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Thermodynamic modeling of complex sediment-water-gas interactions during early diagenesis

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Abstract

The driving force of complex biogeochemical reactions in sedimentary environments during early diagenesis is the irreversible redox-conversion of organic matter. Our modeling approach incorporates interdependent diagenetic reactions evolving into a diffusive multi-component and multi-phase system by means of thermodynamic equilibrium calculations of species distribution. The modeling tool is the PHREEQC (version 2) computer code. Reaction kinetics of organic carbon conversion are integrated into the set of equilibrium reactions by defining the type and amount of converted organic matter at a certain time step. The model has been applied so far in different environmental settings: the gas hydrate dominated sediments of Hydrate Ridge (ODP Leg 204), the high accumulation area of the Amazon Fan, and the upwelling area off Peru.

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Keywords: PHREEQC; hydrogeochemical modeling, methane; early diagenesis; biogeochemistry; gas hydrates.

1. Introduction

Early diagenetic processes in marine sediments are complex and can be investigated by hydrogeochemical models. Of particular interest regarding to methane cycling within marine sediments is the formation of methane hydrate and processes in the transition zone between sulfate reduction and methanogenesis. Here, irreversible remineralization of organic matter triggers the early diagenetic mineral precipitation/dissolution, gas formation and subsequent pore water compositional changes. Sulfate reduction delivers bicarbonate and sulfide to the system, according to the reaction $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$ [1]. When sulfate is exhausted, methanogenesis via the CO_2 reduction pathway is often the dominant biogenic methane formation process in marine sediments [2]. The process can be simplified by

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the reaction: $2CH_2O + Ca^{2+} + H_2O \rightarrow CH_4 + CaCO_3 + 2H^+$. The products of early diagenetic reactions initiate coupled equilibrium reactions that induce a new state of chemical equilibrium. The concurrent and interdependent reactions in an early diagenetic system can be best described by a conceptual modeling approach that considers all reactions and the fundamental principles of mass and charge balance. The hydrogeochemical model presented here is based on chemical thermodynamics. Reaction kinetic data are not considered. Rates of sulfate reduction and methanogenesis result from a defined amount of remineralizable organic carbon that is preassigned and determined by calibration of the model to alkalinity profiles.

In this paper we will compare the modeling results of three different environments: i) gas hydrate dominated sediments of Hydrate Ridge (ODP Leg 204), ii) the high accumulation area of the Amazon Fan (ODP Leg 155) and iii) the upwelling area off Peru (ODP Leg 112/201). This comparison highlights the key factors and processes in early diagenesis, and especially in biogenic methane formation.

2. Environmental settings

Hydrate Ridge is located offshore of Oregon (U.S.A.) in the Cascadia accretionary complex. Site 1246 is located in 870 m water depth. Temperature and pressure at the seafloor are within the range of the gas hydrate stability zone (GHSZ). Thus, methane hydrate is stable within the entire stratigraphic section above the bottom-simulating reflector (BSR) [3].

The Amazon Fan is one of the world’s largest deep-sea fans located on the northern part of the passive Brazilian Equatorial margin. Mass-transport deposits result in very high sedimentation rates. The sediments are located within the GHSZ [4].

Shelf sites off Peru are located within the oxygen minimum zone caused by a well-developed coastal upwelling regime, active since the Miocene period. This specific setting results in the deposition of thick organic-rich sediments. Pressure and temperature conditions at the shelf sites are not appropriate for the formation of methane hydrate within the sediments [5].

Table 1. Most important model input parameters determining early diagenetic processes within the investigated sediments. GHSZ: gas hydrate stability zone.

	ODP Leg 204, Site 1246 Hydrate Ridge	ODP Leg 155, Site 938 Amazon Fan	ODP Leg 112/201, Site 681 Shelf off Peru
Sedimentation rate (cm kyr^{-1})	31	660	8
Type of organic matter	marine	dominant terrestrial	marine
Within GHSZ	yes	yes	no

3. Conceptual model

The approach is based on a 1.7-liter reactor that is filled by present-day seawater and sediments of a defined mineral composition according to sediments from the investigated sites [3, 4, 6]. The driving force for the formation of diagenetic products in the reactor is the irreversible remineralization of organic matter. The accumulation of the organic matter metabolites (e.g. CH_4, CO_2, and H_2) leads to the development of new inorganic equilibrium conditions in the system. Equilibrium species distribution and coupled mass transfer that results from reactions in the modeling reactor are calculated by using the PHREEQC (version 2) program [7].

The model describes a “growing sediment column” (cf. Fig. 1 in [8]). Initially, equilibrium calculations are performed on just one sediment cell that is overlain by 5 cells containing seawater. The time step for each cell was calculated from the sedimentation rate. The main active transportation