Simulation of long-term feedbacks from authigenic carbonate crust formation at cold vent sites

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Abstract

Fluid flow at cold vent sites is usually driven by the ascent of overpressured fluids from subsurface reservoirs. Porosity changes in surface sediments due to precipitation and dissolution of authigenic carbonates affect fluid flow and biogeochemical turnover. From observations, it is known that carbonate precipitates often occur in distinct layers in high concentrations, surrounded by layers with low carbonate content. Using a non-steady state model, we simulate aragonite and calcite precipitation and dissolution in a 2-m long sediment column, located under a bacterial mat at Hydrate Ridge, Cascadia accretionary margin. Assuming a constant pressure gradient over 7000 years, fluid flow, anaerobic oxidation of methane (AOM) rates, and carbonate precipitation and dissolution rates show strong oscillations evoked by changes in permeability and fluid flow over time. The porosity reaches values below 0.35 in the carbonate layers that reduce the fluid flow velocity from an initial value of 30 cm a
-1 to a minimum value of about 2 cm a
-1. These significant changes in the fluid flow system displace the depth of sulfate penetration. The simulation predicts cycles of carbonate crust formation and dissolution with a duration of 2000–2700 years resulting in several distinct carbonate layers. During periods of high fluid flow, AOM reaches rates over 1000 μmol cm
-1 a
-1 and methane fluxes out of the sediment reach 200 μmol cm
-1 a
-1. During periods of low fluid flow, AOM is about 450 μmol cm
-1 a
-1 and the methane flux into the bottom water vanishes completely. The oscillations are dampened so that fluid flow and biogeochemical turnover slowly approach steady state after about 7000 years towards the end of the simulation period, showing a 1-m-thick area at the surface with carbonate concentrations of about 25 wt.%. Flow oscillations may also impact the colonization of chemosynthetic larvae and bacteria in and on the sediment. The frequency of precipitation–dissolution cycles of 2000–2700 years is long enough for vent biota to react to changes in the sediments, for example explaining the occurrence of buried Calyptogena and Acharax mussel shells at former vent sites that are not presently active.

The evaluation of side scan sonar data reveals large areas of cemented sediments and carbonate pavements north of the investigated site. The situation found in the investigated core may be characterized as intermediate stage of carbonate cementation. This ongoing process will also form a solid carbonate pavement at this site in the future.

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1. Introduction

At cold vent sites, advecting fluids transport methane and other geochemical species from deeper horizons upward into the near-surface sediments. Here methane encounters downward diffusing seawater sulfate and is oxidized anaerobically by a microbial consortium, releasing bicarbonate and sulfide into the pore water (Boetius et al., 2000; Hinrichs et al., 1999). This process called anaerobic oxidation of methane (AOM) increases the alkalinity and triggers carbonate precipitation. On a global scale, authigenic carbonates and gas hydrates may have a significant impact on the carbon cycle, due to their temporary or permanent storage capacity of carbon (Dickens, 2002; Judd et al., 2002). Moreover, the amount of sulfide delivered from below triggers the colonization and distribution of different chemosynthetic communities (Sahling et al., 2002) at these sites. These distinct communities are the characteristic indicator for active fluid vent sites at the sea floor.

1.1. Biogeochemical turnover of methane

The main biogeochemical processes occurring in the cold vent environment beneath a bacterial mat, dominated by upward fluid flow, are AOM using sulfate as electron acceptor:

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \quad (1)$$

and precipitation of calcium carbonates (aragonite and calcite):

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3(\text{s}) + \text{CO}_2 + \text{H}_2\text{O}, \quad (2)$$

induced by the increase of carbonate alkalinity during AOM.

Numerical experiments with different velocities of upward fluid flow showed that measurements of the sulfate penetration depth can be used to estimate the sedimentary turnover rates and flux of methane and total CO$_2$ (TCO$_2$) between sediment and bottom water (Luff and Wallmann, 2003). As upward methane delivery increases, the depth of the AOM layer moves upward in order to supply a balancing amount of sulfate derived from overlying seawater (Borowski et al., 1996), causing the sediment zone containing sulfate to decrease in thickness.

These simulations demonstrated that AOM has by far the highest turnover rates in relation to the other biogeochemical processes occurring at cold vent sites (Luff and Wallmann, 2003). The depth and thickness of the AOM horizon mainly depends on the strength of the upward fluid flow and the concentration of methane in the ascending fluids (Luff et al., 2004). Moderate sulfate penetration depths (1–10 cm) are a good indicator of high AOM turnover rates in the sediment, that is supported by moderate advective fluid flow velocities (20–60 cm a$^{-1}$) and high methane concentrations (>50 mmol l$^{-1}$). Under these conditions, methane may break through the sediment surface, but the main portion is still oxidized within the sediment. The enhancement of alkalinity from AOM causes authigenic carbonate formation if sedimentation rates and bioturbation activities are low (Luff et al., 2004). Such crusts might suppress fluid flow completely due to porosity and permeability reduction. On the northern summit of Hydrate Ridge, massive carbonate boulders that paved the seafloor in several layers exists (Greinert et al., 2001). At the southern summit, only randomly distributed carbonate blocks were found on the sediment surface. In the sediments, gas hydrates with carbonate breccias and aragonite layers (0.5–2 cm thick) parallel to stratification occurred (Bohrmann et al., 1998). The carbonate density at the southern summit is significantly lower than on the northern summit of Hydrate Ridge. This may result from a later onset of fluid venting at the southern summit, providing a spatial proxy for temporal evolution of this methane-bearing accretionary ridge (Tre’hu et al., 1999) or from generally lower sedimentary AOM turnover rates.

1.2. Conditions for carbonate cementation

Carbonate formation in sediment pore space takes place when pore-fluids are highly supersaturated with respect to the carbonate phase (e.g. calcite or aragonite) and kinetic factors do not inhibit their precipitation (Burton, 1993; Tucker and Wright, 1990). Because the amount of calcium (Ca$^{2+}$) and carbonate ion (CO$_3^{2-}$) in pore waters is orders of magnitude less concentrated than in the solid-phase carbonates, thousands of pore volumes of fluid must pass through sediments in order to occlude pore space. This amount has to be delivered by an efficient fluid
transport system in order to appreciably affect the solid phase composition of sediment. Calculation of the molarity of supersaturated fluid indicates that many thousand times the pore volumes of fluid must pass through the pore space in order to fill it completely with cement. Sediments with high porosity are initially preferential conduits for fluid flow. Thus, cementation will take place preferentially where active flow transports large quantities of fluid through porous sediment (Tucker and Wright, 1990). These sediments may become impermeable to further fluid flow after cementation. Gas hydrate also builds such impermeable barriers, but its formation is considerably faster than carbonate precipitation, due to the very effective methane transport by gas bubbles into the gas hydrate stability zone and higher formation velocity (Sloan, 1997; Torres et al., 2004). Both gas hydrates and carbonates block fluid pathways and reduce pore fluid transport. The difference between the two species is, that hydrate once formed, still dissociates to keep the surrounding methane pore water concentration in equilibrium with the “solid phase”. Consequently, it permanently contributes methane to pore waters. At the pressure and temperature conditions prevailing at Hydrate Ridge the methane concentration that is in equilibrium with gas hydrate amounts to 68 mmol l$^{-1}$ (Zatsepina and Buffett, 1997). Thus, from the gas hydrate layers, methane is delivered that diffuses upward and promote AOM, whereas unreactive carbonate crusts simply separate the sediment surface from deeper sediment horizons and reduce AOM turnover rates.

Several numerical models have been developed which describe the feedbacks of cementation of porous media by minerals. Canals and Meunier (1995) numerically investigated the cementation of sandstone by quartz cement as a function of time and space including the kinetic control of mineral dissolution and precipitation. Bolton et al. (1999) examined the flow-chemistry feedback from quartz precipitation and dissolution processes. Kinetic effects in a multi-mineralic flow system have been studied by Soler and Lasaga (1996), to predict bauxite formation with an upper gibbsite-rich and a lower kaolinite-rich zone through simulations over 5 Ma. The impact of porosity and its distribution on transport processes has also been emphasized to explain complex pore water profiles in deep sediments offshore Florida, using a numerical 1D model (Rudnicki et al., 2001). These investigations showed that pore water profiles above low porosity horizons are strongly controlled by the changes in the physical properties of the horizons that affect the transport processes in the sediment column. Luff et al. (2004) applied a numerical model to investigate the optimal conditions for carbonate crust formation at cold vent sites. They found that carbonate crusts in the sediments only form if the fluids contain sufficient dissolved methane (>50 mmol l$^{-1}$) and if bioturbation coefficients are low (<0.05 cm$^2$ a$^{-1}$). Moreover, high sedimentation rates (>50 cm ka$^{-1}$) inhibit crust formation while bioirrigation induces a downward displacement of the precipitation zone and accelerates the formation of a solid crust. Crusts only form over a rather narrow range of upward fluid flow velocities (20–60 cm a$^{-1}$), which is somewhat enlarged (up to 90 cm a$^{-1}$) if the overlying bottom waters are supersaturated with respect to calcite.

Here, we present an advanced non-steady state multi-parameter model to simulate the cementation of surface sediments by carbonate layers at cold vent sites. We simulate the formation of aragonite and calcite and the feedbacks affecting biogeochemical turnover and fluid flow over a time period of 7000 years. Based on a biogeochemical data set from Hydrate Ridge (Cascadia margin), the evolution of authigenic carbonate layers, the changes in pore water chemistry, and the feedback mechanisms of fluid fluxes between sediment and bottom water can be characterized and constrained. Moreover, this study provides the first long-term budget of carbon cycling at cold vent sites.

2. Study area and methods

Hydrate Ridge is an accretionary structure (about 25 km long and 15 km wide) at the Cascadia margin (about 90 km off central Oregon) formed as the result of the subduction of the Juan de Fuca plate beneath the North American plate (Goldfinger et al., 1997; Kulm et al., 1986; MacKay et al., 1992). This ridge is characterized by a northern and southern summit with water depths of about 600 and 800 m, respectively (Fig. 1). Hydrate Ridge is also well known for intense fluid venting characterized by expulsion of methane.
bubbles, by seepage of methane-rich and hydrogen sulfide-rich fluids, and by the occurrence of gas hydrates near the sediment surface. Massive authigenic carbonates occur as scattered complexes at the northern summit, and as solitary large structures at the southern summit and in the vicinity (Fig. 1) (Boetius and Suess, 2004; Bohrmann et al., 1998; Greinert et al., 2001; Ritger et al., 1987; Suess et al., 2001; Torres et al., 2002; Tryon et al., 2002). Carbonate pavements are distributed more or less continuously over the entire Hydrate Ridge area (Johnson et al., 2003). Numerous sedimentology, pore water geochemistry
and microbiology projects have conducted at Hydrate Ridge including ODP leg 204 (Tréhu et al., 2004). During the TECFLUX project (RV SONNE Cruise SO-143; August 1999), a TV-guided multicorer (Site: 114-1) recovered an undisturbed 20-cm long sediment core from the southern summit at 786 m water depth from 44°34.210N, 125°08.813W (Fig. 2, small circle). Data for this figure has been acquired during FS SONNE cruise SO-165 in July 2002 using digital 75 kHz Chirp sidescan sonar from the southern Hydrate Ridge. The instrument was towed about 100 m above the seafloor with an average speed of

Fig. 2. 75 kHz sidescan sonar image of southern Hydrate Ridge. High backscatter intensity is shown in light tones and low backscatter is shown in dark tones. Investigated station (SO165/114-1) is marked with a small point. Referred core (SO165/55-2) from Luff and Wallmann (2003) is marked with a small square. The large square represents the area with the highest cold vent activities. From the 16 cores characterized by typical cold vent infauna, taken during the cruise SO-143 from the southern Hydrate Ridge, 12 originate from this area. The large circle marks the area with the strongest backscatter intensity.
3 knots and provides a 1500-m wide swath. The processed data image the distribution of carbonate crusts at the sediment surface and up to a subbottom depth of less than 1 m. The southwestern part of the image shows the carbonate structure Pinnacle (also marked in Fig. 1) with a surrounding depression, shown as black shadow. The north–south striking dark shadows in the area east of the center of the summit originate from the slope and cannot be interpreted as a signal from the sediment. Northeast of the pinnacle an area of alternating patches of high (white) and low (black) backscatter intensity are seen. The white areas can be interpreted as reflections from carbonate crusts in the uppermost sediments. The carbonate crusts in the surface sediments are most densely concentrated in an area centered around 44°34.3′N and 125°08.8′W (large circle in Fig. 2) and decrease slightly towards the northeast and the southeast. The large square, south of the area with the highest reflections, represents the region with the highest cold vent activities. The investigated site is located outside the area where massive crusts occur but inside the area of high seep activities.

The core has been sliced and squeezed for pore water immediately after recovery in a cold laboratory. Pore waters were analyzed on-board for dissolved ammonia, nitrate, phosphate and sulfide using standard photometric procedures (Gieskes et al., 1991; Grasshoff et al., 1983). Total alkalinity was determined by titration (Ivanenkov and Lyakhin, 1987) immediately after pore water separation. pH values were determined in wet sediment samples prior to squeezing. Problems may occur during these procedures by reoxidation (e.g. sulfide) or loss into the atmosphere (e.g. CO₂). Errors where minimized as far as possible by cooling and fast concentration measurements. The remaining pore waters were later analyzed in the shore-based laboratory for dissolved sulfate and calcium using ion-chromatography and optical ICP, respectively. Sub-samples for dissolved calcium analysis were acidified immediately after squeezing to prevent further CaCO₃ precipitation. Total carbon, organic carbon, organic nitrogen and sulfur were determined using a C/N element analyzer (Verado et al., 1990). Solid phase concentrations of Fe and Mn were determined after acid digestion using optical ICP. Samples for XRD analyses to determine the aragonite and calcite portion from the total carbonate concentrations were taken from the grinded bulk sediment that was also used for total carbonate determinations. Quartz reflections were used as internal standard to calibrate the analyses for the determination of pure calcite and Mg-calcite phases. For semi-quantitative estimations of the carbonate phases, we used the integrated peak areas of (104) calcite/Mg-calcite and (111) aragonite reflections (Greinert, 1999; Milliman, 1974). The vertical distribution of dissolved species in pore waters from core 114-1 and its sediment properties were used for this modelling study.

3. Model description

The measured concentrations in the upper 20 cm of the core SO143/114-1 (Table 1) provide the surface boundary conditions for the simulation of a 2-m long core with the numerical model C. CANDI (Luff et al., 2000). Using this dataset as the basis for the numerical simulation, we are able to determine the main processes and turnover rates at this site because the AOM layer, where more than 95% of the total turnover in the surface sediment of cold vent sites occurs (Luff and Wallmann, 2003) is fully resolved by this dataset. C. CANDI based on CANDI (Boudreau, 1996) describes biogeochemical processes at the investigated site over a period of 7000 years by calculating the transport and biogeochemical reactions of 21 species (O₂, NO₃⁻, MnO₂, Mn²⁺, Fe(OH)₃, Fe²⁺, SO₄²⁻, TPO₄, TNH₄, HCO₃⁻, CO₂, CO₃²⁻, CH₄, POC_reactive, POC_refractionary, H₂S, HS⁻, TBOH, Ca²⁺, CaCO₃(aragonite), CaCO₃(calcite)), which occur as dissolved phases in pore water or as solid phases in the sediment. Primary and secondary redox reactions, precipitation and dissolution reactions as well as thermodynamically controlled acid/base reactions are taken into account (Luff et al., 2000). Thermodynamic calculations in the model use the advancement approach as outlined in Luff et al. (2001).

The model includes the formation and dissolution of carbonate crusts and considers changing porosities evoked by the actual carbonate content (Luff et al., 2004). The porosity (φ) is calculated as a function of aragonite and calcite concentration. The total calcium carbonate concentration in weight percent (CaCO₃ wt.% in the considered layer is used to correct the
background porosity ($\varphi_{bg}$) prior to the onset of carbonate precipitation:

$$\varphi = \left(\varphi_{bg} - 0.01[CACO_3]\right) \frac{1}{(1 - 0.01[CACO_3])} \tag{3}$$

Pore water velocity ($v$) is calculated as a function of the minimum value of the porosity in the sediment column (min($\varphi$)) using the relation given by Carman-Kozeny and Blake-Kozeny, e.g. Boudreau (1997):

$$v = \left(w_L - v_0\frac{(\min(\varphi))^3}{(1 - \min(\varphi))^2}\right) \frac{(1 - \varphi_{bg(L)})^2}{\varphi_{bg(L)}^3} \frac{\varphi_L}{\varphi} \tag{4}$$

In this equation, $\varphi_{bg(L)}$ is the background porosity at the core base, $w_L$ represents the sedimentation rate, $\varphi_L$ the porosity and $v_0$ gives the advective fluid flow velocity at the bottom of the core prior to the onset of carbonate precipitation. This description of the fluid flow modified by porosity changes from carbonate precipitation and dissolution has already been used to determine the physical and biogeochemical constraints on crust forming (Luff et al., 2004).

Prescribed species concentrations and physical properties obtained from measurements are summarized in Table 2. The vertical resolution of the modelling grid was set to 6000 layers using a layer thickness of 0.33 mm, representing the upper 2 m of the sediment column. This resolution ensures a good representation of the steep concentration gradients (e.g. near the sediment surface and in the AOM zone) and allows the calculation of realistic fluxes between the sediment and the overlying bacterial mat. The length of 2 m for the simulated core is needed to keep the buried carbonates during the 7000 years of simulation far away from the bottom boundary of the column. This setting prevents artefacts like dissolution or precipitation there. As forcing we assume a constant pressure gradient at the bottom of the core. This constant driving force may not be a realistic assumption, but it is necessary to remove the effects of a changing pressure gradient so that the model can resolve the chemical effects.

A steady state version of this model was fitted to the available dataset to assimilate the main biogeochemical features at this station. At the same time, it delivers an initial dataset for non-steady state simulations considering carbonate precipitation and dissolution. For the non-steady state simulation, a time

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Table 1

Pore water and solid phase concentrations measured in the sediments of the investigated station SO143/114-1

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>TPO$_4$ (μmol l$^{-1}$)</th>
<th>TNH$_4$ (μmol l$^{-1}$)</th>
<th>TA (meq l$^{-1}$)</th>
<th>pH</th>
<th>SO$_4^{2-}$ (mmol l$^{-1}$)</th>
<th>TH$_2$S (mmol l$^{-1}$)</th>
<th>Ca$^{2+}$ (mmol l$^{-1}$)</th>
<th>$C_{org}$ (wt.%)</th>
<th>CaCO$_3$ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.24</td>
<td>4.81</td>
<td>2.46</td>
<td>7.66</td>
<td>26.8</td>
<td>0.11</td>
<td>10.4</td>
<td></td>
<td>34.9</td>
</tr>
<tr>
<td>0.25</td>
<td>198</td>
<td>405</td>
<td>13.2</td>
<td>8.27</td>
<td>22.3</td>
<td>0</td>
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<td>1.77</td>
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<tr>
<td>0.75</td>
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<td>22.2</td>
<td>8.36</td>
<td>12.1</td>
<td>1.1</td>
<td>8.9</td>
<td>1.68</td>
<td>27.6</td>
</tr>
<tr>
<td>1.5</td>
<td>1.69</td>
<td>101</td>
<td>27.7</td>
<td>8.32</td>
<td>4.4</td>
<td>11.7</td>
<td>6.24</td>
<td>1.39</td>
<td>30.3</td>
</tr>
<tr>
<td>2.5</td>
<td>61.4</td>
<td>70.7</td>
<td>31</td>
<td>8.42</td>
<td>2.4</td>
<td>13.3</td>
<td>5.64</td>
<td>1.35</td>
<td>16.1</td>
</tr>
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<td>3.5</td>
<td>70.5</td>
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<td>8.31</td>
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<td>13.8</td>
<td>5.58</td>
<td>1.64</td>
<td>6.4</td>
</tr>
<tr>
<td>4.5</td>
<td>61.3</td>
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<td>34.3</td>
<td>8.31</td>
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<td>14.6</td>
<td>5.13</td>
<td>1.62</td>
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<tr>
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<td>5.17</td>
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<td>1.55</td>
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<tr>
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<td>8.45</td>
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<td>14.4</td>
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<td>33.8</td>
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<td>15.3</td>
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<tr>
<td>14.5</td>
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<td>34.7</td>
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<td>19.7</td>
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<td>23.4</td>
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<td>8.55</td>
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<td>4.63</td>
<td>1.08</td>
<td>33.9</td>
</tr>
<tr>
<td>21.5</td>
<td>89</td>
<td>23.4</td>
<td>31.3</td>
<td>8.55</td>
<td>0</td>
<td>11.4</td>
<td>4.63</td>
<td>1.08</td>
<td>33.9</td>
</tr>
</tbody>
</table>

The underlined values are used to define the surface concentration for the simulations. Additionally, we defined the concentrations of oxygen, nitrate and methane to 0.0, at the surface. The conditions at the lower boundary are extrapolated from the measurements in 20 cm depth. Methane has been assumed to be in equilibrium with gas hydrates in 2 m depth resulting in a prescribed concentration of 68 mmol l$^{-1}$ (Zatsepina and Buffett, 1997).
step of one day for the overall simulation time of 7000 years was chosen to demonstrate the feedbacks in this system.

4. Results and discussion

Steady state simulations have been carried out with the numerical model to describe the biogeochemical situation in the upper 2 m of the sediments at station SO143/114-1. The results of this simulation are used for the non-steady state simulations as initial condition. The non-steady state simulations are performed to demonstrate the internal dynamics of the sediment column at this cold vent site over a period of 7000 years. All boundary values (e.g. species concentrations at the top and bottom, background porosity, kinetic constants, prescribed fluxes and more) are kept constant (Table 1 and 2), so that the dynamics in the sediment column are induced only by changes in porosity due to precipitation and dissolution of carbonates and by the feedbacks of the biogeochemical turnover and transport processes.

4.1. Pore water and sediments measurements

Measured concentrations of sulfate, total phosphate, total ammonium, sulfide, calcium, alkalinity and pH of core SO143/114-1 are used as boundary values for the simulations (Table 1, Fig. 3). The sediment at this site was covered with a thick bacterial mat (Beggiatoa sp.), providing evidence for active pore water flow and high AOM turnover. Jørgensen and Revsbech (1983) and Sweers et al. (1990) have been shown that Beggiatoa sp. can use both dissolved oxygen and nitrate as terminal electron acceptors for the oxidation of sulfide. Thus concentrations of both species are significantly reduced within the mat and therefore the concentrations at the sediment–bacterial mat interface have been set to zero for the numerical simulation (Luff and Wallmann, 2003; Sommer et al., 2002). Unfortunately, no methane measurements are available from that core. Therefore, assumptions for the boundary concentrations have been made. The concentration at the model bottom layer in 2 m depth are assumed in equilibrium with gas hydrates 68 mmol l\(^{-1}\) (Zatsepina and Buffett, 1997) while the bottom water concentrations are close to zero (Luff and Wallmann, 2003). The processes in the bacterial mat do not significantly affect the measured concentrations of the other solutes and thus the concentrations from the overlying bottom water are used for the upper boundary value in the model. The carbonate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Length of the simulated core</td>
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<td>m</td>
</tr>
<tr>
<td>Number of layers for simulation</td>
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<td></td>
</tr>
<tr>
<td>Temperature</td>
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<td>°C</td>
</tr>
<tr>
<td>Salinity</td>
<td>34.30</td>
<td>PSU</td>
</tr>
<tr>
<td>Pressure</td>
<td>78.0</td>
<td>Atm</td>
</tr>
<tr>
<td>Sedimentation rate</td>
<td>27.5 (\cdot) 10(^{-3})</td>
<td>cm(^{-1}) a(^{-1})</td>
</tr>
<tr>
<td>Background porosity at the sediment surface</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Background porosity in 2 m depth</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Porosity depth-attenuation coefficient</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Bioturbation coefficient at the surface (D_b(0))</td>
<td>0.01</td>
<td>cm(^2) a(^{-1})</td>
</tr>
<tr>
<td>Depth where (D_b) is zero</td>
<td>3.0</td>
<td>cm</td>
</tr>
<tr>
<td>Bioirrigation coefficient</td>
<td>0.0</td>
<td>a(^{-1})</td>
</tr>
<tr>
<td>Start fluid flow velocity at the bottom</td>
<td>30</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td>Flux of labile fraction POC to the sediment</td>
<td>55</td>
<td>\mu mol cm(^{-2}) a(^{-1})</td>
</tr>
<tr>
<td>Flux of refractory fraction POC to the sediment</td>
<td>30</td>
<td>\mu mol cm(^{-2}) a(^{-1})</td>
</tr>
<tr>
<td>Calcium carbonate flux to the sediment</td>
<td>0</td>
<td>\mu mol cm(^{-2}) a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of the labile fraction of POC</td>
<td>0.2</td>
<td>a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of the refractory fraction of POC</td>
<td>3.0 (\cdot) 10(^{-4})</td>
<td>a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of aragonite dissolution</td>
<td>0.5</td>
<td>a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of aragonite precipitation</td>
<td>50</td>
<td>mmol cm(^{-3}) a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of calcite dissolution</td>
<td>0.5</td>
<td>a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of calcite precipitation</td>
<td>5</td>
<td>mmol cm(^{-3}) a(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant of AOM</td>
<td>20</td>
<td>cm(^3) mmol(^{-1}) a(^{-1})</td>
</tr>
</tbody>
</table>

The boundary concentrations are summarized in Table 1. Prescribed fluxes of POC at the sediment surface and kinetic constants have been determined by tuning the numerical model to measured data from Hydrate Ridge (Luff and Wallmann, 2003).
contents of the investigated core vary between 8 and 35 wt.% in the upper 20 cm (Fig. 4). This concentration is high enough for XRD analyses to determine the aragonite and calcite portion from the total carbonate concentrations. In this core aragonite represents the most abundant carbonate species in the upper 20 cm with maximal concentrations in the two distinctive layers of over 20 wt.%. The total carbonate concentration exceeds values of over 30 wt.% there, reaching a minimum of 7 wt.% in about 4.5 cm. This distribution illustrates the existence of alternate layers of cemented and non-cemented sediments with one well-developed layer at the surface and one around 20 cm depth. The measured background porosity values of 0.76 at the top and 0.66 at the bottom of the core (Table 2) represent typical values compared with other sampling sites of Hydrate Ridge (Luff and Wallmann, 2003).

This dataset from site 114-1 allows for a model parameter variation to determine unknown process variables (e.g. particular organic carbon (POC) flux to the sediment surface, advective fluid flow velocity, bioturbation coefficient and a number of kinetic constants). The measured and simulated pore water concentrations of the most important species $SO_4^{2-}$, total dissolved sulfide (TH2S=HS$+H_2S$), total alkalinity (TA=$HCO_3^-+2CO_3^{2-}+HS^-+OH^-+BOH_4^-H^+$) and $Ca^{2+}$ at a cold seep site are shown in Fig. 3.

4.2. Steady state simulations

The simulated concentration profiles of core 114-1 are also presented in Fig. 3 for the upper 40 cm. The measured profiles do not show any significant concentration gradients below 10 cm. To achieve bottom boundary values for the simulation of the 2-m core, the measured values have been extrapolated. Fig. 3 shows that the model is able to reproduce the biogeochemical situation at this site. The rate constant of AOM has been determined from the $SO_4^{2-}$,
alkalinity and the TH$_2$S profiles by parameter variations. The value of 20 cm$^3$ mmol$^{-1}$ a$^{-1}$ falls into the range of values found in other sedimentary environments (0–10,000 cm$^3$ mmol$^{-1}$ a$^{-1}$, Iversen and Jørgensen, 1985; Van Cappellen and Wang, 1996). A higher value of this constant would increase the concentration of alkalinity and TH$_2$S and decrease the concentration of SO$_4^{2-}$ in and above the AOM zone significantly. The vertically integrated AOM rate of 1075 µmol cm$^{-2}$ a$^{-1}$ demonstrates the dominance of anaerobic oxidation of methane in this environment. The maximum of AOM occurs in a depth of about 1.8 cm and decreases to zero in about 5 cm depth. This rate represents 95% of the total turnover in the upper 20 cm.

The high advective fluid flow velocity of 30 cm a$^{-1}$ delivers about 1345 µmol cm$^{-2}$ a$^{-1}$ methane from deeper sediment horizons into the AOM zone. Not all of this ascending methane is oxidized within the sediment column. Thus, a methane flux of 283 µmol cm$^{-2}$ a$^{-1}$ into the water column has been found with the model under the prevailing conditions. Disregarding carbonate precipitation and dissolution processes, the second relevant biogeochemical rate is organic matter degradation using sulfate as electron acceptor (53 µmol cm$^{-2}$ a$^{-1}$). This is followed by methanogenesis reaching a rate of about 13.5 µmol cm$^{-2}$ a$^{-1}$. All other considered secondary redox reactions reach in sum a vertical integrated rate of about 3.5 µmol cm$^{-2}$ a$^{-1}$.

The physical parameters that most influence the biogeochemical processes at cold vent sites are the vertical fluid flow velocity and the sediment porosity. Both regulate the amount of methane and sulfide reaching the upper most part of the sediment column and the amount of sulfate that enters the sediment column. The balance of these parameters determines the depth of AOM, which is of special concern for carbonate precipitation. The closer to the sediment surface it is, the larger is the loss of dissolved inorganic carbon (TCO$_2$=CO$_2$+HCO$_3^-$+CO$_3^{2-}$) to the bottom water and therewith the lower is the degree of oversaturation with respect to aragonite and calcite. A deep AOM layer is an indicator for low AOM that releases low amounts of TCO$_2$ into the pore water and also keeps the degree of oversaturation with respect to aragonite and calcite low. The fluid flow velocity determined with the model (30 cm a$^{-1}$) falls into the

![Fig. 4. Concentrations of aragonite and calcite and the total amount of calcium carbonate ($\Sigma$CaCO$_3$) as determined by XRD analyses of sediments in core 114-1. The total amount of calcite is the sum of both calcite and Mg-calcite phases.](image-url)
range of 30–100 cm a\(^{-1}\) measured by Torres et al. (2002) and 10–250 cm a\(^{-1}\) measured by Tryon et al. (2002) at bacterial mat sites on Hydrate Ridge.

In comparison to a previously investigated core, SO143/55-2, also located at the southern summit of Hydrate Ridge and also covered with a bacterial mat (Luff and Wallmann, 2003), the advective fluid flow is faster in the core investigated in this study but the reaction velocity constant of AOM is lower. A similar value of the vertical integrated AOM turnover rate (925 \(\mu\)mol cm\(^{-2}\) a\(^{-1}\)) has been previously found by Luff and Wallmann (2003) but at that station all methane was oxidized in the sediment column. This comparison depicts that even at sites covered with bacterial mats, high variabilities in fluid flow, turnover and exchange flux with the bottom water can be found.

4.3. Non-steady state simulations

The non-steady state simulation illustrates the evolution of authigenic carbonate distribution in the sediment column and the feedbacks in the biogeochemical activities due to porosity changes over a simulation period of 7000 years. The simulation uses the concentration profiles derived from the steady state simulations as initial condition as well as the kinetic constants that have been found by parameter tuning. Additionally, values of the kinetic constants for aragonite and calcite precipitation and dissolution have been defined (Table 2). It is assumed that the bottom water at the upper boundary of the model column is slightly undersaturated with respect to aragonite and oversaturated with respect to calcite (pH 7.66, TCO\(_2\)=2.2 mmol cm\(^{-2}\) a\(^{-1}\)). Within the sediment, the biogeochemical processes (mainly AOM, as shown above) and the transport processes immediately control the saturation state. Thus, the system in the upper sediment column is significantly oversaturated with respect to both carbonate phases. At the bottom of the core, the system is defined as undersaturated with respect to both species (pH 6.8, TCO\(_2\)=28.0 mmol cm\(^{-2}\) a\(^{-1}\)). However, the slow dissolution of buried carbonates maintains saturation with respect to calcite in the lower section of the model column. Thus, the simulation of the carbonate system apart from the boundaries is not significantly affected by the prescribed values. The observed changes in porosity, fluid velocity, fluxes out of the sediment, vertical integrated turnover rates and other sedimentary properties only originate from carbonate precipitation and dissolution. Cementation of the pore space by authigenic carbonates has a significant influence on the physical properties of the sediment and the biogeochemical turnover on that timescale.

Fig. 5 shows the temporal development of aragonite (A), calcite (B) and the resulting porosity (C) in the simulated sediment column over 7000 years. High concentrations of HCO\(_3^-\) and HS\(^-\) in the upper sediment column derived from AOM (Eq. (1)) supersaturate the pore water with respect to calcium carbonate. Hence, aragonite and calcite precipitate in the AOM zone consuming HCO\(_3^-\) and downward diffusing calcium from seawater (Eq. (2)). At the beginning of the simulation, precipitation of aragonite and calcite immediately start near the sediment surface (Fig. 5). After about 100 years, aragonite concentration exceeds 10 wt.%, whereas calcite only reaches concentrations of about 2 wt.%. Due to the assumed constant sedimentation rate of 27.5 \(\times\) 10\(^{-3}\) cm a\(^{-1}\) (Hempel, 1995), the formed carbonates are buried deeper into the sediment. After about 600 years, aragonite reaches its highest concentration of 36.6 wt.% in a very thin layer between 20 and 25 cm depth (Fig. 5A). Comparable aragonite layers of 0.5–2 cm thickness have been found by Bohmann et al. (1998) in sediment samples recovered from the southern summit of Hydrate Ridge. The calculations of the fluid flow velocity (Eq. (4)) takes into account that fluids have to bypass this region with low porosity. Therefore, the cementation of the upper sediment column by the thin aragonite layer reduces the fluid flow velocities in the simulated sediment column from an initial value of 30 to about 2 cm a\(^{-1}\).

At the same time, the supply of methane from below is reduced and the AOM rate decreases significantly from values of over 1100 to about 100 \(\mu\)mol cm\(^{-2}\) a\(^{-1}\) (Fig. 6A). As a consequence, dissolution of aragonite starts as less bicarbonate is supplied to the pore water via AOM (Fig. 6B). Initially, aragonite precipitation dominates dissolution, but after about 600 years dissolution becomes the most important process for the aragonite distribution. At this time, porosity reaches its minimum value of 0.38 in the depth of the centre of the aragonite layer.
In the following 1200 years, the vertically integrated dissolution of aragonite exceeds precipitation (Fig. 6B). Lower AOM turnover caused by the restricted transport of methane from below results in a lower alkalinity concentration in the upper sediment column and aragonite precipitation reaches a minimum (years 600–1300 in Fig. 6B). Because calcite is the more stable calcium carbonate mineral (Burton, 1993), the metastable aragonite recrystallizes into calcite. This process occurs in sediment depths below 25–30 cm where increased concentrations of calcite can be found (Fig. 5B). Between years 600 and 1300, the advective fluid flow out of the sediment is reduced to a value around 2 cm a\(^{-1}\) by this cementation. When the initial aragonite layer becomes thinner (years 1700–2000), the flow increases slowly to more than 4 cm a\(^{-1}\). This higher velocity allows again for more upward transport of methane, increase in AOM turnover (Fig. 6A) and induces again precipitation of aragonite (Fig. 6B) shortly below the sediment surface (Fig. 5A). While aragonite is limited to this very thin layer during the first 2000 years, calcite occurs in a broader layer that is buried constantly deeper into the sediment (Fig. 5B). Indicated by the coeval decrease in aragonite dissolution (Fig. 6B, dashed line) and calcite precipitation (Fig. 6C, solid line), it can be

Fig. 5. Concentration of aragonite and calcite in wt.% and the resulting porosity in the upper 2 m simulating a sediment below a bacterial mat at a cold vent site on Hydrate Ridge for 7000 years.
assumed that calcite precipitation is strongly connected to aragonite dissolution. Thus, a major part of bicarbonate and calcium needed for calcite precipitation originates from aragonite dissolution. AOM evokes mainly precipitation of aragonite near the sediment surface while the calcite portion increases with depth. From year 1900 to the end of the simulation, a constant aragonite layer with concentrations of up to 20 wt.% between 0 and 30 cm depths can be observed (Fig. 5A). This implies precipitation in the AOM layer and dissolution at the base of the aragonite layer, which is more or less equal to precipitation at the top (Fig. 6B).

Surprisingly, rates of AOM and carbonate precipitation do not simply decay over time but their temporal evolution shows the pattern of a dampened oscillation (Fig. 6). Thus, AOM and aragonite precipitation rates reach progressively smaller maxima at years 0, 2000, 4300 and 7000. The period between two maxima increases with time indicating also a decrease in the frequency of the oscillation. Calcite precipitation and aragonite dissolution rates show the same behaviour. These oscillations are caused by the non-linear dynamics of the sedimentary system. Prior to carbonate precipitation fluid flow, AOM and aragonite precipitation proceed at high rates. Permeability and fluid flow are diminished by authigenic aragonite clogging pore space of surface sediments. Consequently, methane delivery from below, AOM and aragonite precipitation are suppressed, whereas calcite is precipitated continuously fuelled also by carbonate released during aragonite dissolution. Aragonite dissolution prevails precipitation until the crust formed at shallow depth is almost completely dissolved so that fluid flow is re-established. The new maximum in AOM and aragonite precipitation attained after 2000 years is smaller than the initial value because fluid flow and methane delivery are reduced by the ongoing calcite precipitation. The new aragonite layer is broadened and has lower carbonate contents so that permeability, fluid flow and AOM are not strongly reduced but attain a moderate level. The oscillation is induced by slow formation and dissolution of aragonite in surface sediments while the dampening and the decrease in frequency is probably caused by the ongoing calcite

![Figure 6. Simulation results showing changing rates of anaerobic oxidation of methane (A), aragonite precipitation and dissolution (B), and calcite precipitation and dissolution (C) over a period of 7000 years in μmol cm$^{-2}$ a$^{-1}$.](image_url)
formation. Similar oscillations have been observed in other geochemical systems where the transport of dissolved species is affected by mineral precipitation and dissolution processes (Böhm et al., 2003; L’Heur-eux and Jamtveit, 2002).

Sulfate penetration depths in the upper part of the sediment and methane concentration in the lower part are shown in Fig. 7 over the simulation time. The AOM layer is clearly visible as the grey/white area with changing thickness during the simulation, characterized by low concentrations of both species. This zone is located close to the sediment surface when AOM turnover rates are high and becomes deeper and broader during the period of low AOM turnover between years 500 and 1500 because of the reduced advective transport. During this time, molecular diffusion is the major process responsible for the species distribution. After about 2500 years, the temporal changes in the sediment system become smaller, the fluid flow velocity increases, the concentration gradients become steeper and therefore the AOM layer thinner again. From Fig. 7, it can be seen that the carbonate occurrences in the deeper sediment column have large influence on biogeochemical and transport processes occurring near the sediment surface due to the porosity reduction. Similar control of physical properties in deeper sediment strata on sedimentary processes above has been reported by Rudnicki et al. (2001).

In our investigated core, most of precipitation takes place above 50 cm, below that depth carbonates stay stable or are dissolved slowly. Main process for the carbonates below 50 cm depth is the burial that is responsible for the export into deeper sediment layers (about 50 μmol C cm⁻² a⁻¹). Naehr et al. (2000) also found that authigenic carbonates recovered from sediment depths up to 10 to 30 m at ODP Site 996 likely formed at or near the sediment surface. Only mass transport of dissolved species and alteration take place in the deeper sediments.

Fig. 8 shows the carbonate concentrations (solid line) and the aragonite concentrations (dotted line) of the whole sediment column every 1000 years predicted by the simulations. This figure mirrors the carbonate contents of the sediment column shown in Fig. 5 in a more common view at seven definite times only. Apart from the beginning, where the aragonite crust dominated the system, the concentrations of calcium carbonate reach up to 33 wt.%, comparable with the measurements. In both, the measurements (Fig. 4) and the simulation results (Fig. 8), distinct carbonate layers in the sediment column can be observed. These layers with higher carbonate concentrations are surrounded by layers with low carbonate contents. These findings are a common feature in sediments of Hydrate Ridge, where the intermediate layers mainly contain soft clay with dispersed carbonate precipitates (Pfannkuche et al., 2002). Fig. 8G shows that at the end of the simulation the entire upper meter of sediment is more or less cemented. The variation in carbonate content within this zone is about 21–27 wt.%. The measurements of the carbonate concentrations in the surface sediments of core 114-1 shows two distinct carbonate layers (Fig. 4). These patterns are also resolved by the simulation, showing a similar structure, a little bit deeper in the column after about 1500–2000 years (Figs. 5 and 8B). From the sidescan sonar reflections (Fig. 2), it can be seen that the area north of site 114-1 already contains dense carbonate crusts in the upper 50 cm to 1 m (large circle). Thus, the carbonate distribution found in core 114-1 (Fig. 4) seems to be an intermediate state of crust formation. Formerly active cold seep areas are already cemented by the high biogeochemical turnover that causes carbonate precipitation and thus, the active sites are displaced southwards. Thus, this ongoing process will form a solid carbonate crust at site 114-1 in the future, comparable to the situation predicted by the model and already found in the encircled area.
Carbonate cementation of the sediment also affects the exchange of dissolved species between sediment and bottom water (Fig. 9). At the beginning of the simulation, without any carbonate occurrences in the sediment, the fluxes have their highest values. \( \text{SO}_4^{2-} \) is diffusing rapidly (about 1100 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \)) into the sediment to replace the consumed amount and \( \text{TCO}_2 \) and \( \text{TH}_2\text{S} \), the products of AOM leave the sediment due to the high concentrations in the upper sediment layers. AOM dominates the fluxes of \( \text{SO}_4^{2-} \), \( \text{TCO}_2 \) and \( \text{TH}_2\text{S} \) during the total simulation time. Sulfate reduction, methanogeneses and carbonate precipitation also have influences on these fluxes, but the turnover is small compared to AOM. The slightly higher \( \text{TCO}_2 \) flux out of the sediment originates from the higher \( \text{TCO}_2 \) flux in the sediment column from below. Not all of the methane can be oxidized in the beginning of the simulation; thus, a flux of about 283 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \) out of the sediment can be observed. Subsequently, fluxes are diminished by cementation of pore space and after less than 250 years, the methane flux out of the sediment is stopped completely (<2 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \)). The lower amount of methane transported from below can be oxidized completely within the sediment column now. The lower AOM rates that directly mirror the reduced transport processes are mainly responsible for the decrease in \( \text{SO}_4^{2-} \), \( \text{TCO}_2 \) and \( \text{TH}_2\text{S} \) fluxes. All fluxes reach their minimum value during the emplacement of the first prominent aragonite crust. The cyclic variation with maximal fluxes during years 2000, 4300 and 7000 corresponds to the lower aragonite concentrations near the sediment surface.

The total carbon turnover in the simulated sediment column reaches values of more than 1700 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \) at the beginning of the simulation. A high portion of \( \text{TCO}_2 \), mostly in form of \( \text{HCO}_3^- \), is exported into the bottom water. This high amount of \( \text{HCO}_3^- \) in the pore water is needed to keep the system constantly oversaturated with respect to calcium carbonate. After the first aragonite layer has been formed, the total carbon turnover decreases to values of about 200 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \) and attains values between 500 and 750 \( \mu \text{mol cm}^{-2} \text{a}^{-1} \) thereafter, also mirrored in the \( \text{TCO}_2 \) fluxes (Fig. 9). Despite these high rates the overall fixation of carbon in carbonates (aragonite and calcite) is only about 3% during the first 100 years reaching values of about 11% after the
crust is formed (year 400) and decreases to values between 10% and 8.5% of the total carbon turnover thereafter.

5. Conclusions

In surface sediments affected by fluid venting, authigenic carbonates often occur in distinct layers, surrounded by layers with lower carbonate concentrations. Crust formation in these sediments may be caused by external changes in the prevailing pressure gradient or by the dynamics of the system itself. Both factors result in changes in the advection velocity, which has a huge influence on crust forming processes. The simulations clearly depict that the investigated system itself is able to produce distinct carbonate layers even under constant forcing and also demonstrates that this system remains far away from steady state over periods of several thousand years. Hence, long-term changes in the abundance of authigenic carbonates and fluid flow observed at Hydrate Ridge (Teichert et al., 2003) are not necessarily caused by external forcing. While the constant pressure gradient in 2-m depth used as driving force for the simulation may not be a realistic assumption, it is necessary to remove the effects of changing pressure gradients so that the chemical feedbacks may be resolved. In reality, the system will be even more complex (Torres et al., 2002; Tryon and Brown, 2001).

Vertical fluid flow is strongly diminished by the formation of carbonate crusts. As a consequence, fluids migrate laterally to be expelled at other vent sites not yet affected by crust formation until fluid flow is again diminished by authigenic carbonates clogging the pore space of surface sediments. From the side scan sonar data, it seems that core 114-1 shows an intermediate state of crust forming (Fig. 2). The future of this site can be seen in the prediction of the model simulations in Fig. 8G. It can be interpreted that the area characterized by strong crust occurrences is moving southward today. The cementation of the surface sediments causes a movement of the active vent area, leaving solid stable crusts behind. The active area shown in the big square in Fig. 2 is probably formed by lateral fluid flow below impermeable surface sediment layers in the north. Such crust formation in the subsurface may also contribute to the focussing of fluid flow and the strong lateral variability in flow rates observed at Hydrate Ridge (Greinert et al., 2001; Sahling et al., 2002; Suess et al., 2001; Tréhu et al., 1999; Tryon and Brown, 2001).

Methane fluxes into the bottom water are strongly enhanced by the focussing of fluid flow because methane can escape AOM only at high fluid flow rates (Luff and Wallmann, 2003, Luff et al., 2004). Hence, crust formation may ultimately enhance methane fluxes into the water column. Moreover, at these single spots, carbonate precipitation can occur above the sediment surface and therewith form the nucleus of huge carbonate structures observed at Hydrate Ridge (Fig. 1).

Due to the slow changes of the geochemical conditions evoked by crust formation, chemoautotrophic fauna can react on the changes in the environment. Locations or periods with higher fluid flow velocities...
and shallow sulfate penetration provide the habitat for bacterial mats. Changes in the carbonate concentrations in the underlying sediment may increase sulfate penetration and decrease upward sulfide flux. This may attract other cold vent fauna like *Calyptogena* sp. or *Acharax* sp. replacing the bacterial mats as long as fluid flow delivers enough but not too much sulfide. Buried mussel shells at sites currently covered with bacterial mats (Pfannkuche et al., 2002) are a good indicator for long-term changes at seep sites.

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