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Case study

PEaCH₄ v.2.0: A modelling platform to predict early diagenetic processes in marine sediments with a focus on biogenic methane – Case study: Offshore NamibiaEsther T. Arning^{a,*}, Steffen Häußler^a, Wolfgang van Berk^b, Hans-Martin Schulz^a^a Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, D-14473 Potsdam, Germany^b Clausthal University of Technology, Department of Hydrogeology, D-38678 Clausthal-Zellerfeld, Germany

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ABSTRACT

The modelling of early diagenetic processes in marine sediments is of interest in marine science, and in the oil and gas industry, here, especially with respect to methane occurrence and gas hydrate formation as resources. Early diagenesis in marine sediments evolves from a complex web of intertwining (bio) geochemical reactions. It comprises microbially catalysed reactions and inorganic mineral–water–gas interactions. A model that will describe and consider all of these reactions has to be complex. However, it should be user-friendly, as well as to be applicable for a broad community and not only for experts in the field of marine chemistry. The presented modelling platform PEaCH₄ v.2.0 combines both aspects, and is Microsoft Excel©-based. The modelling tool is PHREEQC (version 2), a computer programme for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. The conceptual PEaCH₄ model is based on the conversion of sediment-bound degradable organic matter. PEaCH₄ v.2.0 was developed to quantify and predict early diagenetic processes in marine sediments with the focus on biogenic methane formation and its phase behaviour, and allows carbon mass balancing. In regard to the irreversible degradation of organic matter, it comprises a “reaction model” and a “kinetic model” to predict methane formation. Both approaches differ in their calculations and outputs as the “kinetic model” considers the modelling time to integrate temperature dependent biogenic methane formation in its calculations, whereas the “reaction model” simply relies on default organic matter degradation. With regard to the inorganic mineral–water–gas interactions, which are triggered by irreversible degradation of organic matter, PEaCH₄ v.2.0 is based on chemical equilibrium thermodynamics, appropriate mass-action laws, and their temperature dependent equilibrium constants. The programme is exemplarily presented with the example of upwelling sediments off Namibia, ODP Leg 175, Site 1082. The application demonstrates that the modelling platform PEaCH₄ v.2.0 provides a user-friendly, but complex scientific tool that delivers retraceable information about early diagenetic processes and products in marine sediments.

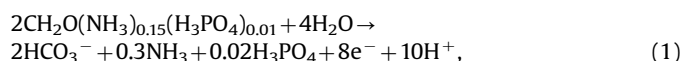
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1. Introduction

The quantification of early diagenetic processes and products is difficult without the help of numerical tools, in marine sediments. The modelling of such processes requires a complex model that considers all of the intertwining geochemical equilibrium reactions and the resulting new state of chemical equilibrium at a minimised level of Gibbs free energy in the system. The interplay between solid, aqueous and gaseous carbon species and many other elemental species (e.g., sulphur, calcium, and iron) are of general interest (Berner, 1982). Further, the site-specific

mineralogical, organic geochemical and sedimentological characteristics have to be taken into account to understand and describe early diagenesis.

During early diagenesis, the reactive part of the initially deposited organic matter is consumed and partly converted to biogenic gas (CH₄, CO₂, and H₂S). The irreversible remineralisation of organic matter can be seen as the transfer of electrons from chemically reduced substances to oxidised substances. It can be simplified by the general oxidation half-cell reaction



given for organic matter of approximate Redfield stoichiometry

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(Redfield, 1958). Sulphate reduction and methanogenesis are of special interest due to their dominant role in organic matter mineralisation of anoxic marine sediments (D'Hondt et al., 2002; Jørgensen, 2006). Organic matter (simplified as CH_2O) is oxidised by sulphate according to the reaction



(and delivers bicarbonate and sulphide to the system) (Jørgensen, 2006). Upon sulphate exhaustion, electrons are transferred due to the reduction of CO_2 (or bicarbonate), leading to the formation of methane (methanogenesis). Methanogenesis via the CO_2 reduction pathway is often the dominant biogenic methane formation process in shallow marine sediments and can be simplified by the reaction (Claypool and Kaplan, 1974; Whiticar et al., 1986)



A second source of biogenic methane is at greater sediment depths and higher temperatures (approximately 40°C ; Zeikus and Winfrey (1976) and Lorant et al. (2008)). Methanogenesis proceeds via the intermediate product acetate (acetoclastic methanogenesis; e.g., Wellsbury et al. (1997) and Parkes et al. (2007)). The intermediate product acetate is produced by acetogens in diverse microbial processes and reactions (e.g., Lever et al. (2010) and Lever (2012)). The reaction steps can be simplified by



and result in the overall reaction $2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2$ (Eq. (7)). Important and in contrast to early biogenic methane formation via the CO_2 reduction pathway (Eq. (3)) is the intermediate product acetate (CH_3COOH) and a more complex reaction chain. However, both sources of biogenic methane have to be considered in a geochemical model that is designed to quantify early diagenetic processes in marine sediments, with special emphasise on the carbon cycle and methane formation.

It was our goal to develop a modelling tool that can be used to retrace diagenetic signals in sediments and to calculate the composition of co-existing pore water, gas, and mineral assemblages. Conceptually, we applied hydrogeochemical modelling using chemical thermodynamics and reaction kinetics. On the one hand, the tool has to be user-friendly and applicable for users with at least little background knowledge in geology and geochemistry; on the other hand, it has to consider most of the complex and intertwining geochemical reactions in marine sediments. The presented modelling platform PEaCH₄ v.2.0 fulfils these requirements. The synonym PEaCH₄ stands for potential of early methane, CH₄.

2. Material and methods

2.1. Samples

The near-surface seawaters off Namibia are mainly influenced by the Benguela Current System (BCS, Hart and Currie (1960), Nelson and Hutchings (1983) and Shannon and Nelson (1996)), and flows northwards along the coast of southwest Africa. The Benguela upwelling area is one of four major eastern oceanic upwelling regions, where the supply of nutrient-rich deep waters to the euphotic zone causes intense primary production. Total organic carbon (TOC) contents of the underlying sediments are

amongst the highest observed in modern sediments (Wefer et al., 1998).

Site 1082 was drilled during Leg 175 of the Ocean Drilling Program (ODP; Wefer et al. (1998)), and is located in the 1279 m deep Northern Cape Basin on the upper slope. The drilling reached a depth of 600.6 m below the sea floor (mbsf). The continuous hemipelagic sediment column covers a time span from the late Miocene to the Holocene (5.8–0 My), and consists of organic-rich calcareous oozes with negligible terrigenous input due to very arid conditions onshore Namibia since the late Miocene (van Zinderen Bakker, 1984). The TOC content of the sediments continuously increases from the middle Miocene to the Pliocene due to the establishment and the intensification of the upwelling system (Siesser, 1980; Meyers and Keswani, 1984). The measured TOC contents of the sediments have to be seen as relicts since higher amounts of easily degradable sediment-bound organic matter present at the time of sediment deposition were already degraded.

2.2. PEaCH₄ v.2.0

PEaCH₄ v.2.0 is a Microsoft Excel® – based modelling platform to predict early diagenetic processes in marine sediments. It is the update of a first version (PEaCH₄) which, e.g., was exclusively based on the “reaction model” approach, etc. The modelling tool is PHREEQC (version 2), a computer programme for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations (Parkhurst and Appelo, 1999; cf. Section 2.3). PHREEQC is coupled to an entry mask of the Excel®-format that enables the user to define geochemical and mineralogical initial boundary conditions and to visualise PHREEQC calculation results in Excel®. Buttons are presented on the spreadsheets each one linking to the action of respective macros (Figs. 2–7), programmed in visual basics (VBA).

The main task of PEaCH₄ v.2.0 is to quantitatively determine (i) the formation of biogenic methane ($\text{CH}_{4(\text{aq})}$, $\text{CH}_{4(\text{g})}$, CH_4 -hydrate_(s)), (ii) the fraction of other gases (CO_2 , N_2 , H_2S) within the multi-component gas, (iii) the amount of precipitated diagenetic minerals and mineral dissolution, and (iv) the pore water chemical composition. In the end, carbon, sulphur, and iron mass balance calculations are performed and presented. PEaCH₄ v.2.0 offers the possibility for calculation of various depositional environments, and a variety of geological and sedimentological scenarios: (i) open systems with diffusion being the important transport mechanism for dissolved and gaseous species, (ii) compaction systems with a significant decrease in porosity to depth, (iii) systems that are within the gas hydrate stability (GHSZ) zone or not, (iv) siliciclastic sediments, and (v) carbonate-dominated sediments.

The entry mask provides the user with the opportunity to define sedimentological and physical parameters like sedimentation rate, water depth, initial bottom water temperature, or the initial composition of the sedimentary mineral phase assemblage (Figs. 1–4 and Table 1). Further, the ratio between marine and terrestrial organic matter and the amount of the converted organic matter has to be defined by the user (Figs. 1 and 5). Finally, the user can choose between a calculation by the pure reaction model or the kinetic model. The last also enables to calculate the “second” biogenic methane formation at a temperature optimum of 40°C (Fig. 5). Background calculations whether sediments are within the GHSZ or not are directly performed by PEaCH₄ v.2.0 and PHREEQC is started automatically when the input is completed. Model results are visualised automatically at the end of the model run. The user can compare the model results with measured data of pore water, gas, and mineral composition, check results at different time steps, and may change input data and run the model again to reach a best fit (Figs. 1, 6, and 7).

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