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Research paper

Hydrogeochemical models locating sulfate-methane transition zone in marine sediments overlying black shales: A new tool to locate biogenic methane?

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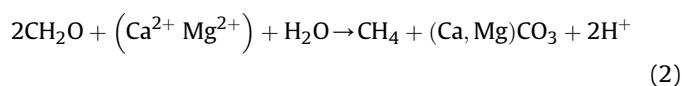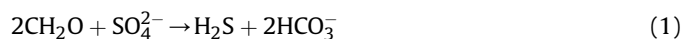
ABSTRACT

Precise hydrogeochemical modeling of early diagenesis is a key in the reconstruction of sedimentary basin models. This determines the mineralogical evolution of the sediment and consequently the porosity of the rock. During early diagenesis also part of the initial organic matter is converted into biogenic gas: CH_4 CO_2, and H_2S. These processes are part of complex reaction chains during sedimentation, and biogeochemical reactions leave different signals that can be observed today. In this work, we reproduce the early diagenetic processes as integrated signals over geological times in sediments of the Demerara Rise by applying chemical thermodynamics using the PHREEQC (version 2) computer code. The investigated sediments are characterized by the presence of black shales in 410—490 mbsf and by a diagenetic barite layer above in 300—350 mbsf at depth of sulfate-methane transition (SMT). We determine the parameters that influence the location of diagenetic barite peaks in sediments overlying black shales by means of a novel modeling approach. Crucial parameters are the amount of bacterial organic matter mineralization, sedimentation rates and bottom water sulfate concentrations. All parameters are intertwining and influence the sulfate-methane cycle. They affect the location of the SMT visualized by diagenetic barite peaks. However, our model approach opens a wide field in exploring early diagenetic reactions, processes and products (such as biogenic methane) over geological times mirrored by diagenetic minerals and pore water concentration profiles that can be detected in present-day sediments.

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1. Introduction

Early diagenesis in marine sediments is a process of various intertwining biogeochemical reactions, which are difficult to quantitatively investigate without the help of numerical tools. A precise quantification of these reactions is thus a necessary addition for general basin modeling. Indeed, this determines the mineralogical evolution of the sediment and consequently the porosity of the rock. During early diagenesis also part of the initial organic matter is consumed and partly converted to biogenic gas: CH_4, CO_2, and H_2S. Sulfate reduction and methanogenesis are of special interest due to their dominant role in organic matter remineralization in anoxic marine sediments (D'Hondt et al., 2002; Jørgensen, 2005). Organic matter (simplified as CH_2O) is primarily

oxidized by sulfate until sulfate depletion (Eq. (1)), and is furthermore converted by methanogenesis (simplified by the reaction: Eq. (2); Claypool and Kaplan, 1974; Whiticar et al., 1986).

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad (1)$$

$$2CH_2O + \left(Ca^{2+} \ Mg^{2+}\right) + H_2O \rightarrow CH_4 + (Ca, Mg)CO_3 + 2H^+ \qquad (2)$$

The hotspot of microbial and diagenetic processes is within the sulfate-methane transition (SMT). The SMT and its development over time are difficult to characterize and to determine. However, recently, diagenetic barite has been found to be an indicator of this reactive zone (e.g. Arndt et al., 2006; Riedinger et al., 2006; Henkel et al., 2012; Kasten et al., 2012).

In the cycle of barium and sulfate in seawater and sediment, primary biogenic barite particles are formed in the water column in

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association with the degradation of organic matter (Dehairs et al., 1980; Bishop, 1988; Dymond et al., 1992; Francois et al., 1995). SO_4 is progressively reduced by bacteria in the sediment column until an almost total disappearance in the SMT. Primary barite gets undersaturated in sulfate-depleted pore waters below the SMT, and will be dissolved. Subsequently, barium ions are released in high concentrations (100—300 ppm) into the pore water, diffuse upwards into sulfate-enriched sediments, and re-precipitate as diagenetic barite (Fig. 1; Eq. (3)) in a distinct zone slightly above the SMT, where the presence of sulfate allows the precipitation of barite (e.g. Gingele and Dahmke, 1994; Torres et al., 1996a; Dickens, 2001; Aloisi et al., 2004; Arndt et al., 2006; Riedinger et al., 2006; Henkel et al., 2012; Kasten et al., 2012).

$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4 \qquad (3)$$

The SMT represents an important redox-boundary in organic matter-rich sediments with respect to the diagenetic barium cycle and locates the beginning of the production biogenic methane (Borowski et al., 1999). Through advection and diffusion methane migrates upwards from deeper sediment layers while sulfate migrates downwards. At the SMT sulfate and methane are contemporaneously consumed through anaerobic oxidation of methane (AOM; e.g. Reeburgh, 1976; Iversen and Jørgensen, 1985; Niewöhner et al., 1998; Hoehler et al., 1994; Boetius et al., 2000, Eq. (2)).

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad (4)$$
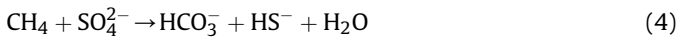
The location of the SMT is determined by the sulfate-methane interplay. Changes in, for example, methane fluxes induce a

migration of the SMT relative to the sediment surface (Kasten et al., 2003). In turn, the location of the diagenetic barite front is dependent on the SMT location and the period of time the SMT is fixed at a defined sediment depth (e.g. Dickens, 2001; Riedinger et al., 2006; Snyder et al., 2007). It has been applied successfully to determine upward fluxes of methane from gas hydrate systems of the Blake Ridge (Dickens, 2001; Snyder et al., 2007) and of the northern Congo Fan (Kasten et al., 2012), from Cretaceous black shales in deposits of the Demerara Rise (Arndt et al., 2009), and in sediments in the Benguela upwelling system (Riedinger et al., 2006). Diagenetic barite fronts may serve as indicators for past and present location of redox fronts due to changing methane and sulfate fluxes, and for hiatuses in sedimentation and changes in sedimentation rates (van Os et al., 1991; Bréhéret and Brumsack, 2000; Dickens, 2001). However, authigenic minerals are sensitive against diagenetic alteration. For instance, diagenetically formed barite fronts may dissolve and re-precipitate under changing redox-conditions over time. The evaluation of measured data about authigenic minerals in sediments may thus be difficult and may lead to misinterpretations. Regarding to this, geochemical
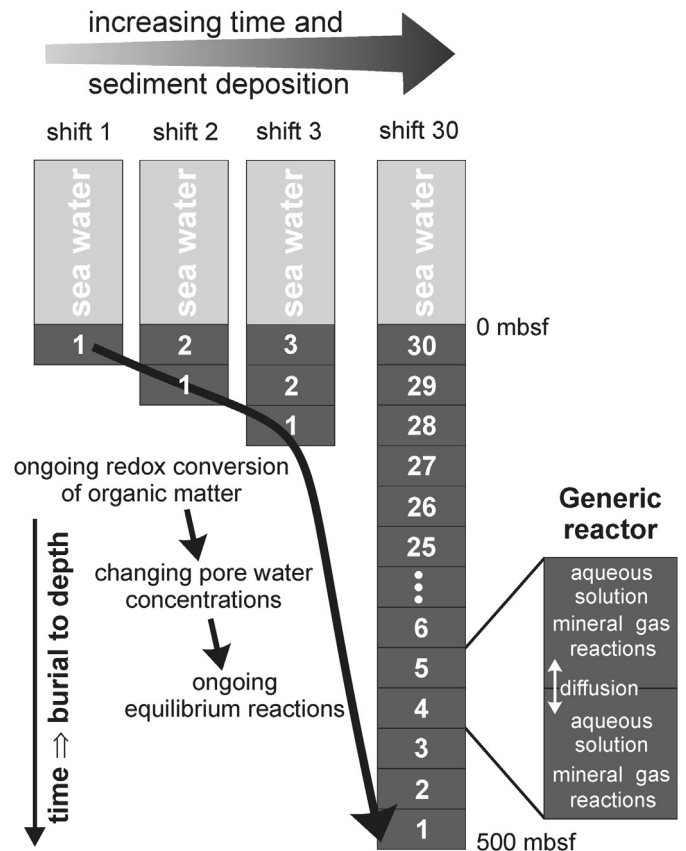
Figure 2. Concept of the PHREEQC model. The model describes the development of geochemical conditions in a growing sediment column with time. Each shift corresponds to a time step of 1,307,692 years. Diffusion regulates the exchange of dissolved species within the sediments and at the sediment—water interface. Equilibrium reactions between aqueous solution, solids, and gaseous phases occur within the cells and determine aqueous solution, mineral, and gas composition in each cell at each time step. The right column describes the recent situation within the modeled sediments after calculations of the last time step (shift 30). At each time step, equilibrium reactions are calculated "cell by cell" followed by remineralization of defined amount of organic carbon and calculation of species distribution. The remineralization of organic matter induces irreversible redox reactions. The time step is ended with calculations of new equilibrium conditions resulting from diffusion and sediment burial. The next time step begins with "cell by cell" equilibrium calculations (modified from Arning et al., 2011).
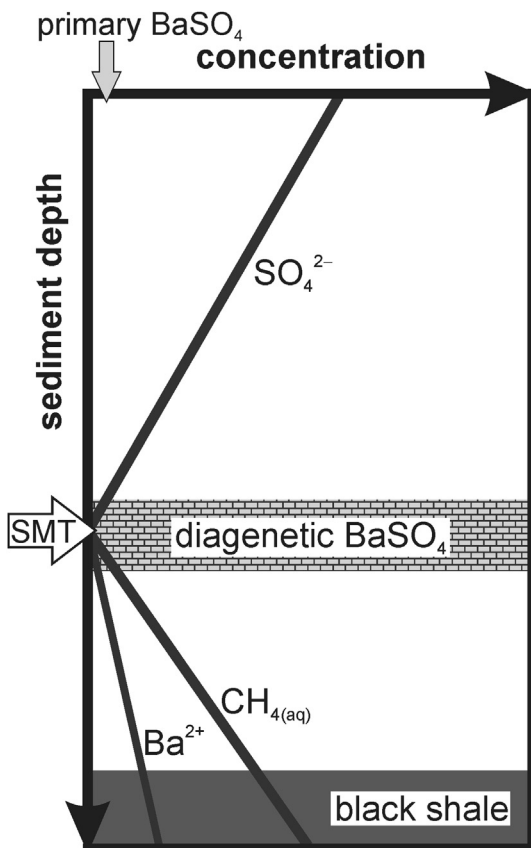
Figure 1. Scheme of important parameters in diagenetic barite ($BaSO_4$) formation in marine sediments overlying black shales. SMT: sulfate-methane transition.