolution of biogenic barites. The released barium reprecipitates as authigenic barite at the top of the sulfate depletion zone and serves as an indicator for the location of the sulfate-methane interface.

Reaction rate constants were determined by inverse modeling techniques. Due to the low metabolic activity in the deep biosphere, estimated rate constants are orders of magnitudes lower than those observed in the shallow subsurface. Model-determined methanogenic rate constants (1- 3.5 10^{-9} a^{-1}) compare well with those estimated by the empirical power law (Middelburg, 1989). In addition, methanotrophic reaction rates (10^{-2} μM a^{-1}) are similar to experimentally determined rates at other deep biosphere sites (ODP Leg 201). Transient model simulations indicate that the initial reactivity of the black shale organic matter must have been already low (ca. $1 \cdot 10^{-6}$ a^{-1}) during its deposition 100 Ma ago. The decrease of organic matter reactivity and the associated decrease in methanogenic rates, as well as changing sedimentation rates lead to significant shifts of the sulfate methane interface over the past 100 Ma. The associated vertical migration of the barite precipitation zone is well recorded in the barite depth profile and supports our transient model results.

Refercences

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Phosphogenesis in recent upwelling areas: The importance of microbial communities indicated by lipid biomarkers

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The burial of phosphorus and the formation of phosphorites (phosphogenesis) in marine sediments represent an important sink in the global phosphorus cycle. Numerous basin-scale phosphorite deposits were formed in the geological past (e.g., Trappe 1998). Phosphogenesis is not only found in ancient settings, it is reported in recent sediments of upwelling regions as for example off Namibia, Peru, and Chile (Föllmi 1996).

These sediments contain dense populations of large nitrate-storing sulfide-oxidizing bacteria *Thiomargarita*, *Beggiatoa*, and *Thioploca*, respectively. Due to metabolic activities of the thiotrophs generating sulfate, a close spatial connection to sulfate-reducing bacteria is established. Differences in the motility of the thiotrophs at the three study sites lead to different distributions of sulfate reducers in sediments off Namibia, Peru, and Chile. Profiles of lipid biomarkers attributed to sulfate reducers (10Me$C_{16:0}$ fatty acid, *ai*-$C_{15:0}$ fatty acid, and mono-*O*-alkyl glycerol ethers) document the close association to thiotrophs. Depth profiles of mono-*O*-alkyl glycerol ethers have been found to correlate best with the occurrence of large sulfur bacteria. This suggests a particularly close link between mono-*O*-alkyl glycerol ether-synthesizing sulfate reducers and thiotrophs. Lipid biomarker profiles indicate that the interaction between thiotrophs and sulfate-reducing bacteria favors phosphate enrichment, triggering phosphorite formation in upwelling areas.

Studying recent phosphogenic environments provides a basis to better understand micobial influence on phosphogenesis and to better constrain the role of microorganisms in the formation of ancient phosphorites.

References

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