PEaCH₄ v.2.0: A modelling platform to predict early diagenetic processes in marine sediments with a focus on biogenic methane– Case study: offshore Namibia

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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.

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 oxidized substances. It can be simplified by the general oxidation half-cell reaction

given for organic matter of approximate Redfield stoichiometry (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 CH₂O) 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 CO₂ (or bicarbonate), leading to the formation of methane (methanogenesis). Methanogenesis via the CO₂ reduction pathway is often the dominant biogenic methane formation process in shallow marine sediments and can be simplified by the reaction

A second source of biogenic methane is at greater sediment depths and higher temperatures (approximately 40°C; Zeikus and Winfrey, 1976; Lorant et al., 2008). Methanogenesis proceeds via the intermediate product acetate (acetoclastic methanogenesis; e.g., Wellsbury et al., 1997; Parkes et al., 2007). The intermediate product acetate is produced by acetogens in diverse microbial processes and reactions (e.g., Lever et al., 2010; 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 emphasize 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; 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 1,279 m deep Northern Cape Basin on the upper slope. The drilling reached a depth of 600.6 meters 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 visualize PHREEQC calculation results in Excel®. Buttons are presented on the spreadsheets each one linking to the action of respective macros (Figs. 2 to 7), programmed in visual basics (VBA).

The main task of PEaCH₄ v.2.0 is to quantitatively determine i) the formation of biogenic methane (CH_{4(aq)}, CH_{4(g)}, CH_{4-hydrate(s)}), ii) the fraction of other gases (CO₂, N₂, H₂S) 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, 2, 3, and 4, 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 visualized 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).

2.3 Conceptual model

The model approach and description are adopted and modified from Arning et al. (2011, 2015).

The model aims to reproduce the measured depth distribution of present-day compositional data (depth profiles) in order to retrace the diagenetic evolution of sediments due to organic carbon remineralization. Problems that may arise from this modelling are that i) the filling of free model parameters may not completely reflect the real (palaeo)oceanographic situation and data of the recent situation were not measured, or that ii) the measured datasets maybe explained by several model set ups.

However, the long-term redox processes at shallow sediment depth are mainly triggered by the microbial degradation of organic matter. Therefore, our model approach is based on and adjusted with the amount of labile organic matter that has been degraded. The modelled redox-conversion of organic matter leads during its final step to a methane enrichment in the pore water of sediments when organic matter oxidation with oxygen, nitrate, manganese(III/IV), iron(III), and sulphate is finished. When the maximum methane solubility in pore water is reached, a free gas phase establishes. Presuming pressure and temperature conditions appropriate for methane hydrate formation (e.g., Kvenvolden, 1993; Sloan, 1998; Xu and Ruppel, 1999 and references therein), methane hydrate forms instead of a free gas phase. Prominent examples for the co-occurrence of methane hydrate and intense microbial methanogenesis in marine sediments are at Hydrate Ridge in the Pacific Northwest off Oregon (e.g. Tréhu et al., 2004), at the northern Cascadia accretionary margin (Whiticar et al., 1995; Pohlman et al., 2009), in high accumulation areas like the Amazon submarine fan (Flood et al., 1995; Tanaka et al., 2003), or at the slope off Peru (Shipboard Scientific Party, 2002). The ODP data set (Wefer et al., 1998) enables calibration of our model and definition of well-defined input parameters.

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174 2.3.1 Model approach

175 Numeric hydrogeochemical 1-dimensional reactive transport models can reflect the complex
176 web of early diagenetic processes in marine sediments. The modelled sediment column is
177 composed of 30 cells ("generic reactors"; Table 1). The generic 1.7 l reactor is filled with an
178 aqueous solution of present-day chemical seawater composition (Nordstrom et al., 1979),
179 and with sediments of a defined mineralogical composition according to sediments from ODP
180 Leg 175, Site 1082 (Wefer et al., 1998). Equilibrium species distribution and coupled mass
181 transfer that result from reactions in the modelling reactor are calculated by using the
182 PHREEQC (version 2) programme (Parkhurst and Appelo, 1999). Calculations are based on
183 mass action laws that include all species of Ca, Mg, Na, K, Al, Fe, Ba, Si, Cl, C, S, N, P, H₂O,
184 and their corresponding equilibrium constants. Species, mass-action equations, and
185 equilibrium constants are listed in the thermodynamic database "wateq4f.dat" (Parkhurst and
186 Appelo, 1999) and Table 2. Conceptually, the equilibrium species distribution is triggered by
187 the irreversible redox conversion of organic matter, which proceeds in pre-assigned
188 amounts. The accumulation of the organic matter metabolites leads to the development of
189 new inorganic equilibrium conditions in the system.

190 The modelled sediment column is 400 m thick (representing the zone most crucial for
191 early diagenetic reactions at ODP Leg 175, Site 1082), and is subdivided into thirty 13.3 m
192 thick cells (Table 2). Each cell is an original reactor (expressed as representative volume
193 (RV)), and contains 1 l of pore water (V(aq)) and 1.89 kg of solid sediment. Hence, the
194 average porosity (ϕ) is 0.59 and the average specific weight of solids ($\rho(s)$) is 2.7 kg l⁻¹. The
195 model design is based on a growing sediment column. Initially, equilibrium calculations are
196 performed on one sediment cell that is overlain by five cells containing seawater. At a second
197 time step, the first cell is instantaneously buried to a depth of 13.3 m. The time step for each
198 cell (166,250 yrs; Table 2) is calculated from the sedimentation rate (Table 2; Wefer et al.,
199 1998). The total time modelled is 4,987,500 yrs.

200 Freshly deposited sediments at the sediment-water interface form the second cell in
201 the growing sediment column. After 30 time steps the modelled sediment column consists of
202 30 cells and represents the upper 400 meters of the investigated site. Once all calculations
203 have been completed, the mineral assemblage and pore waters of the first cell (from the first
204 time step) shift from the sediment-water interface to the base of the modelled sediment
205 column at a depth of 386.7 to 400 mbsf.

206 The active transportation processes considered in this model are 1) one-dimensional
207 molecular diffusion of aqueous species, and 2) burial of solids and aqueous species,
208 according to the observed sedimentation rate, which also represents advection, and possibly

3) compaction flow. Diffusion enables the transportation of dissolved species between all cells during sediment deposition and burial. A mean diffusion coefficient ($0.86 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$) for all aqueous species is calculated from diffusion coefficients (corrected for tortuosity) according to Giambalvo et al. (2002) who investigated similar sediments from the South Atlantic.

The upper boundary of the model is defined as a constant concentration boundary within the topmost cell of the seawater column. The lower boundary is defined as a boundary closed for diffusion. Diffusive exchange between seawater and pore water takes place at the sediment-water interface, between each deposited sediment cell and the overlying cell containing seawater. The temperature increases linearly throughout the modelled sediment column and is consistent with the geothermal gradient (Table 2; Wefer et al., 1998). The input parameters that define both primary and secondary equilibrium phases (minerals and gas) and physical boundary conditions are given in Table 2. A detailed description of the physical and chemical considerations and the calculation scheme of the applied model are given in Arning et al. (2011).

2.3.2 Model calibration and organic matter remineralization

In the presented case study about sediments off Namibia, organic matter remineralized in the model (Redfield- CH_2O) was assumed to be dominantly of marine origin with minor terrestrial contributions (Wefer et al., 1998) and is defined with an approximate Redfield stoichiometry of C:N:P equal to 100:15:1 (Redfield, 1958). In our model, the organic matter is considered as a whole, and reaction rates are included by converting different amounts of Redfield- CH_2O during each time step. It has to be noted that the stoichiometry of the remineralized organic matter is an approximation as the Redfield ratio of organic matter depositing on the sea floor is not necessarily conserved. However, minor contributions of organic matter from other sources like that aeolian transport of terrestrial carbon from remote regions or transport of nearly buoyant organic matter from terrestrial vegetation cannot be fully excluded. As no direct evidence exist for that and we cannot quantify its contribution to the TOC, it cannot be included in the model of ODP Leg 175, Site 1082.

There is the likelihood that aeolian transport of terrestrial C can be from remote regions. Also, transport of nearly buoyant organic matter from terrestrial vegetation could make its way to the sediment.

The measured pore water alkalinity profiles are used for calibration. The background behind this conceptual proxy is that the release of CO_2 from the conversion of organic matter and subsequent water-mineral-gas interactions controls the pore water alkalinity. These

reactions are given in Table 2. Most important with respect to pore water alkalinity are carbonate, iron sulfide, and methane formation. To calibrate the model, the amount of organic matter (simplified as $(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z$) that can be converted in each representative volume at each time step is readjusted until the modelled alkalinity profiles of the investigated site nearly match the general trend of the measured alkalinity profile.

4. Results and Discussion

4.1 Balancing usability and complexity

PEaCH4 v. 2.0 offers the opportunity to test different scenarios on their feasibility of methane formation, phase behaviour and storage. The user can check, which conditions are required for significant methane generation, e.g., to quantify the amount of organic matter, or the influence of sedimentation rate and composition. Furthermore, carbon mass balance calculations and quantifications can be used to conclude whether a high amount of methane is worth more detailed investigation. Beyond predicting possible reservoirs of biogenic methane, the platform predicts hydrate formation and may be used as a tool to plan drilling in sensitive areas with shallow methanogenic sediments.

Early diagenesis in sediments involves a complex network of geochemical equilibrium reactions, biological processes, and aqueous mass transport all dependent on sedimentological and physical environmental conditions. The professional consideration leading to the combination of all of these processes in one modelling platform is a challenging task, especially when the modelling platform should be applicable for users with only basic knowledge in biogeochemistry, as well. We enable this balancing act between usability and complexity in the presented modelling platform PEaCH₄ v.2.0. This is possible due to buttons that guide the user through the platform (Figs. 2 to 7) and that provide the opportunity to choose special calculation methods and input parameters. The complex calculations run in the background.

In the simplest form the user has to consider basic input parameters to fill in the Excel[®] entry mask. The PHREEQC programme that performs the geochemical equilibrium calculations (Parkhurst and Appelo, 1999) starts automatically by using the respective button. The “summary”-sheet will provide a meaningful and quick overview of the results without the necessity to review the raw data. Buttons on the “summary”- and “mass balance”-sheets allow an uncomplicated change and adjustment of the input data (Figs. 6 and 7). However, more advanced and interested users can survey the PHREEQC input sheet that will be given at the end of the Excel[®] entry mask or the raw data, or may change initialised reaction rates.

PEaCH₄ v.2.0 is applicable for scientists working in the fields of (bio)geochemistry, mineralogy, and sedimentology as well as for users from the oil and gas industry. The outcome is a wealth of detailed results on pore water and sediment chemistry with a special focus on methane and other carbon species. Moreover, PEaCH₄ v.2.0 automatically calculates and displays carbon, sulphur, and iron mass balances. To adapt the programme to application for the oil and gas industry, the units for methane are given in “standard cubic feet per m³” (scf m⁻³) besides the conventional mmol L⁻¹ used in science. Moreover, porosity changes can be calculated, formation of gas hydrates and the amount of producible biogenic methane can be predicted, and changes over time can be visualized. Especially this may be of special interest to reconstruct changing environmental conditions in Earth history (e.g., Arning et al., 2015).

4.2 Reaction vs. kinetics

Two methods for the calculation of the reaction of convertible organic matter are integrated in PEaCH₄ v.2.0. The user can choose between the “reaction” method and the “kinetic” method by pressing the respective button (Fig. 5). The fundamental difference between both methods is that the reaction method does not consider the model time for the calculation of the reaction of convertible organic matter, whereas calculations by the kinetic method depend on the model time.

In the reaction method, the amount of the organic matter that is converted in each time step is defined for each cell by a constant and is independent from increasing or decreasing total model time. In the first cell 22 % of the given convertible organic matter reacts, in the second cell the amount decreases to 17 % and will further decrease to the last model step. In the end 100 % of the initially convertible organic matter has reacted in the 30 model cells of the sediment column.

The kinetic option in PEaCH₄ v.2.0 uses the model time for the calculation of the reaction amount of organic matter. Rate calculations of the organic matter amount that reacts in each time step and in each cell are calculated for the pre-assigned model time by PHREEQC. Rate calculations are based on defined sulphate reduction rates (0.03 mmol C L⁻¹ a⁻¹) and rates of methanogenesis (0.03 mmol C L⁻¹ a⁻¹). Consequently, the amount of the converted organic matter decreases with the model time. However, the defined rates for sulphate reduction and methanogenesis are still problematic to assess. Some rates of organic matter conversion strongly differ for different environmental settings and are a somehow arbitrary assumption. The rates used in PEaCH₄ v. 2.0 are chosen to the best of our knowledge and were compiled from literature (Finke et al., 2007; Parkes et al., 2007; Finke and Jørgensen 2008; Lorant et al., 2008; Burdige 2011; Hubert et al., 2009, 2010;

Robador et al., 2010; Ijiri et al., 2012). The used rates could be changed by the user supposed that better adapted data are known.

The kinetic model option is an important tool to include the calculation of the second biogenic methane formation at higher temperatures. This integration of a second source of biogenic methane has been one challenging task in the development of PEaCH₄ v. 2.0. It is a complex step to integrate the kinetic reactions and ambiguous rates in the PHREEQC model and to automate the calculation process. In addition, the reaction products of the kinetically controlled degradation of organic carbon are integrated into the complex web of water-mineral-gas interactions. Furthermore, uncertainties still arise from a lack of information about microbial reactions in nature and corresponding rate calculations. Finke and Jørgensen (2008) found in experimental studies that microbes can adapt their temperature optimum on the local conditions in marine sediments. Sulphate reduction in Wadden Sea sediments, e.g., is possible up to a temperature of 40°C. Organic matter can thus be microbially converted over a large sediment depth interval. Studies by Hubert et al. (2009, 2010) reveal similar results. In a fundamental study, Zeikus and Winfrey (1976) have determined the rate of methane production according to temperature from lake sediments and found highest rates at a temperature of around 40°C.

The formation of methane by microorganisms at a temperature optimum of 40°C as a second source of biogenic methane is integrated in the kinetic model option (Fig. 5). The kinetic approach is based on the Monod equation

$$\mu = \mu_{max} \cdot S / (K_s + S) \text{ (eq. 7)}$$

μ is the specific growth rate of the microorganisms; μ_{max} is the maximum the specific growth rate; S is the concentration of the limiting substrate for growth; K_s is the “half-velocity constant” (Monod 1949) and on the assumption that microbial reaction rates are temperature dependent (Lorant et al., 2008; Zeikus and Winfrey, 1976). The kinetic PHREEQC model uses an empiric model for temperature dependant microbial rate calculations, the so-called Ratkowsky model. It describes the microbial growth rate (μ_m)

$$\mu_m = [b_3(T - T_{min})]^2 \cdot \{1 - \exp[c_3(T - T_{max})]\} \text{ (eq. 8)}$$

with b_3 and c_3 as the two parameters for adaption, T_{min} the minimum temperature and T_{max} the maximum temperature (Ratkowsky et al. 1982; Zwietering et al 1991).

In conclusion, different conceptual approaches to calculate biogenic methane formation exist between the “reaction model” and the “kinetic model”, and result in the observed differences of the model results (Fig. 8). A similar amount of organic matter in the reaction (red dots) and the kinetic model (black dots) leads to discrepancies in the modelled alkalinity, methane, and sulphate concentrations. Strong organic matter conversion within the

upper model cells induces high methane generation and –as by-product- alkalinity in the kinetic model. These concentrations are noticeably higher than the measured data. Furthermore, the sulphate pool is exhausted at the very top of the sediment column which deviates from the measured data. The results of the reaction model, in contrast, fit the measured sulphate profile very well and tolerably fit the measured alkalinity data. The methane concentrations increase with depth peaking around 150 mbsf and are exhausted in the upper 20 mbsf reflecting methane oxidation by sulphate (e.g., Reeburgh 1976; Iversen and Jørgensen 1985; Hoehler et al., 1994; Niewöhner et al. 1998; Boetius et al., 2000). However, the measured methane concentrations are significantly lower than the modelled data, but that could be explained by analytical difficulties or methane outgassing during the coring.

The calibration of the kinetic model (blue dots) requires a detailed consideration of the input parameters as either escalating alkalinity values may occur or sulphate depth profiles may penetrate too deep into the modelled sediment column (Fig. 8). In such a case the content of convertible organic matter has to be reduced in the upper cells to fit the modelled and measured alkalinity profiles. However, this may result in low methane concentrations in the upper part of the model column. Due to the conceptual approach, the modelled methane concentrations increase with increasing sediment depth as the conversion rate of the organic matter is temperature dependent. Given a local geothermal gradient of $20^{\circ}\text{C km}^{-1}$ (Wefer et al., 1998) 11.7°C prevails in 400 mbsf. In total, less organic matter is converted in the calibrated kinetic model ($7,563 \text{ mmol L}^{-1}$) in comparison to the calibrated reaction model ($8,275 \text{ mmol L}^{-1}$). Even though the modelled methane concentrations are higher than the measured ones in all model calculations, the results gained by the reaction model match the measured sulphate profile and reflect a typical shape of a methane concentration profile with a distinct zone of methanogenesis as observed in other upwelling sediments as well (e.g. off Peru; Suess et al., 1988, Arning et al., 2012).

An approach to calculate the biogenic methane formation at higher temperatures similar to our “kinetic model” has been applied by the programme BIOGENIX (Clayton 1992, 2008). This programme can be used to calculate methane formation at greater sediment depth. In contrast to PeaCH₄ v.2.0, it lacks the option to calculate the early diagenetic formation of biogenic methane in the upper few hundred meters of marine sediments. Hence, this approach neglects that organic matter conversion predominates over the upper few hundred meters of marine sediments (e.g., Westrich and Berner, 1984; Middelburg, 1989; Parkes et al., 1994; Cragg et al., 1996; Cragg et al., 1997; Lipp et al., 2008). Further, biogeochemical reactions, interactions between minerals and fluids, and the corresponding changing chemical equilibriums are not integral parts of Biogenix. Thus, Biogenix is

applicable for deep biogenic methane formation calculations, but lacks the holistic approach of PEaCH₄. Further, problems with uncertain reaction rates similar to the kinetic method of PEaCH₄ v.2.0 have to be taken into account.

4.3 Amount of organic matter conversion – Case study: ODP Leg 175, Site 1082

Primary productivity is an important feature in oceanography to determine consequences of trophic levels due to, e.g., currents or climates (Gupta and Kawahata, 2006; Arning et al., 2011). In marine geosciences, geologists use the reconstruction of productivities to develop palaeo-oceanographic models. The reconstruction of ancient primary productivities, i.e. the amount of organic matter that has been converted during early diagenesis in marine sediments, may thus allow quantifications about the contents of primarily deposited organic matter. In contrast to our modelling study, Hatcher et al. (2014) used experimental analyses (Fourier transform infrared spectroscopy; FTIR) and nuclear magnetic resonance spectroscopy (¹³C NMR) to determine diagenesis rates. They attributed changes in the molecular composition of sedimentary organic matter to its diagenetic fate and behaviour, and calculated rates of organic matter conversion. The calculated rates decrease with increasing sediment depth from 5.6 to 0.2 mol C m⁻³kyr⁻¹. This decrease is in accordance with decreasing organic matter conversion with sediment depth as calculated by the PEaCH₄ v.2.0 model.

However, the total amount of converted organic matter calculated by the reaction model (*cf.* chapter 4.2; 8,275 mmol L⁻¹) is approximately 1.5 times higher as calculated by Hatcher et al. (2014; 4,995 mmol L⁻¹) for the same sediments of ODP Leg 175, Site 1082. Minor organic matter degradation as calculated by Hatcher et al. (2014) may be due to the fact that the composition of the organic matter in 7 mbsf has been chosen for calculation. The authors stated that an organic matter composition characteristic for deposition at the sediment/water interface would allow a more accurate calculation. Our model results, in contrast, may result in an overestimation, as methane concentrations are at least twice as high as the measured ones (Fig. 8). Nevertheless, a direct data input of the lower total organic matter conversion number calculated by Hatcher et al. (2014) leads to significantly low alkalinities and to an unrealistic deep sulphate penetration into the modelled sediment column.

Discrepancies in the alkalinity may be explained by additional CO₂ production by low-temperature cracking of the kerogen. It has been observed that this process produce CO₂ and asphaltenes, which could fuel biological methane formation and may be an additional

methane source at the ODP Leg 175 (personal comment). However, as this study is not published, yet, we cannot comment on this further or include the data in our discussion.

5. Conclusions

It was our goal to develop a user-friendly modelling platform that retraces and quantifies early diagenetic processes in marine sediments by hydrogeochemical modelling using chemical thermodynamics. A major focus was to overcome discrepancies between usability and complexity of the presented modelling platform PEaCH₄ v.2.0.

The developed programme PEaCH₄ v.2.0 offers the opportunity i) to estimate the amount of generated biogenic gas, ii) to resolve the timing of CH₄ and CO₂ generation, iii) to determine whether methane will be dissolved in interstitial waters, will be present as gas phases, or will be stored in the form of hydrates, iv) to calculate mineral precipitation and dissolution driven due to these processes, v) to calculate carbon mass balances, and vi) to determine pore water composition.

The process and the numerical solution of biogenic methane formation at higher temperatures, as a second source of biogenic methane, are integrated in the platform. Despite missing or controversial fundamental data about microbial rate calculations, complex kinetic reactions and ambiguous rates were integrated in the PHREEQC model and allow an automation of the calculation process. As a result, PEaCH₄ v. 2.0 reaches good numerical estimations about the biogenic methane formation at higher temperatures.

The comparison between experimental data and our modelling approach highlights the difficulties to exactly determine organic matter degradation rates in the complex reaction web during early sedimentary diagenesis. It further illustrates the importance to continue the development of model approaches that can quantify and calculate (bio)geochemical processes in marine sediments under consideration of their total complexity.

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Figure captions

Fig. 1. Abstraction of the modelling platform PEaCH₄ v.2.0. The user can define sedimentological and geochemical input parameters in different Excel[®] worksheets. Hydrogeochemical calculations are performed by PHREEQC (version 2), a computer programme for speciation, batch-reaction, one-dimensional transport, and inverse

geochemical calculations. The output is visualized in Excel® and the user has the opportunity to compare modelled results with measured data and eventually to adjust input parameters.

Fig. 2. Screen view of PEaCH₄v.2.0. Input sheet where the user can define basic sedimentological parameters. The button “next” is linked to the action of a macro that opens the next sheet.

Fig. 3. Screen view of PEaCH₄v.2.0. The user is shown whether sediments of interest are located within the gas hydrate stabilization zone or not.

Fig. 4. Screen view of PEaCH₄v.2.0. Here, the user can define the primary mineralogy of the model column. Two buttons are present with each one guiding the user to the respective next sheet.

Fig. 5. Screen view of PEaCH₄ v.2.0. Here, the user can define the amount of the organic matter that will be converted in the model. Two buttons are present on the spreadsheet with each one linking to the action of respective macros and set up either the “reaction model” or the “kinetic model.”

Fig. 6. Screen view of PEaCH₄v.2.0. The summary sheet gives an overview on the modelling results that can be compared to measured data, if available. Five buttons are present on the spreadsheet with each one linking to the action of respective macros.

Fig. 7. Screen view of PEaCH₄v.2.0. The mass balance sheet provides mass balances on carbon, sulphur, and iron species. Two buttons are present on the spreadsheet with each one linking to the action of respective macros.

Fig. 8. Modelled (dots) and measured (white squares) pore-water alkalinity, sulphate concentration and methane concentration profiles in mmol L⁻¹ (mM). The calibrated “reaction model” (red dots) has a total organic carbon conversion of 8,275 mmol L⁻¹. The “kinetic model” that is not calibrated (black dots) was run with the same total carbon amount as the reaction model (8,275 mmol L⁻¹). Total carbon conversion of the calibrated “kinetic model” was 7,563 mmol L⁻¹. Measured pore-water concentration data are taken from Wefer et al. (1998).

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A	B	C	D	E	F	G	H	I	J
Input parameters									
total model thickness [m]	700								
sedimentation rate [cm kyr ⁻¹]	50								
water depth [m]	870								
geothermal gradient [°C km ⁻¹]	30								
bottom water temperature [°C]	4								
Sediment column									
cell length [m]	23.3								
number of cells - sediment	30								
number of cells - total	35								
sedimentation rate [m yr ⁻¹]	0.0005								
average sediment mass [g]	1500								
Modelling time									
total modelling time [yr]	1398000								
time step per cell [yr]	46600								
time step per cell [s]	1.46958E+12								
Temperature and pressure parameters									
geothermal gradient [°C m ⁻¹]	0.03								
temperature change [°C/cell]	0.699								
hydrostatic pressure water depth [atm]	87.00								
hydrostatic change sediment [atm/cell]	2.33								
Additional model parameters									
diffusion coefficient [m ² s ⁻¹]	8.60E-10								
cation exchange capacity	1.2								

How to use this spreadsheet:

1. Orange fields have to be filled by the user.
2. Choose the parameters carefully.
(Some values for guidance are on the right site)
3. Press the "next" button when the input is completed.

Next

670

671

How to use this spreadsheet:

1. Automatic analysis, if gas hydrates occur in the sediment column with the given input parameters (orange line).
2. Press the "next" button

Potential of gas hydrate formation to a sediment depth of 1310 meter below sea level

Next

672

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A B D E F G H I K L M N O P R S T U

Next

Secondary minerals

How to use this spreadsheet:

1. Orange fields can be filled by the user.
2. Change the initial amount of primary phases in the sediment column.
3. Optional: Choose with the active/inactive menu, which primary phases occur in the sediment column.
4. Optional: Press the "secondary minerals" button for a more detailed mineral composition.
5. Press the "next" button when the input is completed.

Goethite					Calcite					Aragonite				
Cell	Depth [mbsf]	active	Amount [wt.%]	Amount [mol/cell]	Cell	Depth [mbsf]	active	Amount [wt.%]	Amount [mol/cell]	Cell	Depth [mbsf]	inactive	Amount [wt.%]	Amount [mol/cell]
30	5	1	1.0	0.1688	30	5	1	0.00	0.0000	30	5	0	0.00	0.0000
29	15	1	1.0	0.1688	29	15	1	0.00	0.0000	29	15	0	0.00	0.0000
28	25	1	1.0	0.1688	28	25	1	0.00	0.0000	28	25	0	0.00	0.0000
27	35	1	1.0	0.1688	27	35	1	0.00	0.0000	27	35	0	0.00	0.0000
26	45	1	1.0	0.1688	26	45	1	0.00	0.0000	26	45	0	0.00	0.0000
25	55	1	1.0	0.1688	25	55	1	0.00	0.0000	25	55	0	0.00	0.0000
24	65	1	1.0	0.1688	24	65	1	0.00	0.0000	24	65	0	0.00	0.0000
23	75	1	1.0	0.1688	23	75	1	0.00	0.0000	23	75	0	0.00	0.0000

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	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V																																										
	<p>How to use this spreadsheet:</p> <ol style="list-style-type: none"> 1. Orange fields can be filled by the user. 2. The OM amount is the key parameter of the model. Gas hydrate formation, alkalinity and pH depend on the amount of convertible organic matter. 3. Please change the initial amount of convertible organic matter in the sediment column. This input limits the total conversion of organic matter. Don't use measured TOC data! 4. Please change the ratio between marine and terrestrial organic matter. 5. Choose the type of organic matter degradation: <div> <div>Reaction is very simple and independent of time and temperature (no 40°C maximum); compaction is not possible (very fast calculation)</div> <div>Kinetic model is dependent of time and temperature (fast calculation)</div> </div> 6. Keep in mind, that these two models differ in the OM conversion. Just clicking on an other button without changing the amount of organic matter doesn't work. 																																																										
Reaction																																																											
Kinetic model																																																											
	<div> <div>Initial amount of convertible organic matter</div> <table border="1"> <thead> <tr> <th>Model time step</th> <th>Time [k yr]</th> <th>OM amount [wt %]</th> <th>OM amount [mmol/cc]</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>47</td> <td>2.0</td> <td>1250</td> </tr> <tr> <td>2</td> <td>94</td> <td>2.0</td> <td>1250</td> </tr> <tr> <td>3</td> <td>141</td> <td>1.8</td> <td>1125</td> </tr> <tr> <td>4</td> <td>188</td> <td>1.8</td> <td>1125</td> </tr> <tr> <td>5</td> <td>235</td> <td>1.6</td> <td>1000</td> </tr> </tbody> </table> </div> <div> <div>Ratio of organic matter origin</div> <table border="1"> <thead> <tr> <th></th> <th>Marine</th> <th>Terrestrial</th> </tr> </thead> <tbody> <tr> <td>parts [%]</td> <td>50</td> <td>50</td> </tr> </tbody> </table> </div> <div> <p>Guidance:</p> <table border="1"> <thead> <tr> <th>Amount of TOC in recent sediments</th> <th>wt %</th> </tr> </thead> <tbody> <tr> <td>Continental slope</td> <td>1.5 - 3.0</td> </tr> <tr> <td>Cascadia Basin</td> <td>1.0 - 1.5</td> </tr> <tr> <td>Amazonas deep sea fan</td> <td>0.3 - 1.2</td> </tr> <tr> <td>Arctic</td> <td>0.1 - 0.4</td> </tr> <tr> <td>Baltic Sea</td> <td>0.8 - 4.7</td> </tr> </tbody> </table> </div>																	Model time step	Time [k yr]	OM amount [wt %]	OM amount [mmol/cc]	1	47	2.0	1250	2	94	2.0	1250	3	141	1.8	1125	4	188	1.8	1125	5	235	1.6	1000		Marine	Terrestrial	parts [%]	50	50	Amount of TOC in recent sediments	wt %	Continental slope	1.5 - 3.0	Cascadia Basin	1.0 - 1.5	Amazonas deep sea fan	0.3 - 1.2	Arctic	0.1 - 0.4	Baltic Sea	0.8 - 4.7
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How to use this spreadsheet:

1. Check the plotted modelling results.

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684 **Table 1.** PHREEQC model setup and input parameters of ODP Leg 175, Site 1082 for the
685 calibrated model. RV: representative volume, CEC: cation exchange capacity.

Input parameters	ODP Site 1082 ^a
Setup parameters	
number of RV	30
height RV [m]	13.3
V _{tot} RV [L]	1.7
V _{aq} RV [L]	1.0
time per shift [yrs] ^b	166,250
total model time [yrs] ^c	4,987,500
sediment depth [m] ^c	400
CEC [meq RV ⁻¹] ^d	1.2
diffusion coefficient [m ² s ⁻¹] ^e	0.86E ⁻⁰⁹
database	wateq4f.dat ^f
Physical parameters	
bottom water temperature [°C]	4
geothermal gradient [°C km ⁻¹]	20
sedimentation rate [cm kyr ⁻¹]	8
water depth [m]	1279
Geochemical parameters	
starting solution	sea water ^g
<i>primary phases [wt.%]</i>	
SiO ₂ (amorph)	20
Illite	20
Montmorillonite	20
Chlorite 14A	18.9
Kaolinite	20

Goethite	0.6 to 3.5
Calcite	10

686 ^a: data are from Wefer et al. (1998)

687 ^b: calculated from sedimentation rate

688 ^c: calculated from sedimentation rate, number and height of RVs

689 ^d: cation exchange capacity, depends on the clay mineral content, estimated according to Jasmund
690 and Lagaly (1993)

691 ^e: mean value for all dissolved species, calculated according to diffusion coefficients given in
692 Giambalvo et al. (2002)

693 ^f: Parkhurst and Appelo (1999)

694 ^g: after Nordstrom et al. (1979)

695

696 **Table 2.** Equilibrium phases, mass-action equations and equilibrium constants (log K, at
697 25°C and 1bar pressure). Equilibrium constants are from the “wateq4f.dat” data set
698 (Parkhurst and Appelo, 1999).

Equilibrium phase	Equilibrium reaction	log K
Barite	$\text{BaSO}_4 = \text{Ba}^{2+} + \text{SO}_4^{2-}$	-9.97
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48
Chlorite14A	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 16\text{H}^+ = 5\text{Mg}^{2+} + 2\text{Al}^{3+} + 3\text{H}_4\text{SiO}_4 + 6\text{H}_2\text{O}$	68.38
CH4Hydrate	$\text{CH}_4:6\text{H}_2\text{O} = \text{CH}_4 + 6\text{H}_2\text{O}$	-1.07 ^a
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$	-1.0
Greigite	$\text{Fe}_3\text{S}_4 + 4\text{H}^+ = 2\text{Fe}^{3+} + \text{Fe}^{2+} + 4\text{HS}^-$	-45.03
Illite	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2 + 11.2\text{H}_2\text{O} = 0.6\text{K}^+ + 0.25\text{Mg}^{2+} + 2.3\text{Al}(\text{OH})_4^- + 3.5\text{H}_4\text{SiO}_4 + 1.2\text{H}^+$	-40.27
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	7.44
Montmorillonite	$\text{Ca}_{0.01}\text{Na}_{0.31}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 12\text{H}_2\text{O} = 0.01\text{Ca}^{2+} + 0.31\text{Na}^+ + 2.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4 + 2\text{H}^+$	-45.03
Sepiolite(d)	$\text{Mg}_2\text{Si}_3\text{O}_{7.5}\text{OH}:3\text{H}_2\text{O} + 0.5\text{H}_2\text{O} + 4\text{H}^+ = 2\text{Mg}^{2+} + 3\text{H}_4\text{SiO}_4$	18.66
Struvite	$\text{MgNH}_4\text{PO}_4:6\text{H}_2\text{O} = \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$	-13.26 ^b
CO ₂ (g)	$\text{CO}_2 = \text{CO}_2$	-1.47
CH ₄ (g)	$\text{CH}_4 = \text{CH}_4$	-2.86
N ₂ (g)	$\text{N}_2 = \text{N}_2$	-3.26
H ₂ S(g)	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	-6.99

699 ^a: calculated from Gibb's free energy ($\Delta G = 5.736 \text{ kJ mol}^{-1}$), pressure (P = 10MPa), and temperature
700 (T = 279.55 K) after Lu et al. (2008).

701 ^b: defined after Ronteltap et al.(2007).

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