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Quantitative geochemical modeling along a transect off Peru: Carbon cycling in time and space, and the triggering factors for carbon loss and storage

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[1] Early diagenetic processes in Peruvian shelf and slope sediments are numerically reproduced by applying chemical thermodynamics in a complex, universal approach using the PHREEQC (version 2) computer code. The reaction kinetics of organic carbon remineralization are integrated into a set of equilibrium reactions by defining the type and the amount of converted organic matter in a certain time step. We calculate the most intense remineralization of organic carbon for present-day shelf sites, and the final carbon pool is dominated by secondary carbonates. This serves to highlight the influence of organic matter degradation and anaerobic oxidation of methane (AOM) on diagenetic mineral formation. The enrichment of aqueous methane and the formation of methane hydrate only takes place in slope sediments with high sedimentation rates that prevent diffusive loss of methane (e.g., Sites 682 and 688). Moreover, AOM prevents the diffusion of dissolved methane into overlying seawater. Throughout the Miocene period, these sites were located on a former shelf and the total carbon loss from the sediments was significantly higher in comparison with the present-day. Compared with the present-day shelf site, organic matter remineralization is high, and methane is produced but not stored within the sediments. Our model calculations rule out the possibility of present-day and former shelf site sediments off the coast of Peru as methane reservoirs. Remineralized TOC has to be considered, particularly in older sediments, when interpreting TOC profiles and calculating mass accumulation rates of total organic carbon (MARTOC). The more organic matter has been remineralized during the depositional history, the larger the difference between MARTOC calculated from measured TOC data, and from the sum of modeled and measured TOC data. Consequently, most reliable primary productivity calculations are based on the sum of measured relict TOC and the amount of remineralized organic carbon determined by modeling.

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1. Introduction

[2] The marine sedimentary carbon cycle is driven by the early diagenetic remineralization of organic carbon. Carbon storage and carbon release are crucial in the overall mass balance. The sedimentation of carbon as organic matter, the formation of dissolved inorganic carbon, authigenic carbonates that serve as a long-term sink for carbon, and methane formation in sediments are key processes [Berner, 1982;

Berner, 1991]. A simplified scheme that summarizes the points of interest of the sedimentary carbon cycle regarding our present study is given in Figure 1. Early diagenetic processes lead to the remineralization of solid organic carbon into gaseous and aqueous carbon species during sediment deposition. The final destiny of this early diagenetic carbon pool is controlled by the specific hydrogeochemical conditions in the pore space and by interaction with the surrounding mineral matrix. With further burial, organic carbon remineralization decreases until the labile parts are exhausted [Arning *et al.*, 2011].

[3] The fixation and release of carbon can result from hydrogeochemical reversible and irreversible equilibrium reactions, triggered by organic matter remineralization via sulphate reduction ($2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$) [from Jørgensen, 2006] and methanogenesis ($2\text{CH}_2\text{O} + (\text{Ca}^{2+}, \text{Mg}^{2+}) + \text{H}_2\text{O} \rightarrow \text{CH}_4 + (\text{Ca}, \text{Mg})\text{CO}_3 + 2\text{H}^+$). Precipitation of carbonates ($\text{Ca}^{+2} + \text{CO}_3^{-2} \leftrightarrow \text{CaCO}_3$) and

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Figure 1. Simplified scheme of points of interest of the sedimentary carbon cycle regarding our present study. Authigenic carbonates and recalcitrant organic carbon are stored within the sediments and display a long-term sink for carbon. Methane hydrate dissociates in deeper sediments below the gas hydrate stability zone. Gaseous methane may re-enter this zone again. Changing pressure (P; e.g., as a result of changing sealevel) and temperature (T) conditions methane hydrates may cause dissociation of the hydrates and methane can diffuse into the overlying seawater.

sulphides ($2\text{Fe}^{+3} + \text{Fe}^{+2} + 4\text{HS}^- \leftrightarrow \text{Fe}_3\text{S}_4 + 4\text{H}^+$), as well as anaerobic oxidation of methane (AOM; $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$) [e.g., Boetius *et al.*, 2000], are important processes in early diagenesis (within the upper few 100s of meters of sediment).

[4] With regard to methane cycling within marine sediments, the formation of methane hydrate is of particular interest, as are processes in the sulphate-methane transition zone (SMTZ). There are several recent studies that focus on the loss of carbon at the SMTZ [e.g., Davie and Buffett, 2001; Davie and Buffett, 2003; Luff and Wallmann, 2003; Torres *et al.*, 2004; Hensen and Wallmann, 2005; Wallmann *et al.*, 2006; Bhatnagar *et al.*, 2007; Sivan *et al.*, 2007; Snyder *et al.*, 2007; Wang *et al.*, 2008; Chatterjee *et al.*, 2011, and references therein], but diagenetic processes in the sediments below the SMTZ to several 100 m depth need further investigations.

[5] The early diagenetic carbon cycle in anoxic environments is complex and comprises of the interplay between solid, aqueous and gaseous carbon species, and many other elemental species (e.g., sulphur, calcium, and iron) [Bernier, 1982]. Numerical retracing of these organic-inorganic interactions shows that the formation of diagenetic carbonates and the generation of methane are key processes in the sedimentary carbon cycle and that a dominant output of carbon is HCO_3^- through the seafloor [e.g., Luff and Wallmann, 2003; Wallmann *et al.*, 2006; Snyder *et al.*, 2007; Arning *et al.*, 2011].

[6] The methane pool in sediments – as one example of a carbon species – potentially consists of three internal components: 1) dissolved gas 2) gas hydrates, and 3) free gas. This methane is present in also in the study of climate change [Dickens, 2003; Kvenvolden, 1999]. Numerical simulations show the importance throughout Earth's history of methane release from gas hydrates, and they can explain major negative $\delta^{13}\text{C}$ excursions, for example at the Paleocene/Eocene boundary [Dickens, 2003]. Current literature [see Dickens, 2011, and references therein] suggests that between 170 and

12,700 gigatonnes of organic carbon are stored within gas hydrates. Methane emissions from continental shelves are estimated to be between 8 and 65 Tg $\text{CH}_4 \text{ yr}^{-1}$ [Hovland *et al.*, 1993]. On continental slopes, methane hydrates can occur in sediments, which are located within the gas hydrate stability zone and may serve as an intermediate methane sink [e.g., Luff and Wallmann, 2003; Snyder *et al.*, 2007; Riedinger *et al.*, 2010] (cf. Figure 1).

[7] The carbon cycle in a high productivity environment, in particular carbon storage in the form of carbonates and methane formation, will be elucidated upon further within this manuscript. Questions that will be answered are: (i) Which portion of organic carbon is recycled by diagenetic processes and what are the relevant processes? (ii) How much carbon is stored within the sediments, and is methane hydrate formation possible? We chose as our modeling site a transect from the shelf of the lower slope off Peru. This transect is one of the best studied transects across an upwelling center [e.g., D'Hondt *et al.*, 2003; Suess *et al.*, 1988]. It covers shelf sites with high primary productivity, underlying an oxygen minimum zone, as well as slope sites with very high sedimentation rates. Furthermore, site locations differ in the Miocene time due to sea level changes and the subsidence history [von Huene and Suess, 1988]. This allows for comparison between present-day and ancient conditions, to help decipher conditions and sites that favor carbon storage and methane hydrate formation today and in the Miocene period. Interpretation of the results shall quantitatively determine carbon gain and loss across the Peruvian margin for Miocene period and recent sediments. Furthermore, it is the aim of this manuscript to emphasize the consequences for palaeoceanography. Detailed data sets from several boreholes across the transect can be used as input data for a generic reactor that stores or releases carbon.

2. Transect off the Coast of Peru

[8] The investigated transect off Peru (11°S to 12°S ; Figure 2) includes sites on the shelf (ODP Leg 112, Sites 681

Figure 2. Transect of investigated stations off the coast of Peru. The present-day oxygen minimum zone is located in a water depth between 50 and 650 m (modified after *von Huene and Suess* [1988]). Dashed line represents an approximation of the present phase boundary for methane hydrates extending as a lens down the slope [cf. *Dickens*, 2001].

and 680, corresponding to ODP Leg 201, Sites 1229 and 1228, respectively), on the shelf edge (ODP Leg 112, Site 679), and on the lower slope (ODP Leg 112, Sites 682 and 688) to the open ocean (ODP Leg 201, Site 1231) [*D'Hondt et al.*, 2003; *Suess et al.*, 1988]. Pressure and temperature conditions at the slope sites are appropriate for the formation of methane hydrate within the sediments, but not at the shallow shelf sites [e.g., *Sloan*, 1998, and references therein]. A well-developed coastal upwelling regime, active since the Miocene period, coincides with the subduction of the Nazca Plate. This specific setting results in the deposition of thick organic-rich sediments [*Kvenvolden and Kastner*, 1990].

[9] Recent major upwelling cells are located at 7° to 8°S, 11° to 12°S, and 14° to 16°S [*Suess et al.*, 1987]. The shelf sites are located beneath the strongest wind-driven upwelling areas of the Peru Current regime. They are located within the present-day oxygen minimum zone (OMZ) at a water depth of 50 to 650 m over the shelf and slope (Figure 2). Typically, the OMZ is defined for oxygen concentrations below 0.5 ml l⁻¹ [*Helly and Levin*, 2004]. In the geological past, sites 682 and 688 were located within the OMZ at lower sea level stands [*von Huene and Suess*, 1988].

[10] Shelf and upper slope sediments from the Quaternary and in particular the late Pliocene period contain alternately laminated and bioturbated diatomaceous mud units. Prior to at least 4 to 5 Ma, the Salaverry Basin (Sites 680, 681, and 679) was exposed to high-energy bottom currents. The Basin probably existed as a shallow water environment located inshore of the present center of coastal upwelling. This palaeo-environment prohibited the deposition of organic-rich muds. Thus, early Pliocene sediments from Sites 680, 681, and 679 contain more terrigenous clastics than late Pliocene sediments [*Suess and von Huene*, 1988]. Sites 682 and 688 on the present lower slope exhibit laminated, organic-rich diatomaceous muds from the late Miocene and early Pliocene ages. Deposition of the upwelling sediments at these locations is consistent with the inferred seaward shift of upwelling activity [*von Huene and Suess*, 1988]. The Peruvian margin receives only limited input from riverine discharge. The provenance of such terrigenous material is the arid Peruvian Andes and the Atacama desert. Peruvian rivers provide most of the terrigenous material: Eolian dust from the desert has a minor input. [*Böning et al.*, 2004].

[11] A detailed description of the investigated sites is given in section 1 of the auxiliary material.¹

3. Conceptual Model

[12] Hydrogeochemical models can reflect the complex web of early diagenetic processes in marine sediments. Of particular interest regarding to methane cycling within marine sediments, the formation of methane hydrate and processes in the transition zone between sulphate reduction and methanogenesis have been studied in great detail [e.g., *Davie and Buffett*, 2001; *Hensen and Wallmann*, 2005; *Wang and van Cappellen*, 1996]. Additionally, rates of sulphate reduction, methanogenesis, and organic matter degradation have been modeled [*Sivan et al.*, 2007; *Wallmann et al.*, 2006 and references therein], but the modeling of early diagenetic remineralization of organic matter has often been limited to the upper few centimeters of marine sediments [*Boudreau*, 1996; *Luff et al.*, 2000; *Luff and Wallmann*, 2003; *Wang and van Cappellen*, 1996]. More advanced models of microbial respiration and organic matter degradation have resolved complex microbial mechanisms involved in the anaerobic degradation of organic matter [*Jin and Bethke*, 2003; *Jin and Bethke*, 2005; *Wirtz*, 2003]. So far, most of the applied models have focused on isolated hydrogeo- or biochemical reactions that are only part of a complex web of reactions evolving into a multi-component and multiphase system. Reactions are interrelated due to reaction products and reactants that are involved at different steps of process chains.

3.1. Approach

[13] The modeled sediment columns are composed of 50 cells ("generic reactors"), each. The generic 1.7 l reactor is filled with an aqueous solution of present-day chemical seawater composition [*Nordstrom et al.*, 1979], and with sediments of defined mineral composition according to sediments from ODP Leg 112, Sites 679, 680, 681, 682, and 688, and Leg 201, Site 1231 [*Shipboard Scientific Party*, 2003; *Suess et al.*, 1988]. Equilibrium species distribution and coupled mass transfer that results from reactions in the

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GB004156.

modeling reactor are calculated by using the PHREEQC (version 2) program [Parkhurst and Appelo, 1999]. Calculations are based on mass action laws that include all species of Ca, Mg, Na, K, Al, Fe, Si, Cl, C, S, N, P, H₂O, and their corresponding equilibrium constants. Species, mass-action equations, and equilibrium constants are listed in the thermodynamic database “wateq4f.dat” [Parkhurst and Appelo, 1999] and Table S2.8 of the auxiliary material. The reaction kinetics of organic carbon remineralization are integrated into the set of equilibrium reactions by defining the type and the amount of remineralized organic matter in a certain time step. The accumulation of the organic matter metabolites (e.g., CH₄, CO₂, and H₂) leads to the development of new inorganic equilibrium conditions in the system.

[14] The modeled sediment column is 495 m thick (representing the zone crucial for early diagenetic reactions), and is subdivided into fifty 10-m-thick cells (Tables S2.2–S2.7). Each cell is an original reactor (expressed as representative volume (RV); $1.7 \text{ l} = 10 \text{ m} \cdot 0.013 \text{ m} \cdot 0.013 \text{ m}$) and contains 1 l of pore water (V_{aq}) and 1.89 kg of solid sediment. Hence, the average porosity (ϕ) is 0.59 and the average specific weight of solids (ρ_{s}) is 2.7 kg l^{-1} . The model design displays a growing sediment column [cf. Arning et al., 2011, Figure 1b]. Initially, equilibrium calculations are performed on one sediment cell that is overlain by five cells containing seawater. At a second time step, the first cell is instantaneously buried to a depth of 10 m. The time step for each cell (Tables S2.2–S2.7) is calculated from the sedimentation rate (Tables S2.2–S2.7) [Shipboard Scientific Party, 2003; Suess et al., 1988]. Freshly deposited sediments at the sediment-water interface form the second cell in the growing sediment column. After 50 time steps the modeled sediment column consists of 50 cells and represents the upper 495 m of the investigated sites. Once all calculations have been completed, the mineral assemblage and pore waters of the first cell (from the first time step) shift from the sediment-water interface to the base of the modeled sediment column at a depth of 485 to 495 m below seafloor (mbsf).

[15] The active transportation processes considered in this model are 1) the one-dimensional molecular diffusion of aqueous species, and 2) the burial of solids (including methane hydrate) and aqueous species, according to the observed sedimentation rate, which also represents advection. Porosity changes that occur within the upper few meters and toward greater sediment depths [Shipboard Scientific Party, 2003; Suess et al., 1988] cannot be resolved by the model, hence compaction flow and advection are not incorporated. 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].

[16] The upper boundary is defined as a constant concentration boundary (overlying seawater). The lower boundary is defined as a closed boundary for diffusion in models designed for Sites 679, 682, 688, and 1231. For the Sites 680 and 681, our model defines the lower boundary as a constant one with regard to water influx from subsurface brine [Kastner et al., 1990]. Diffusive exchange between seawater and pore water takes place at the sediment-water interface, between each newly deposited sediment cell and the lowermost cell containing seawater.

[17] Temperature increases linearly throughout the modeled sediment column consistent with the geothermal gradient (Tables S2.2–S2.7) [Shipboard Scientific Party, 2003; Suess et al., 1988]. A constant pressure (Tables S2.2–S2.7, calculated as hydrostatic pressure according to water depth and 250 m of sediments) was selected for calculations of gas solubility because of software limitations, as the effect of varying the total pressure on aqueous species distribution and associated solid phases is minor (cf. Table S2.1).

[18] Secondary minerals and gas phases (Tables S2.2–S2.7) are not present at the beginning of the equilibrium calculations but are by default allowed to form and react during the model run. Saturation indices (SI; $SI = \log(IAP/K)$ with IAP the ion activity product and K the equilibrium constant) with respect to the mineral phases of interest are initially set to 0 except for dolomite, siderite, and Ca-rhodochrosite (Tables S2.2–S2.7). Supersaturation for these carbonates is assumed due to phosphate adsorption onto calcium carbonate, in accordance with observations by Raiswell and Fisher [2004] and Warren [2000]. Equilibrium phases that are not present within the used database wateq4f.dat, such as those for struvite, carbonate fluorapatite (CFA), Ca-rhodochrosite, and CH₄-hydrate, are defined separately (Table S2.8).

[19] Given in situ pressure and temperature conditions, sediments of Sites 682, 688, and 1231 are within the gas hydrate stability zone [e.g., Sloan, 1998, and references therein]. Therefore, methane hydrate is defined as an additional equilibrium phase in these model scenarios. The equilibrium constant for methane hydrate is calculated from Gibb's free energy ($\Delta G = 5.736 \text{ kJ mol}^{-1}$) of the methane dissolution reaction: $\text{CH}_4 \cdot 6\text{H}_2\text{O}_{(\text{s})} = \text{CH}_{4(\text{aq})} + 6\text{H}_2\text{O}$, pressure ($P = 10 \text{ MPa}$), and temperature ($T = 279.55 \text{ K}$) after Lu et al. [2008].

[20] Input parameters that define primary and secondary equilibrium phases and physical boundary conditions are given in Tables S2.2–S2.7 of the auxiliary material. A detailed description of the physical and chemical considerations and the calculation scheme of the applied model are given in Arning et al. [2011].

3.2. Model Calibration and Organic Matter Remineralization

[21] Measured pore water alkalinity profiles (Figures 3b and 6b) are used for calibration. The release of CO₂ from the organic matter and its subsequent dissolution influences pore water alkalinity. 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 (Figures 3a and 6a) is readjusted until the modeled alkalinity profiles of investigated sites match measured alkalinity profiles (Figures 3b and 6b).

[22] Remineralized organic matter in the models (Redfield-CH₂O) designed for Sites 680, 681, 682, 688, and 1231 is assumed to be primarily of marine origin, with a minor contribution from terrestrial input. This organic matter is defined with an approximate Redfield stoichiometry of C:N:P equal to 100:15:1 [Redfield, 1958]. In the model for site 679, organic matter of marine origin is converted in Holocene period to upper Miocene sediments (5 to 235 mbsf), whereas in older sediments (245 to 495 mbsf) mixed marine/terrestrial organic matter (C:N:P = 100:12:1) is converted. In our

Figure 3. (a) Amounts (mmol and wt.%) and rates ($\text{mmol m}^{-3} \text{ yr}^{-1}$) of organic matter remineralized in each representative volume (RV) of the shelf and lower slope sites, as well as measured total organic carbon (TOC) content (wt.%). (b) Modeled and measured alkalinity profiles of the shelf and lower slope sites. (c) Modeled and measured ammonia concentration profiles of the shelf and lower slope sites. Grey dots: modeled data, diamonds: measured data. Measured pore water concentration data are taken from *Suess et al.* [1988]. Red numbering indicates sedimentary units according to *Suess et al.* [1988].

model, the organic matter is considered as a whole, and reaction rates are included by converting different amounts of Redfield-CH₂O in each time step. It has to be noted, that the stoichiometry of the remineralized organic matter is an approximation as in organic matter landing on the seafloor the Redfield ratio did not be necessarily conserved. The good fit between measured and modeled ammonia concentration profiles (Figure 3c, except for sites 680 and 681; see explanation in section 4.2) support our assumptions of organic matter composition.

[23] Rates of organic carbon remineralization at Sites 681, 680, 679, and 682 are comparable (Figure 3a). Some higher rates are only modeled in the Quaternary sediments of the shelf sites 681 and 680. Organic carbon remineralization at Site 679 is relatively constant, whereas at Site 682 most organic carbon was remineralized during the middle Miocene period. The amounts of remineralized organic carbon are twice as high in the Miocene sediments of site 682 compared with the Miocene sediments of Site 679. Organic carbon remineralization was suppressed in Site 682 sediments older than the Miocene period. By far most organic carbon was remineralized within the Quaternary sediments of Site 688 (up to 3.2 wt.%). The most inactive site is the open ocean Site 1231 with less than 0.05 wt.% of organic matter remineralized (Figure 6a). To calculate rates and carbon amounts for Miocene sediments, the calibrated models were run for less time steps covering sediment depths from the Miocene period.

3.3. Calculations

[24] The diffusive flux J [mol/(m² · s)] of HCO₃⁻, dissolved CO₂, and dissolved CH₄ into the sulphate-methane transition zone (SMTZ) is calculated from the modeled pore water profiles using Fick's first law:

$$J = -\phi \cdot D_{sed} \cdot dc/dx, \quad (1)$$

where ϕ is porosity (–), D_{sed} is the specific diffusion coefficient in pore space of a sediment (m²/s), and dc/dx is the concentration gradient (mol/(m³ · m)).

[25] D_{sed} can be calculated as:

$$D_{sed} = D^{sw} / \theta^2 \quad (2)$$

with D^{sw} diffusion coefficient in solution [m²/s] taken from Schulz [2006] and θ^2 tortuosity (estimated from porosity ϕ : $\theta^2 = 1 - \ln(\phi^2)$ [after Boudreau, 1997]). The fluxes are calculated for the present-day and the Miocene situation. It is not meant that these fluxes are continuous over time.

[26] Mass accumulation rates of total organic carbon (MARTOC) (g/(cm² · kyr)) are calculated following the equation developed by van Andel *et al.* [1975]:

$$MARTOC = TOC \cdot 100^{-1} \cdot SR \cdot (WBD - 1.025PO \times 100^{-1}), \quad (3)$$

where TOC is total organic carbon (%), SR is the mean sedimentation rate (cm kyr⁻¹), WBD is wet bulk density (g/cm³), and PO is porosity (%). Using mass accumulation rates, dilution effects by inorganic compounds can be excluded, and the data can be interpreted in terms of changes in sediment supply and thus primary productivity.

From MARTOC we can calculate the primary productivity (PP) (g/(cm² · kyr)):

$$PP = MARTOC \cdot 100 / EP, \quad (4)$$

where EP is the export production (%). In the present-day high productivity area on the Peruvian shelf, 10% of primary productivity from the photic zone of the ocean reaches the seafloor [Fossing, 1990]. High alkalinity in the pore water of lower slope sites (Figure 3b) suggests high organic matter remineralization on these sites, as well. We, therefore, assume that 10% of the primary productivity has constantly reached the seafloor at the shelf and lower slope sites off the coast of Peru. It has to be noticed that this is an approximation.

4. Results

[27] Detailed data sets exist for the drilling sites of ODP Legs 112 and 201 [D'Hondt *et al.*, 2003; Suess *et al.*, 1988]. They contain information on the geological setting, including a sedimentological and structural model. Furthermore, information is available about pore water and gas geochemistry, lithology, cement geochemistry, mineralogy, and porosity. Sedimentation rates can be calculated from age-depth plots based on established biostratigraphical findings. Results from the shelf and upper slope sites 679, 680, 681, 682, and 688 are presented together in Figures 3–5. Results for the open ocean site 1231 are given in Figure 6.

4.1. Solid Phase

[28] Remineralization of organic matter in the PHREEQC model results in the formation of secondary mineral phase assemblages including calcite (CaCO₃), dolomite (CaMg(CO₃)₂), Ca-rhodochrosite (Ca_{0.1}Mn_{0.9}CO₃), siderite (FeCO₃), carbonate fluorapatite (CFA; Ca_{9.316}Na_{0.36}Mg_{0.144}(PO₄)_{5.3}(CO₃)_{1.2}F_{0.98}), struvite (MgNH₄PO₄ · 6H₂O), and greigite (Fe₃S₄; Figures 5 and 6). The amount of secondary mineral phases varies in the sediments of different sites (Figure 5a).

[29] In addition to calcite and dolomite, a calcium-rich rhodochrosite formed generically in Site 679 sediments (Figure 5a) and corresponds to the analytical findings and pore water concentration profiles of calcium, magnesium, strontium and alkalinity (Figure 3b and Figure S3.2 of the auxiliary material) [Kastner *et al.*, 1990; Meister *et al.*, 2009]. Model calculations for carbonate formation in the Site 682 sediments result in minor amounts of Ca-rhodochrosite and predominating siderite in sediments older than the Quaternary period (Figure 5a). The highest amounts of secondary carbonates were calculated for the Quaternary sediments of Site 688 (Figure 5a).

[30] Greigite formation was calculated to be at the highest levels in the Quaternary sediments of Sites 680, 679, and 682 (Figure 5c). At site 1231, greigite reaches maximum amounts in the deeper section. Due to the low sedimentation rate and low organic matter remineralization, sulphate can penetrate deep into the sediments, inducing sulphate reduction and thus iron sulphide precipitation. The highest amounts of modeled secondary carbonates and greigite correlate with sediment depths, known as hot spots of microbial

Figure 4. (a) Modeled (mM) and measured (ppm) methane concentration profiles of the shelf and lower slope sites and amounts of methane hydrate (mmol/RV) at site 688 (b) Modeled and measured sulphate concentration profiles of the shelf and lower slope sites. (c) Modeled and measured phosphate concentration profiles of the shelf and lower slope sites. Gray dots: modeled data, diamonds: measured data, RV: representative volume. Measured pore water concentration data are taken from *Suess et al.* [1988]. Red numbering indicates sedimentary units according to *Suess et al.* [1988].

Figure 5. (a) Modeled carbonate contents (mol/RV) in sediments of the shelf and lower slope sites. (b) Modeled carbonate fluorapatite (CFA) contents (mol/RV) in sediments of the shelf and lower slope sites. (c) Modeled greigite (Fe_3S_4 ; mol/RV) and total sulphur (TS; wt.%) contents in sediments of the shelf and lower slope sites. Gray dots: modeled data, diamonds: measured data, RV: representative volume. Measured pore water concentration data are taken from *Suess et al.* [1988]. Red numbering indicates sedimentary units according to *Suess et al.* [1988].

Figure 6. Amounts and rates of organic matter remineralized, modeled and measured concentration profiles, as well as modeled carbonate and sulphur contents of the open ocean site 1231. (a) Amounts (mmol and wt.%) and rates (mmol m⁻³ yr⁻¹) of organic matter remineralized in each representative volume, as well as measured total organic carbon (TOC) content (wt.%). (b) Modeled and measured alkalinity profile. (c) Modeled and measured ammonia concentration profiles. (d) Modeled and measured phosphate concentration profiles. (e) Modeled (mM) and measured (ppm) methane concentration profiles. (f) Modeled and measured sulphate concentration profiles. (g) Modeled carbonate contents. (h) Modeled greigite (Fe₃S₄; mol/RV) and total sulphur (TS; wt.%) contents. Grey and blue dots: modeled data, diamonds: measured data, RV: representative volume. Measured pore water concentration data are taken from *Shipboard Scientific Party* [2003]. Red numbering indicates sedimentary units according to *Shipboard Scientific Party* [2003].

activity, and with enhanced formation of these minerals (including dolomite [e.g., *Meister et al.*, 2007]).

[31] The formation of carbonate fluorapatite (CFA) requires a complex additional model layout, and is therefore a topic of the companion manuscript II. In brief summary, most of the CFA is present in the Miocene sediments of site 682 (up to 0.0035 mol/RV; Figure 5b). A peak in CFA content was also calculated for the Pliocene/Pleistocene boundary at Site 680. In Site 688 sediments, CFA content is one order of magnitude lower in comparison with other sites, and results in the formation of struvite due to very high organic matter remineralization and high ammonia release (Figures 3a and 3b).

4.2. Pore Water

[32] Modeled concentrations of ammonia fit very well with measured concentrations at Sites 679, 682, and 688 (Figure 3c). In general, modeled ammonia concentrations from the shelf sites 680 and 681 are distinctly lower than at the shelf edge and lower slope sites. Furthermore, modeled ammonia concentrations are one order of magnitude lower than the measured ones (Figure 3c). This difference may be caused by an external source of nitrate and ammonia due to the subsurface brine [*Kastner et al.*, 1990], and this modeling feature also occurs in Site 1231 sediments within the upper 70 m (Figure 6c). Down to a sediment depth of 100 mbsf, measured concentrations decrease sharply and approximate modeled concentrations.

[33] Measured sulphate concentrations mirror modeled sulphate concentrations in deeper sediments at all sites and are slightly lower in the upper sediments (Figures 4c and 6f). Modeled concentrations from Sites 679 and 682 are exhausted at shallower sediment depths in comparison to measured ones. The models are run with an average sedimentation rate (except for Site 688), however Quaternary sedimentation rates are much higher compared with older sedimentation processes. Furthermore, measured sulphate concentrations are not completely exhausted at all sites, as minimum sulphate concentrations are likely the result of seawater contamination of the samples [*Kastner et al.*, 1990]. At the two shelf sites 680 and 681 sulphate concentrations decrease close to zero in the upper 45 mbsf and increase below that depth. Modeled sulphate is depleted in sediments from Sites 679, 682, and 688 within the first 45, 5, and 15 m, respectively. Site 1231 sulphate concentrations decrease only slightly with depth.

[34] Phosphate concentrations are difficult to model due to the unknown formation processes of authigenic phosphate mineral phases. Phosphate concentrations strongly depend on the composition of carbonate fluorapatite, and this is not known in detail. Therefore, modeled phosphate concentrations (Figures 4c and 6d) do not match the measured ones in the presented approach, and will be the topic of companion paper II.

4.3. Methane

[35] Our modeled concentration profiles of dissolved methane ($\text{CH}_{4(\text{aq})}$) mirror the trends from measured data, except for at Sites 688 and 1231 (Figures 4a and 6e). Measured methane concentrations are lower than modeled ones, however. Concentrations of modeled and measured dissolved methane are incomparable: a portion of methane was

lost during the sampling procedure, and so only residual methane has been measured [*Kvenvolden and Kastner*, 1990].

[36] The methane concentration profiles at the brine-influenced shelf sites 680 and 681 exhibit distinct peaks within Quaternary sediments at 40 and 50 mbsf, respectively (Figure 4a). This is due to a second zone of sulphate reduction [*D'Hondt et al.*, 2003; *Kastner et al.*, 1990; *Meister et al.*, 2007]. Modeled dissolved methane concentrations are up to 0.00004 mM at Site 680 and 0.00025 mM at Site 681. In the sediments of site 679, dissolved methane starts to accumulate below 50 mbsf, and increases to a depth of up to 54 mM and down to the end of the model column (495 mbsf).

[37] For the slope sites, model results indicate that methane formation starts within the uppermost sediments of Site 682. Concentration increases with sediment depth, reaches a maximum concentration of 60 mM at 250 mbsf, and remains constant below 250 mbsf. Dissolved methane formation within the top sediments is also predicted for Site 688 with a similar trend as for site 682. In general, methane solubility increases with depth due to increasing pressure and temperature within the gas hydrate stability zone (GHSZ). Below the base of the GHSZ, methane solubility should again decrease [e.g., *Bhatnagar et al.*, 2007]. In our modeling approach dissolved methane concentrations remain constant below distinct depths, because all cells of the model are exposed to the same pressure. This is due to limitations with PHREEQC in terms of gas pressure. Methane hydrate starts to form at a sediment depth of 165 mbsf (Site 688), reaches a maximum content of 1480 mmol/RV at 245 mbsf, and decreases to a minimum of 10 mmol/RV at 335 mbsf. Below 335 mbsf, methane hydrate contents are calculated to be around 60 mmol/RV.

[38] Methane concentrations are minor within sediments of the open ocean site 1231, (Figure 6a). A dissolved methane concentration of 0.0003 μM is calculated within a sediment depth of 15 mbsf. Methane concentration increases within a sediment depth of up to 0.003 μM and down to the end of the model column (495 mbsf).

4.4. Mass Accumulation Rate of Total Organic Carbon (MARTOC)

[39] Mass accumulation rates of total organic carbon (MARTOC) have to be calculated as the base for primary productivity (PP) calculations (see section 3.3). MARTOC are highest in the Quaternary sediments of Site 688 and one order of magnitude lower in the Quaternary sediments of the other Sites (679, 680, 681, and 682). MARTOC have been calculated from i) the organic carbon content remineralized in the model (MARTOC-model), ii) the sum of the organic carbon content remineralized in the model and measured TOC content (MARTOC-model + meas), and iii) the measured TOC content (MARTOC-meas). Detailed results from Site 679 are shown to illustrate the differences in these calculations and are compared to literature data for verification.

[40] Our MARTOC-model at Site 679 is lower in Quaternary sediments (0.001 to 0.004 $\text{g cm}^{-2} \text{ kyr}^{-1}$) and reaches values around 0.01 $\text{g cm}^{-2} \text{ kyr}^{-1}$ in deeper sediment layers from the Pliocene and Miocene age (Figure 7). MARTOC have also been calculated from measured TOC values for Site 679 by *ten Haven et al.* [1990]. The accumulation rates are two orders of magnitude higher in the Quaternary section

Figure 7. Mass accumulation rates of organic carbon (MARTOC) and primary productivities (PP) of the shelf and lower slope sites calculated by means of modeled and measured organic carbon data. Red numbering indicates sedimentary units according to *Suess et al.* [1988].

($0.26 \text{ g cm}^{-2} \text{ kyr}^{-1}$) and within the same range from Pliocene and Miocene sediments (0.02 to $0.07 \text{ g cm}^{-2} \text{ kyr}^{-1}$). These differences are due to the organic carbon remineralization rates. While in Quaternary sediments the amount of remineralized organic carbon is low (Figure 3a), the amount of remineralized organic carbon in the Pliocene and Miocene sediments is higher. The measured TOC content inversely correlates with these observations: high TOC contents correspond to organic carbon remineralization. A larger portion of the initially accumulated TOC has been remineralized in older sediments and is lost to analyses. Therefore, MARTOC-model + meas leads to slightly higher rates in Pliocene and Miocene sediments. In contrast, MARTOC-model + meas in the Quaternary sediments match those calculated from measured TOC contents (MARTOC-meas), because measured TOC contents are almost consistent with the TOC amount that was accumulated initially.

5. Discussion

5.1. Primary Productivity off the Coast of Peru

[41] One key parameter in palaeoceanography and in the carbon cycle is primary productivity. Commonly, measured (relict) TOC contents from marine sediments are consulted when reconstructing the primary productivity of Earth history. Present-day measured TOC profiles in marine sediments, however, only give information on relict organic matter. Information on the fraction of organic matter that has already been converted can only be achieved by means of modeling (Figure 7).

[42] Slope sites 682 and 688 make it most obvious that remineralized organic carbon should be of great importance within the study of palaeoceanography. (Figure 7). The more organic matter that has been remineralized during early diagenesis (Figure 3a) the larger the difference between MARTOC calculated from measured TOC data (MARTOC-

meas) and from the sum of modeled and measured values (MARTOC-model + meas). At Site 682, most organic matter was remineralized in the Miocene sediments (Figure 3a) and the largest differences between MARTOC-meas and MARTOC-model + meas are observed. Differences are lower in the Oligocene and Eocene sediments that are accompanied by less organic matter remineralization. Remineralization rates are lower because of lower initial TOC contents, due to the periodic influx of coarse clastic sediments to a shallow marine basin [von Huene and Suess, 1988].

[43] Past and present-day primary productivity (Figure 7) can be calculated from MARTOC (see section 3.3), but it has to be critically interpreted. Our results are not reasonable for all investigated sites. For example, the input of allochthonous organic-rich sediments from the shelf to the lower slope at Site 688 during the Quaternary period precludes reliable calculation of primary productivity from modeled as well as from measured TOC values. Also the two shelf sites 680 and 681 exhibit special features, which have to be taken into account when calculating primary productivity from measured TOC. Due to brine reflux at the shelf sites according to *Kastner et al.* [1990], two enrichment horizons are present of microorganisms and enhanced microbial activity [Cragg et al., 1990; Meister et al., 2007; Meister et al., 2008]. These horizons mirror peaks in the measured TOC contents of the sediments. Therefore, measured TOC values lack direct correlation with TOC contents derived from primary productivity, because microorganisms are an in situ organic carbon source in marine sediments. Obviously, primary productivity calculated by generically converted organic carbon is distinctly lower, especially at the enrichment horizons, than primary productivity based on measured values (Figure 7).

[44] Primary productivity today and in the geological past can be determined from Site 679 and 682 model calculations and TOC measurements. Calculated primary productivities

Figure 8

Figure 9. Ratio between measured preserved total organic carbon ($\text{TOC}_{\text{measured}}$) and modeled secondary inorganic carbon ($\text{IC}_{\text{modeled}}$). Measured data are taken from *Suess et al.* [1988]. Red numbering indicates sedimentary units according to *Suess et al.* [1988].

(based on MARTOC-model + meas) for the Quaternary period at the shelf edge for upwelling areas off Peru (Site 679; 19 to $199 \text{ gC cm}^{-2} \text{ kyr}^{-1}$) are in the same range as measured primary productivities (between 21 and $110 \text{ gC cm}^{-2} \text{ kyr}^{-1}$ [Antoine et al., 1996]) [Behrenfeld and Falkowski, 1997a, 1997b; Fossing, 1990]. Model calculations yield a higher primary productivity during Quaternary times at the shelf edge (Site 679) than at the lower slope site 682. Furthermore, model calculations indicate that primary productivity changed from the Miocene period up to today. During the Miocene period different palaeoceanographic conditions induced higher primary productivity at Site 682, located at the shelf (approximately half of what was calculated for Quaternary times at Site 679). On the other hand, Site 679 was located inshore of the centers of present-day upwelling [Suess and von Huene, 1988] with a consequently low primary productivity (Figure 7). Furthermore, our model calculations show that more terrigenous organic material was deposited during the middle Miocene period at Site 679. This concurs with our assumption of a more landward location of this site during Miocene time.

5.2. The Carbon Cycle of Peru Shelf and Slope Sediments: Present-Day and Miocene

[45] Carbon mass balance calculations highlight the influence of organic matter remineralization on diagenetic carbonate formation (Figure 8). Secondary carbonate minerals

dominate the final carbon pool after remineralization of the organic carbon. Not included is the relict TOC that dominates over modeled IC especially in the upper sediments (Figure 9).

[46] Carbonate formation is crucial to the carbon cycle of the sediments. It is associated with, and determines concentrations of dissolved inorganic carbon (DIC; dissolved CO_2 and pore water alkalinity) (Figure 3b). The total carbon losses of the investigated sites are calculated based on the carbon mass balance calculations shown in Figures 8 and 10. It is the sum of carbon losses and gains across all grid cells. It considers the amount of remineralized organic carbon, of initial inorganic carbon (seawater alkalinity as well as primary carbonates at sites 679, 682, and 688), and of final carbon (secondary carbonates, DIC and methane). As can be seen in Tables 1 and 2, the most carbon is diffusive loss of bicarbonate (HCO_3^-). The loss of total carbon in sediments at Site 680 is less than at Site 681, because of the formation of intensified authigenic carbonates. The whole sediment columns have a moderate carbon loss of 1153 mmol ($=7\%$) and 2166 mmol ($=14\%$) of total carbon ($\text{C}^{(+IV)} + \text{C}^{(-IV)} + \text{C}^{(0)}$), respectively (Table 3).

[47] The loss of total carbon at the shelf edge site 679 ($1846 \text{ mmol} = 7\%$) is comparable to the general carbon loss at all the shelf sites. The total amount of remineralized organic carbon is higher, however, compared with the other shelf sites, and consequently more authigenic carbonates are

Figure 8. Carbon mass balance calculations of the present-day situation of all investigated stations. Calculations are based on summed amounts of each cell after the last time step. Prior to model calculations, inorganic carbon is present only in low amounts in each cell ($\text{alkalinity} + \text{CO}_{2(\text{aq})} = 4.62 \text{ mmol C}$). In the left diagram the amount of remineralized organic carbon is given. Amounts and species distribution of carbon for each cell after complete remineralization of organic carbon are given in the middle diagram. In the right diagram carbon mass balance calculations as difference between the final carbon present ($\text{alkalinity} + \text{CO}_{2(\text{aq})} + \text{carbonates} + \text{CH}_{4(\text{aq})} + \text{CH}_4\text{-hydrates}$) and the initial carbon ($\text{alkalinity} + \text{CO}_{2(\text{aq})} + \text{remineralizable organic carbon}$) are given. Negative values indicate loss of carbon from cells and positive values indicate carbon gain in cells due to diffusion. It is shown a snapshot in the Miocene time and not a continuous carbon loss and gain. The mass balance calculation does not include the relict organic carbon that remains within the sediments. RV: representative volume.

Figure 10. Carbon mass balance calculations in the Miocene for stations 679, 682, and 688. Calculations are based on summed amounts of each cell after the last time step. Prior to model calculations, inorganic carbon is present only in low amounts in each cell ($\text{alkalinity} + \text{CO}_{2(\text{aq})} = 4.62 \text{ mmol C}$). In the left diagram the amount of remineralized organic carbon is given. Amounts and species distribution of carbon for each cell after complete remineralization of organic carbon are given in the middle diagram. In the right diagram carbon mass balance calculations as the difference between the final carbon present ($\text{alkalinity} + \text{CO}_{2(\text{aq})} + \text{carbonates} + \text{CH}_{4(\text{aq})} + \text{CH}_4\text{-hydrates}$) and the initial carbon ($\text{alkalinity} + \text{CO}_{2(\text{aq})} + \text{remineralized organic carbon}$) are given. Negative values indicate loss of carbon from cells and positive values indicate carbon gain in cells due to diffusion. It is shown a snapshot in the Miocene time and not a continuous carbon loss and gain. The mass balance calculation does not include the relict organic carbon that remains within the sediments. RV: representative volume.

formed. Furthermore, dissolved methane becomes significant in the final carbon pool. In contrast to younger sediments, higher organic matter remineralization within sediments from the Miocene age leads to a loss of carbon in the deeper sediments and a gain in the upper sediments due to upward diffusion of dissolved carbon species (Figure 8). The opposite process can be observed in sediments from Site 680.

[48] Carbon-cycling in the Peruvian shelf and lower slope environments is affected by the width of the sulphate reduction zone that is followed instantaneously by a methanogenic zone. The range of depth in the sulphate reduction zone determines the sulphate methane transition zone (SMTZ). At the slope sites 688 and 682 this zone is close to the sediment surface, whereas at Site 679 it is located deeper within the sediments (cf. Figures 4a and 4b). Within the shelf sediments there are two SMTZs due to the influx of subsurface brine. Anaerobic oxidation of methane (AOM; $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$) [Boetius et al., 2000] takes place where methane and sulphate profiles meet due to the upward diffusion of dissolved methane. AOM is calculated by our model in correspondent cells, reflected by enhanced alkalinity, and enhanced authigenic carbonate precipitation, and

sulphide mineral formation (Figures 3b, 5a, and 5c). Our model most likely overestimates the rates of AOM, which it expresses in lower methane and sulphate concentrations compared to the measured values (Figures 4a and 4b). The AOM process prevents methane from escaping into the water column [Boetius et al., 2000; Niewöhner et al., 1998; Treude et al., 2005] and therefore the modeled methane is exhausted at the top of the sediment column.

[49] The influence of diffusional fluxes (Table 1) becomes obvious at the lower slope site 682, which has the highest total carbon loss ($47,911 \text{ mol} = 92\%$). High organic matter remineralization in the upper sediment layers already leads to sulphate depletion in the upper layers of the sediments (Figures 3a and 4b) and high levels of CO_2 and methane production close to the sediment surface (Figures 4a and 8). Contemporaneous low sedimentation rates (Table S2.5) favor the diffusive loss of DIC into the overlying seawater and less carbonates precipitate. The amounts of authigenic carbonates in the sediments of Site 682 are comparable to the amounts in the shelf edge site 679 sediments, even though, in total, much more organic carbon was converted at the lower slope site 682 (Figure 3a). On the other hand, our

Table 1. Flux at the Present Day From Deep Sediments Into the Sulphate Methane Transition Zone Close to the Sediment Surface^a

J sed (mmol/(m ² *yr))	688	682	679	680	681
HCO_3^-	31.3859928	32.9552924	4.3155740	16.6738087	21.7740325
$\text{CO}_{2(\text{aq})}$	0.1459784	0.0889141	0.0331769	0.1092184	0.1234181
$\text{CH}_{4(\text{aq})}$	6.0675077	5.2238352	0.0000000	0.0000324	0.0000809

^aSpecific diffusion coefficients (D^{sw}) at 5°C were taken from Schulz [2006]: $D^{\text{sw}}_{\text{HCO}_3^-} = 6.09\text{E-}10 \text{ m}^2/\text{s}$, $D^{\text{sw}}_{\text{CO}_{2(\text{aq})}} = 1.03\text{E-}10 \text{ m}^2/\text{s}$, $D^{\text{sw}}_{\text{CH}_{4(\text{aq})}} = 8.97\text{E-}10 \text{ m}^2/\text{s}$.

Table 2. Flux in the Miocene From Deep Sediments Into the Sulphate Methane Transition Zone Close to the Sediment Surface^a

J sed (mmol/(m ² *yr))	688	682	679
HCO ₃ ⁻	15.692996	19.616245	9.572728
CO _{2(aq)}	0.045121	0.059718	0.046448
CH _{4(aq)}	0.000000	48.540061	0.000000

^aSpecific diffusion coefficients (D^{sw}) at 5°C were taken from Schulz [2006]: $D^{sw}_{HCO_3^-} = 6.09E^{-10}$ m²/s, $D^{sw}_{CO_2(aq)} = 1.03E^{-10}$ m²/s, $D^{sw}_{CH_4(aq)} = 8.97E^{-10}$ m²/s.

calculations prove that most of the remineralized carbon is stored within the sediments of the lower slope site 688. This is due to very high sedimentation rates during the Quaternary period, (Table S2.6) and also due to AOM that prevents methane from diffusion into overlying seawater. Thus, Site 688 reveals moderate present-day total carbon loss (5487 mmol = 11%) that is comparable to the loss calculated for all shelf sites (Table 3). The relatively moderate carbon loss can be explained by carbonate formation that takes place in the Quaternary sediments with enhanced organic matter remineralization. Very high rates of organic matter remineralization (6–8 mmol) (Figure 3a) in sediment depth between 160 mbsf and 260 mbsf are responsible for the formation of final carbon amounts of more than double the levels found at other sites. Comparison of the pie diagrams in Figures 11a and 11b obviously demonstrate the carbonate formation at site 688 to be a recent phenomenon of Quaternary times. Enhanced carbonate formation did not take place during Miocene time when this site was located on a former shelf.

[50] The established model also provides a tool to unravel the ancient carbon cycle of the investigated sediments. Carbon mass balance and flux calculations were performed for the Miocene section at Sites 679, 682, and 688, and were compared with the present-day situation (Figure 10 and Tables 2 and 3). Sites 682 and 688 were the most interesting to evaluate due to changes in the sea level and the subsidence history. Throughout the Miocene period these sites were located on a former shelf and influenced by upwelling [Suess and von Huene, 1988; von Huene and Suess, 1988]. The total carbon loss from sediments on both sites is thus significantly higher compared with the present-day situation, especially at Site 688 (Table 3). At Site 688, less organic carbon remineralization and a much lower sedimentation rate in the Miocene period lead to conditions of suppressed carbonate and methane formation within the sediment column. Loss of carbon from the Miocene sediments of Site 682 can be determined by noting the high methane flux from deep sediments into the SMTZ close to the sediment surface

(Table 2). Comparable to the present-day shelf site, organic matter remineralization is at a high level (Figure 3a) and methane is produced, but not stored, within the sediments.

[51] Comparison of both the present-day and the ancient situation at shelf and lower slope sites off the coast of Peru indicates that hydrogeochemical conditions within pore waters and sediments, as well as sedimentological conditions, determine the carbon cycle within marine sediments. Our modeling results, summarized in Figure 11, agree with the assumption that in the present-day ocean, continental slope sediments, rather than shelf sediments, act as major carbon sinks [Henrichs and Reeburgh, 1987; Reimers et al., 1992; Walsh, 1991; Walsh et al., 1985]. Work on the reconstruction of climate benefits from knowledge of whether carbon is stored within, or removed from, marine sediments.

5.3. Methane Accumulation in Marine Sediments off the Coast of Peru

[52] Knowledge of methane cycling today and during Earth's history is crucial as methane is an important greenhouse gas and energy source. Geochemical modeling helps to quantify methane accumulation in, or release from, marine sediments, and identifies factors and mechanisms that are responsible for methane storage. Crucial to the methane cycle is the diffusive flux of methane toward the SMTZ that is controlled by sedimentation rates and concentration gradients (dc/dx).

[53] Our model results demonstrate that most methane is temporarily stored within sediments of the present-day lower slope site 688 (Figures 4a, 8, and 10). Here, very high sedimentation rates are caused by slumpings that transport huge amounts of organic carbon-rich sediments from the shelf to the lower slope [Suess et al., 1988]. These sediments are quickly buried and a high rate of organic matter remineralization becomes feasible in deeper sediment layers. Deep sulphate penetration into the sediments is prohibited due to AOM and high sedimentation rates (Figure 4b). Consequently, enhanced methane production takes place in the deep sediments. Methane accumulation leads to methane concentrations that are at equilibrium concentration with methane hydrates. Methane hydrates form due to appropriate pressure and temperature conditions at the lower slope, and they transiently retain most of the generated methane (Figures 4a and 8). Importantly, our modeled methane hydrate occurrence fits observations made by Suess and von Huene [1988].

[54] Our model calculations further rule out the possibility of present-day and former shelf site sediments off the coast of Peru acting as a methane reservoir, even though rates of organic matter remineralization have been high in these

Table 3. Total Carbon Loss/Gain of the Modeled Sediment Columns Today and in the Miocene^a

	681		680		679		682		688		1231 ^b	
	mmol	%	mmol	%	mmol	%	mmol	%	mmol	%	mmol	%
Present day	-2166	-14	-1153	-7	-1846	-7	-47911	-92	-5487	-11	+558	+21
Miocene	—	—	—	—	-863	-5	-35379	-109	-613	-44	—	—

^aThe total carbon loss/gain is calculated on the basis of the carbon mass balance calculations shown in Figure 8. It is the sum of carbon losses and gains across all grid cells. It considers the amount of remineralized organic carbon, of initial inorganic carbon (seawater alkalinity as well as primary carbonates at sites 679, 682, and 688), and of the final carbon (secondary carbonates, DIC, and methane). The seafloor area of the reactor is 0.000169 m².

^bThe open ocean site 1231 is the only one with a total carbon gain due to minor organic carbon remineralization and diffusion of alkalinity from the seawater into the sediments.

Figure 11. Summary of carbon species that are stored within the sediments, methane fluxes into the sulphate-methane transition zone (SMTZ), and fluxes of dissolved inorganic carbon (DIC; HCO_3^- and $\text{CO}_{2(\text{aq})}$) out of the sediments into overlying seawater. (a) Present-day situation. (b) Miocene situation. The size of pie diagrams is relative to the amounts of stored carbon species (cf. Figures 8 and 9). The size of arrows is relative to the amount of organic carbon remineralized (gray arrows; cf. Figures 8 and 9) and to methane flux from deep sediments into the sulphate methane transition zone close to the sediment surface (white arrows; cf. Tables 1 and 2). Note: the SMTZ is only illustrative and not according to its real sediment depth.

settings (Figure 3a). The levels of carbon stored are minor compared with lower slope environments (Figure 11). Methane flux is at a high level in the Miocene period shelf sediments from deep layers in the SMTZ (Site 682; $0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$) (Table 2) and is comparable with methane flux calculated for present-day surface sediments in the Gulf of Mexico ($1.1 \pm 0.2 \text{ mol m}^{-2} \text{ yr}^{-1}$) [Wankel et al., 2010]. On the other hand, methane flux from present-day slope sites with methane hydrate formation ($0.006 \text{ mol m}^{-2} \text{ yr}^{-1}$) is comparable with the flux from sediments overlying a major gas hydrate deposit at the Carolina Rise and Blake Ridge ($0.018 \text{ mol m}^{-2} \text{ yr}^{-1}$) [Borowski et al., 1996]. At present-day shelf sites, however, methane concentrations and fluxes are several orders of magnitude lower (Figure 4b and Table 1), due to methane oxidation from sulphate that derived from sub-surface brines. The brine transports sulphate into the system (Figure 4b), and a second zone of methane oxidation is established within deeper sediments (Figure 4a). Enhanced sulphate reduction can also be retraced by modeled iron sulphide formation. The highest iron sulphide content occurs in the zones of methane oxidation (Figure 5c), and matches the measured values determined in surface sediments from the same area by Suits and Arthur [2000].

[55] Remineralization of organic matter drives methane formation as well as carbonate formation. It is crucial to

consider carbonate formation when looking at methane formation, as it influences the $\text{HCO}_3^-/\text{CO}_{2(\text{aq})}$ pore water concentration. This appears obvious when comparing the present-day shelf sites 680 and 681. Levels of modeled authigenic carbonate formation are twice as high in Site 680 sediments compared with site 681 sediments (Figure 5a), correlated with modeled methane concentrations that are one order of magnitude lower (Figure 4a).

6. Conclusions

[56] Hydrogeochemical modeling, together with carbon mass balance and flux calculations, enable insights into the present-day and the Miocene period carbon cycle. Furthermore, our model can be applied to answer palaeoceanographic questions. Several conclusions can be drawn from the modeling of shelf and slope sites off Peru:

[57] 1. The established model provides a tool to unravel the present-day and ancient carbon cycles of marine sediments. Thus, results from the developed geochemical model contribute to a better understanding of interrelations between sedimentological settings, geochemical conditions, and carbon cycles within the marine realm.

[58] 2. Mass balance calculations show that carbonate formation is crucial for carbon storage. Most carbon is stored

when organic matter is remineralized in deeper sediment layers, together with high sedimentation rates that prevent dissolved carbon species from diffusion into the uppermost sediment layers. Furthermore, the process of anaerobic oxidation of methane (AOM) is crucial to carbon storage (in the form of authigenic carbonates) within marine sediments.

[59] 3. Regarding the methane cycle, slope sites are important for methane storage. Model calculations further rule out the possibility of methane reservoirs in present-day and former shelf site sediments off the coast of Peru, because of the intense anaerobic oxidation of methane by sulphate in these sediments.

[60] 4. In palaeoceanography it is important to consider the remineralized organic carbon that can be determined only from model calculations, especially in sediments that have passed through intense organic matter remineralization and have low measured total organic carbon content.

[61] 5. Ancient primary productivity can be calculated from the mass accumulation rates of total organic carbon that are based on i) the amount of organic carbon that has been remineralized (known only from model calculations) and ii) the amount of relict organic carbon that has been retained in the sediments (known from measurements). The calculated primary productivity of Quaternary shelf sediments is proven by its accordance with measured primary productivity data from the same area. Primary productivity is an important factor in the carbon cycles of marine sediments and is significant in the carbon mass balance of the ocean. Thus, the model can be applied to calculated ancient primary productivity and allows for the reconstruction of palaeoceanographic conditions.

[62] In summary, our model results clarify that several geochemical and sedimentological parameters have to be taken into account when examining methane cycles in marine sediments. Sedimentation rates and organic matter contents are as important as the rate of sulphate reduction and authigenic carbonate formation.

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