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 deploration of sulfate in the methanenrich 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 ($10^{-2}$ $\mu$M a$^{-1}$) are similar to experimentally determined rates at other deep biosphere sites (ODP Leg 201). Transient model simulations indicate that the initial reactionivity of the black shale organic matter must have been already low (ca. $10^{-9}$ 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.

References