Repeated occurrences of methanogenic zones, diagenetic dolomite formation and linked silicate alteration in southern Bering Sea sediments (Bowers Ridge, IODP Exp. 323 Site U1341)

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ABSTRACT

Diagenetic precipitates, such as dolomite, and the chemistry of residual deeply buried porewater often represent the only traces of past biogeochemical activity in marine sediments. A 600 m thick sedimentary section, recently drilled at Integrated Ocean Drilling Program (IODP) Site U1341 on Bowers Ridge (southern Bering Sea), provides insight into such a 4.3 Ma old paleo-diagenetic archive. Hard-lithified calcite–dolomite layers, and laminae of disseminated carbonate, were recovered in diatom-rich sediments over a depth range of 400 m. Carbon isotope values of the diagenetic carbonates between −16.6 and −14.4‰ (VPDB) and strontium isotope ratios of dolomites close to past seawater values suggest carbonate precipitation induced by the production of dissolved inorganic carbon (DIC) during elevated rates of organic carbon mineralization, primarily via sulfate reduction, at shallow sediment depth below the paleo-seafloor. Diagenetic carbonates at 280–440 m below seafloor were likely also produced by the intermittent onset of sulfate reduction coupled to the anaerobic oxidation of methane (AOM) at sulfate–methane transition zones (SMTZ). These microbially mediated processes do not occur in the sediment at this site at present but were likely connected to the presence of a methanogenic zone at 2.58–2.51 Ma. A minimum in sulfate concentrations in modern porewaters and low sedimentary Ba/Al ratios resulting from former sulfate depletion are reminiscent of the presence of this large methanogenic zone. The minimum in sulfate concentrations is reflected in a minimum in magnesium concentrations, less radiogenic strontium and isotopically light calcium in the porewater. It is proposed that magnesium was removed from the porewater during carbonate precipitation and volcanic ash alteration which occurred in the former methanogenic zone and also released strontium with a less radiogenic isotope ratio and isotopically light calcium into the porewater. The isotopic composition of porewater calcium was also influenced by ammonium–calcium exchange on clay minerals and carbonate recrystallization. Our study elucidates the response of porewater element concentrations and isotopic profiles interlinked with the formation of diagenetic carbonates to changes in the deposition of organic carbon in sediments of deeper water sites (> 2000 m water depth) over prolonged timescales. It shows that variations in biogeochemical processes in response to changes in oceanographic conditions and a dynamic subseafloor biogeochemical zonation have to also be taken into account at these deep water sites for a global assessment of organic carbon burial fluxes and remineralization.

1. Introduction

Biogeochemical processes in deeply buried marine sediments, mediated by a large and diverse microbial community, strongly modify the composition of porewaters and solid-phase constituents (D’Hondt et al., 2002, 2004; Teske and Sørensen, 2008). These processes facilitate important transformations of the sedimentary carbon cycle that ultimately control the amount of dissolved inorganic carbon (DIC) that is released...
back into the ocean and the fraction of carbon that is buried in the sedimentary record over longer time scales (Schrag et al., 2013).

Organic carbon reaching the seafloor is degraded via fermentation and hydrolysis and organic intermediates are oxidized by terminal electron acceptor processes (TEAP) in the sequence of decreasing redox potential (Froelich et al., 1979). The main TEAP in anoxic marine sediments is sulfate reduction (Fenchel and Jørgensen, 1977; Emerson et al. 1980; Jørgensen, 1982, 2006). Below the depth of porewater sulfate depletion, organic matter is degraded by hydrogenotrophic and acetoclastic methanogenesis (Martens and Berner, 1974; Sansone and Martens, 1981; Ferry, 1992; Whiticar et al., 1986; Whiticar, 1999). Methane produced here is mostly oxidized via anaerobic oxidation of methane (AOM) coupled to sulfate reduction in the sulfate–methane transition zone (SMTZ) (Hoehler et al., 1994; Boetius et al., 2000; Valentine and Reeburgh, 2000), and typically results in the precipitation of diagenetic carbonate minerals. Bicarbonate produced during TEAPs such as organoclastic sulfate reduction links their formation to a particular diagenetic setting, i.e., the SMTZ (Baker and Burns, 1985; McKenzie, 1982; Baker and Burns, 1985; Compton and Siever, 1986; Burns et al., 1988). They were also discovered in recent marine sediments at several Deep-Sea Drilling Program (DSDP) sites (Pischiotto and Mahoney, 1981; Kelts and McKenzie, 1982; Baker and Burns, 1985). Dolomite found in hemipelagic sediments has a wide range of carbon isotopic values; δ13C links their formation to a particular diagenetic setting, i.e., the sulfate reduction or methanogenic zones (Kelts and McKenzie, 1982; Mazzullo, 2000). These zones, however, often span very broad intervals of several tens to hundreds of meters in marine sediments. In recent studies the role of AOM as a driver for authigenic dolomite formation was emphasized (Raiswell, 1988; Moore et al., 2004; Meister et al., 2007; Ussler and Paull, 2008). The occurrence and isotopic composition of diagenetic dolomites were therefore suggested to represent a specific signature to reconstruct past seafloor biogeochemical conditions, in particular at the SMTZ (Rodriguez et al., 2000; Malone et al., 2002; Meister et al., 2007, 2008). So far, an extended record of multiple generations of carbonate diagenesis in seafloor sediments was only recovered from ODP Leg 201 Site 1229 on the Peru Margin (Thornburg and Suess, 1990; Meister et al., 2006, 2007).

In conjunction with dolomite formation, porewater DIC, calcium and magnesium concentration profiles often show distinct excursions at microbial interfaces in marine sediments, particularly at the SMTZ (Baker and Burns, 1985; Moore et al., 2004; Ussler and Paull, 2008; Wehrmann et al., 2011). These studies suggest that dolomite formation is linked to the prevailing microbially mediated diagenetic processes and explain the occurrence of confined authigenic dolomite layers in otherwise unaltered siliciclastic sediments. They indicate that authigenic carbonate layers in deeply buried sediments may provide information on the paleo-diagenetic setting, i.e., past biogeochemical processes that may not be traceable in modern porewater profiles. For example, changes in the sedimentary burial of organic carbon linked to variations in surface water productivity and sedimentation rates, may not only be imprinted in the solid-phase total organic carbon (TOC) composition and paleoproductivity indicators such as the biogenic opal content, but also in temporary variations of carbonate diagenesis (Malone et al., 2002; Meister et al., 2007).

Despite detailed studies of subseafloor biogeochemistry, we are still far from understanding how oceanographic conditions control the onset and decline of diagenetic interfaces, for example methanogenic zones, on a global scale and over geological time. Tracing episodic changes in subsurface biogeochemical conditions is essential for a global estimate of carbon burial and remineralization rates (Schrag et al., 2013). So far, studies have used different approaches at specific locations to document the history of the SMTZ based on diagenetic minerals, such as carbonates (see above), iron sulfides (Riedinger et al., 2005; März et al., 2008) and diagenetic barite (Torres et al., 1996; Dickens, 2001). Also reaction-transport modeling (Adler et al., 2000; Hensen et al., 2003; Arndt et al., 2006, 2009; Wehrmann et al., 2013) and lipid biomarker records (e.g., Bian et al., 2001; Birgel and Peckmann, 2008) have proven to be useful tools to decipher the biogeochemical history of marine sediment sites.

Here we report new findings on dolomite layers and associated porewater element profiles over a 400 m thick interval within a 620 m thick sedimentary sequence drilled at a water depth of 2177 m on the western margin of Bowers Ridge in the southern Bering Sea (Integrated Ocean Drilling Program (IODP) Expedition 323, Site U1341). Its location in the marginal sea of the North Pacific and its excellent stratigraphic resolution make this site ideal to study the link between subseafloor biogeochemical activity and paleoceanographic conditions (Takahashi et al., 2009).

During the past 4.3 Ma the accumulation rates of organic matter and biogenic opal at Site U1341 have generally decreased, and are inferred to reflect a long-term reduction of primary productivity (Aiello and Ravelo, 2012; März et al., 2013). These trends were punctuated by excursions to much higher accumulation rates of opal and increased delivery of reactive organic carbon, particularly at 2.58–2.51 Ma (353–373 mbsf; März et al., 2013; Wehrmann et al., 2013). Previous studies propose that this event led to the onset of methanogenesis, the development of sulfate–methane transition zones for a time period on the order of 103 yrs, and the subsequent decline of these processes (Wehrmann et al., 2013). Due to the high burial rates at Site U1341, this event is preserved in the porewater sulfate profile, associated sulfur isotope composition of sulfate and low solid-phase Ba/Al ratios at 304–435 mbsf (Fig. 2A; März et al., 2013; Wehrmann et al., 2013).

Authigenic carbonate layers and deeply buried porewater signals in the sediment offer the opportunity to gain additional insight into paleo-diagenetic processes, particularly to resolve shorter or less pronounced changes at this site before and after the event at 2.58 Ma. We investigate the distribution, mineralogy, and carbon and strontium isotope compositions of authigenic carbonate layers. Additionally, we analyze the present-day porewater concentrations and isotope compositions of key ions such as calcium, magnesium and strontium affected by microbially mediated diagenetic processes and carbonate formation. The goal is to evaluate carbonate diagenesis in relation to the prevailing past and present biogeochemical processes in the sediment and to shed light on additional processes controlled by changes in organic carbon turnover rates and the occurrence of intermittent methanogenesis.

2. Study area

2.1. Oceanographic and geological background

Site U1341 is located at a water depth of 2177 m on the western flank of the central Bowers Ridge in a depression 40 km west of the ridge crest (Fig. 1). Bowers Ridge is approximately 800 km long and 200 km wide, and rises more than 3500 m above the Bering Sea abyssal plain at the connection to the Aleutian Arc massif (Fig. 1). The ridge slope is draped by up to 2 km thick diatomaceous sediments and mudstones on both flanks (Ben-Avraham and Cooper, 1981; Wanke et al., 2012). The ridge is composed of subalkaline basalts, basaltic andesites and alkaline basaltic trachyandesites, which occur as volcanic conglomerates and volcanic
sandstones (Kawabata et al., 2011; Wanke et al., 2012). Bowers Ridge formed as a result of island arc volcanism that ceased in the Oligocene (Wanke et al., 2012). Volcanic rocks with an age of 26–32 Ma were dredged from Bowers Ridge suggesting that the ridge developed after the formation of the Aleutian Arc and the initiation of subduction along the Aleutian Trench (Jicha et al., 2006; Wanke et al., 2012). The subsurface geothermal gradient (67.8 °C/km; Expedition 323 Scientists, 2010) is more than double typical oceanic crust values, suggesting residual volcanic heat at depth. On the northern and eastern side, Bowers Ridge is framed by a subduction zone with a sediment-buried trench at the ridge’s base (Cooper et al., 1981; Wanke et al., 2012). The western side of the ridge forms a passive margin, which formed during opening of the Bowers Backarc Basin in the Cenozoic (Cooper et al., 1992).

Surface waters along the eastern Bering Sea shelf break, known as the Bering Sea Green Belt, are among the world’s most productive ocean regions (Kinder and Coachman, 1978; Springer et al., 1996; Okkonen et al., 2004). In contrast, the open marine domain of the Bering Sea is regarded as a High-Nutrient-Low-Chlorophyll (HNLC) region (Banse and English, 1999; Leblanc et al., 2005; Tyrrell et al., 2005; Aguilar-Islas et al., 2007; Sambrotto et al., 2008; Brown et al., 2011). Diatoms such as *Neodenticula seminae* represent the dominant primary producers in the Bering Sea and contribute to a large flux of biogenic opal to Bering Sea sediments (Takahashi, 1999, 2005, Takahashi et al., 2002).

Paleo-environmental investigations of Site U1341 on Bowers Ridge suggest overall higher opal accumulation rates driven by higher diatom productivity during the Pliocene and a long-term trend to lower opal accumulation rates during the Pleistocene, particularly after the onset of Northern Hemisphere Glaciation (NHG) (Aiello and Ravelo, 2012; März et al., 2013). Excursions in opal accumulation rates to higher values at around 2.58–2.51 Ma were driven by the onset of strong water column stratiﬁcation in the North Paciﬁc, which caused the leakage of nutrient-rich deep/intermediate North Paciﬁc waters into the Bering Sea via the Kamchatka Strait.

2.2. Lithostratigraphy

Diatom ooze with a varying sponge spicule component and diatom-bearing mud are the two main sediment types at Site U1341 (Fig. 2A). Sediments also contain minor amounts of volcanic ash, foraminifers, and calcareous nannofossils. Silt-sized feldspar, quartz, clay, mica, and rock fragments are the most abundant terrigenous grain types at this site (Expedition 323 Scientists, 2010). Discrete ash layers are frequently found in Bering Sea sediments; at Site U1341 they can be found throughout the sediment column. They are black, light gray, reddish gray or light gray and occur as distinct thin layers or intermixed with biogenic and silicilastic sediment as a result of bioturbation (Expedition 323 Scientists, 2010). Carbonate-rich intervals comprising disseminated micrometer-scale micrite as well as distinct semi-lithiﬁed to lithiﬁed dolostone layers were observed in U1341 sediments below 140 mbsf (Fig. 2A). The background total inorganic carbon (TIC) content of U1341 sediments averages 0.17 ± 0.2 wt% (Fig. 2C). A few outliers from this distribution may be due to the analysis of layers containing disseminated diagenetic carbonates. Total organic carbon contents (TOC) of background samples from this site average 0.5 ± 0.2 wt% (Fig. 2C).

2.3. Shipboard porewater geochemistry

Sulfate concentrations at Site U1341 decrease from seawater-like values at the sediment surface to values around 23.4 mM in
At greater depths, sulfate concentration values decrease further to a minimum value of 11.9 mM at 448 mbsf. Sulfate concentrations then increase to a value of 17 mM at 600 mbsf (Fig. 3A) (Expedition 323 Scientists, 2011b). Chloride concentrations decrease slightly from values around 570 mM in the uppermost sediment section to values around 550 mM in the deepest section of the sediment (Fig. 3A).

In the uppermost 160 m porewater magnesium concentrations are slightly above seawater values at around 56 mM. The concentration of porewater magnesium displays a trend similar to the observed sulfate concentrations in the deeper sediment sections (Fig. 3B). Below 160 mbsf magnesium concentrations decrease to a minimum value of 29 mM at around 485 mbsf and increase again below this depth to a value of 37 mM in the deepest sample (Fig. 3B) (Expedition 323 Scientists, 2011b).

The calcium concentration profile contrasts with that of magnesium. In the uppermost 160 m of the sediment, calcium concentrations vary between 8.8 and 10.6 mM with a small minimum at around 80 mbsf (Fig. 3C). At greater depths, calcium concentrations decrease to a minimum value of 6.7 mM at 290 mbsf and increase again below this depth to a maximum value of 13.9 mM at 534 mbsf. The deepest sediment section is characterized by a slight decrease in calcium concentrations to a value of 11.7 mM at 602 mbsf (Fig. 3C) (Expedition 323 Scientists, 2011b).

The porewater DIC concentration profile shows an increase in the top 30 m from seawater values at the shallowest depth to a maximum value of 12.4 mM. Below 30 mbsf, DIC concentrations decrease to a value of 3.9 mM at 601 mbsf (Fig. 3D) (Expedition 323 Scientists, 2011b).

Porewater strontium concentrations show an overall increase with depth from a value of 69 μM at 1.3 mbsf to a value of 131 μM at 591 mbsf (Fig. 3E). Porewater potassium concentrations at Site U1341 range from 8.8 mM to 11.3 mM with no depth-trend (Fig. 3F) (Expedition 323 Scientists, 2011b). The ammonium concentration profile displays a general trend to increasing values with depth to maximum values around 5 mM at 400–500 mbsf. Ammonium concentrations decrease slightly below this depth interval (Fig. 3G).

3. Methods

3.1. Shipboard and post-cruise sampling

Sampling procedures for porewater analyses onboard JOIDES Resolution during IODP Expedition 323 followed standard protocols (Gieskes et al., 1991; Pimmel and Claypool, 2001). Sediment depths are reported in corrected core composite depth below sea floor (CCSF-B) reported in meters below sea floor (mbsf). This depth scale corrects for effects of core expansion and incomplete core recovery, so the length of the cored section is the same as the drilled depth. The CCSF-B depth scale allows for measurements from multiple holes to be used on a common depth scale. It provides an accurate depth scale for absolute calculations of sedimentation rates and fluxes (Mix et al., 2003).

Sediment cores were retrieved by Advanced Piston Coring (APC, down to 458 m drilling depth below sea floor, mdsf) and Extended Coring Barrel (XCB, down to 602 mdsf). Cores for whole-round sediment samples were taken on the ship’s catwalk immediately after retrieval. Porewater was extracted from whole-rounds using a Manheim-type hydraulic press (Manheim et al., 1994). For DIC carbon isotope composition analyses porewater samples were retrieved by Rhizon sampling (Seeberg-Elverfeldt et al., 2005) from the top 80 m of the sediment. Chemical laboratory analyses for shipboard work are described in detail in Expedition 323 Scientists (2011a). Shipboard data presented in this manuscript are available in Expedition 323 Scientists (2011b) and shipboard TOC, chloride, sulfate and DIC data were displayed in Wehrmann et al. (2013).
Hard diagenetic mineral fragments and semi-lithified authigenic mineral phases were hand-picked at the IODP Core curation facility in Kochi, Japan, based on visual core description carried out during the cruise. Samples were retrieved from U1341 Holes A and B and correlated based on CCSF-B calculations. In a few cases carbonate concretions were only found in one of the two holes; all concretions are listed in Table 1. Carbonate phases that could be traced in both holes in parallel are only shown as one layer in Fig. 2A. A list of concretions that were not analyzed because no sample was available, and concretions that are only composed of minor amounts of carbonate, is included in Table S1 of the supplementary material to this manuscript.

3.2. X-ray diffraction analyses

The mineralogical composition of carbonate concretions from Site U1341 was analyzed with a Philips XPERT pro X-ray diffractometer at the University of Bremen, Germany. CuKα radiation was used and the samples were scanned from 3° to 85° (2θ) (Fig. 4). Semi-quantitative proportions of different minerals were estimated from integrated peak areas. Dolomite stoichiometry was calculated from the displacement of the (104) peak using the equation of Lumsden (1979). Disseminated carbonate phases were only analyzed in a few cases onboard (see Expedition 323 Scientists, 2011b) and also by the above described method at the University of Bremen. The distribution of calcite and dolomite in petrographic thin sections was analyzed by the alizarin red stain method (Dickson, 1966).

3.3. Stable isotope analyses

3.3.1. Carbon and oxygen isotope analyses of carbonates

Carbon and oxygen isotopes in powdered bulk sediment were analyzed with a Finnigan MAT 251 mass spectrometer coupled to
measurements. Powdered Solnhofner Plattenkalk calibrated from the deepest sediment section. The chloride calculation of paleo-temperature values for carbonates, particularly global ice volume, which may introduce a small error in the assumption at 90° of dolomites were corrected for dolomite (Rosenbaum and Sheppard, 1986). The ¼ oxygen isotope fractionation factor by Vasconcelos et al. (2005) to calculate formation temperatures for dolomite based on the 13C, and 18O values are reported relative to VPDB. All 18O values of dolomites were corrected for dolomite-phosphoric acid fractionation at 90 °C using the fractionation factor of 1.0093 (Rosenbaum and Sheppard, 1986). The 18O values were used to calculate formation temperatures for dolomite based on the oxygen isotope fractionation factor by Vasconcelos et al. (2005) [1000 ln(δ18O dolomite-H2O) = 2.730 × 106/T2 + 0.26] and assuming that porewater δ18O values were similar to modern seawater. There are likely limitations to this assumption since seawater δ18O values were not constant over the last 4.3 Ma, due to changes, e.g., in global ice volume, which may introduce a small error in the calculation of paleo-temperature values for carbonates, particularly from the deepest sediment section. The chloride concentration in porewaters (Fig. 4A) has no significant downcore trend, implying that an assumption of a constant porewater δ18O value for purposes of this carbonate formation temperature is reasonable with a temperature uncertainty of about 1 °C.

3.3.2. Carbon isotope analyses of dissolved inorganic carbon (DIC)

Stable carbon isotope analyses of DIC were performed at the Oregon State University College of Earth, Ocean and Atmospheric Sciences (OSU/CEOAS) Stable Isotope Mass Spectrometer Facility by continuous-flow mass spectrometry using a GasBench-DeltaV system with dissolved sodium bicarbonate and solid-phase calcium carbonate standards following Torres et al. (2005). Method precision is ±0.03‰ for δ13C. Carbon isotope values are reported relative to VPDB.

3.3.3. Strontium isotope composition of dissolved porewater strontium and diagenetic dolomite

Nine diagenetic dolomite samples were chosen for strontium isotope analyses based on their mineralogy (Table 3). Ground

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth [mbsf]</th>
<th>Calcite [%]</th>
<th>Dolomite [%]</th>
<th>δ13C [% PDB]</th>
<th>δ18O [% PDB]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite concretions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>323-U134IA-23H-3, 80–98 cm</td>
<td>200.5</td>
<td>2.3</td>
<td>70.1</td>
<td>−16.2</td>
<td>5.0</td>
</tr>
<tr>
<td>323-U134IA-22H-3, 98–112 cm</td>
<td>200.7</td>
<td>1.2</td>
<td>81.1</td>
<td>−15.7</td>
<td>4.9</td>
</tr>
<tr>
<td>323-U134IA-50H-7, 0–17 cm</td>
<td>221.1</td>
<td>0.0</td>
<td>96.3</td>
<td>−16.6</td>
<td>5.1</td>
</tr>
<tr>
<td>323-U134IA-25H-4, 36–41 cm</td>
<td>225.1</td>
<td>0.0</td>
<td>93.7</td>
<td>−16.6</td>
<td>5.1</td>
</tr>
<tr>
<td>323-U134IA-25H-4, 104–106 cm</td>
<td>225.7</td>
<td>0.0</td>
<td>92.7</td>
<td>−16.3</td>
<td>5.1</td>
</tr>
<tr>
<td>323-U134IA-3OH-2, 87–97 cm</td>
<td>301.2</td>
<td>0.0</td>
<td>95.3</td>
<td>−16.0</td>
<td>4.0</td>
</tr>
<tr>
<td>323-U134IA-3OH-1, 0–10 cm</td>
<td>308.3</td>
<td>2.8</td>
<td>75.4</td>
<td>−16.3</td>
<td>4.6</td>
</tr>
<tr>
<td>323-U134IB-42H-3, 100–109 cm</td>
<td>371.5</td>
<td>2.1</td>
<td>53.9</td>
<td>−14.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Mixed calcite-dolomite concretions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>323-U134IB-58X-3, 38–42 cm</td>
<td>471.1</td>
<td>0.0</td>
<td>84.8</td>
<td>−15.6</td>
<td>4.2</td>
</tr>
<tr>
<td>471.1</td>
<td>0.0</td>
<td>92.9</td>
<td>−15.7</td>
<td>4.7</td>
<td></td>
</tr>
</tbody>
</table>

| Disseminated carbonate phases |
| 323-U134IA-16H-5, 50–55 cm | 142.9 | 45.1 | 13.9 | −15.5 | 3.7 |
| 323-U134IB-17H-2, 135–150 cm | 152.4 | 53.8 | 21.5 | −16.0 | 3.8 |
| 323-U134IB-17H-3, 0–10 cm | 152.5 | 44.7 | 26.9 | −14.4 | 3.7 |
| 323-U134IA-18H-5, 36–72 cm | 161.4 | 41.6 | 39.7 | −16.2 | 4.6 |
| 323-U134IB-51H-4, 81–87 cm | 436.5 | 46.8 | 4.3 | −15.8 | 3.1 |
| 323-U134IB-69X CC, 11–16 cm | 573.4 | 0.0 | 94.6 | −16.6 | 3.2 |

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samples were treated with 1 N acetic acid (suprapur) at 70 °C for 3 h and centrifuged subsequently. The supernatant was used for strontium isotope analyses. This treatment dissolves the major part of the dolomite and yields reliable results for subsequent strontium isotope analysis (Meister et al., 2007). For Sr-separation shrink Teflon columns were filled with 100 μl Sr-spec resin (50–100 μm mesh, Eichrom). Each porewater or supernatant sample was loaded in 3 N HNO₃ and the strontium washed out with ultra-pure water. Strontium was measured on a Thermo-Fisher Triton T1 Thermal Ionization Mass Spectrometer (MIRC, University of Münster, Germany) in static mode. Aliquots of the samples (300–500 ng) were loaded with HCl and TaF₅ on tungsten filaments in sandwich technique (c.f., Arning et al., 2009). Mass correction is based on a ⁸⁶Sr/⁸⁸Sr ratio of 0.1194. Total procedural blanks for the 104 peak towards lower ²θ angles.

3.3.4. Calcium isotope composition of porewater calcium

For calcium isotope analyses, porewater samples were mixed with a ⁴⁴Ca–⁴⁰Ca double-spike (Gussone et al., 2011) to correct for isotope fractionation during ion chromatography and data acquisition in the mass spectrometer. Calcium in the sample was isolated using a 300 μl column volume HCl-chemistry with MCI Gel CK08P, 75–150 μm (Ockert et al., 2013). Of the purified solution, about 300 ng calcium recovered in 2.5 N HCl were loaded on an out-gassed Re-single filament with a Ta-activator in sandwich technique. Calcium isotope ratios were determined using a Thermo-Fisher Triton T1 Thermal Ionization Mass Spectrometer (MIRC; University of Münster, Germany). Fractionation correction was carried out using the exponential law and the data reduction follows the description in Heuser et al. (2002). Replicate procedural blank measurements were usually below 1% of total calcium and never exceeded 3%. The calcium isotope values are expressed as ⁴⁴/⁴⁰Ca values (δ⁴⁴/⁴⁰Ca [%,SRM915a]=[(⁴⁴Ca/⁴⁰Ca)sample/(⁴⁴Ca/⁴⁰Ca)standard−1]×1000) relative to SRM915a from the U.S. National Institute of Standards and Technology (NIST). Analyses of IAPSO seawater standard yielded a mean value of 1.87‰. SRM915a with a 2 s.d. of 0.05‰ (σ=2). This value lies within the range of previously published values for IAPSO seawater standard (c.f., Hippler et al., 2003; Teichert et al., 2009). The average 2 s.d. of the samples was determined to be 0.09‰ by replicate measurements.

4. Results

4.1. Mineralogy and petrographic description of diagenetic carbonates

Diagenetic carbonate layers at Site U1341 occur in several intervals around 150 mbsf, between 200 and 240 mbsf, at around 300 mbsf, 350 mbsf, 435 mbsf and below 470 mbsf (Fig. 2A and Table 1). Hard, lithified diagenetic carbonate fragments at Site U1341 are composed of varying mixtures of calcite and dolomite (Fig. 2A and Table 1). The petrographic texture shows only micrite with large amounts of diatoms. A few planktonic foraminifera tests occur and are well preserved, i.e., not replaced by dolomite. Generally, concretions found at a sediment depth of 140–160 mbsf and at 436 mbsf contain ca. 40–55% of calcite and less than 40% dolomite while carbonate concretions in the remaining sediment column contain large proportions of dolomite of up to 97% and less...
than 5% calcite. Other mineral phases found in these layers are clay, quartz, and feldspar. Diffractograms show a sharp 104 peak and typical superstructure ordering peaks of dolomite are present (Fig. 4). A considerable shift of the 104 peak to lower 2\(^\theta\) angles indicates Ca-rich dolomite with MgCO\(_3\) content varying between 40 and 50 mol% (average 45.9 mol%).

Disseminated carbonate layers were observed sporadically at several depth intervals (Fig. 2A). A sample subset was analyzed by XRD. Shipboard and shore-based analyses revealed that disseminated and friable carbonates at 209–210 mbsf are primarily composed of dolomite.

4.2. Stable isotope composition

4.2.1. Carbon and oxygen isotope compositions of bulk diagenetic carbonates

Carbon isotope values of the semi-lithified to lithified carbonate concentrations display a small range of ~16.6 to ~14.4% and no trend with depth (Fig. 5B and Table 1). Oxygen isotope values of the same samples range from 1.7 to 5.3‰ (Fig. 5C and Table 1). Carbon and oxygen isotope values are not correlated (R\(^2\) < 0.1).

4.2.2. Carbon isotope composition of dissolved inorganic carbon (DIC)

Carbon isotope values of DIC show increasing depletion in \(^{13}\)C in the uppermost 20 m with values ranging from ~2.5‰ at 0.5 mbsf to a value of ~10.5‰ at around 20 mbsf. Below this depth, \(^{13}\)C values of DIC average ~10.8‰ (Fig. 3D).

4.2.3. Srontium isotope composition of dissolved porewater strontium and diagenetic dolomite

The \(^{87}\)Sr/\(^{86}\)Sr isotope ratio of porewater strontium at Site U1341 is ~0.7091 in the top 150 m of the sediment column. The ratio decreases below this depth to progressively less radiogenic values and reach a minimum value (0.70865) at 485 mbsf. Below this depth strontium isotope ratios show a trend to more radiogenic values (Fig. 3E and Table 2).

The \(^{87}\)Sr/\(^{86}\)Sr isotope ratio of the diagenetic dolomite shows values between 0.70837 and 0.70884 throughout the sediment column, with the exception of the dolomite layer at 471.32 mbsf which has an isotopic value of 0.70826 (Fig. 5D and Table 3).

### Table 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth [mbsf]</th>
<th>Normalized (^{87})Sr/(^{86})Sr</th>
<th>(^{44}/40)Ca [%SRM915a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1341A-2H-1</td>
<td>4.4</td>
<td>0.70918</td>
<td>1.56</td>
</tr>
<tr>
<td>U1341A-3H-6</td>
<td>39.6</td>
<td>0.70918</td>
<td>1.49</td>
</tr>
<tr>
<td>U1341A-12H-6</td>
<td>105.2</td>
<td>0.70914</td>
<td>1.60</td>
</tr>
<tr>
<td>U1341A-22H-6</td>
<td>205.2</td>
<td>0.70896</td>
<td>1.66</td>
</tr>
<tr>
<td>U1341A-30H-6</td>
<td>271.0</td>
<td>0.70893</td>
<td>1.42</td>
</tr>
<tr>
<td>U1341B-41H-5</td>
<td>365.2</td>
<td>0.70877</td>
<td>0.85</td>
</tr>
<tr>
<td>U1341B-50H-5</td>
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<td>n.d.</td>
</tr>
<tr>
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</tr>
<tr>
<td>U1341B-63X-6</td>
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<td>0.93</td>
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<td>0.70879</td>
<td>1.02</td>
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<tr>
<td>U1341B-71X-6</td>
<td>600.9</td>
<td>0.70882</td>
<td>1.25</td>
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</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth [mbsf]</th>
<th>Normalized (^{87})Sr/(^{86})Sr</th>
</tr>
</thead>
<tbody>
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<td>U1341A-22H-3</td>
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<td>U1341A-25H-4</td>
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<td>U1341A-34H-2</td>
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<td>U1341A-38H-1</td>
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<tr>
<td>U1341B-58X-3</td>
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<td>0.70826</td>
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<tr>
<td>U1341B-58X-5</td>
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<td>U1341B-58X-9</td>
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</tr>
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<td>U1341B-69X-cc</td>
<td>573.43</td>
<td>0.70891</td>
</tr>
</tbody>
</table>

Oxygen isotope values of carbonate concretions indicate paleotemperature values of 3.6–16.3 °C (Fig. 5E).

### Fig. 5

(A) Downcore distribution of diagenetic carbonate phases, (B) carbon isotope composition (\(^{13}\)C) of diagenetic carbonate phases and porewater dissolved inorganic carbon (DIC), (C) oxygen isotope composition of diagenetic carbonate phases, (D) strontium isotope ratios (\(^{87}\)Sr/\(^{86}\)Sr) of strontium in porewater and diagenetic carbonates and, (E) carbonate formation temperatures (°C) calculated from \(^{18}\)O values in diagenetic carbonates, Temperature values for disseminated carbonate phases are not included.

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4.2.4. Calcium isotope composition of porewater calcium

In the uppermost 200 m, the calcium isotope composition of porewater calcium shows a decrease from seawater value (1.88‰) to 1.5‰ at about 40 mbsf and a subsequent increase to values of about 1.66‰ (Fig. 3C and Table 2). At depths > 200 mbsf, calcium isotope values show progressive depletion in the heavier isotope with depth to minimum values of ~0.84‰ between 360 and 490 mbsf. In deeper sediments, calcium isotope values increase again to a value of 1.25‰ (Fig. 3C and Table 2).

5. Discussion

5.1. Diagenetic carbonate formation in U1341 subseafloor sediments

Diagenetic carbonate layers occur in several intervals between 150 mbsf and 600 mbsf at Site U1341 (Fig. 2A and Table 1). The diagenetic carbonate layers at 300 and 350 mbsf, and likely the mixed calcite/dolomite layers at 436 mbsf, can be assigned to the previous occurrence of two SMTZs framing a large methanogenic zone that developed ca. 2.58–2.51 Ma ago (Wehrmann et al., 2013). These authors suggest that low solid-phase Ba/Al ratios between 304 and 433 mbsf (Ba-depletion zone; Fig. 2A) mark the maximum extent of former sulfate depletion and the location of the paleo-methanogenic zone. Complete porewater sulfate depletion results in the dissolution of solid-phase barite which reduces the solid-phase Ba/Al ratio (Brumsack and Gieskes, 1983; Von Breymann et al., 1992; McManus et al., 1998). The source of sulfate for the upper SMTZ was downward-diffusing sulfate while a deep sulfate source, likely associated with the underlying basement or the lateral inflow of seawater into deeper sediment sections, provided sulfate to the lower SMTZ (Wehrmann et al., 2013). This time interval was characterized by elevated reactive organic carbon delivery to the seafloor (evidenced in the sediment by high opaline silica contents) which was interpreted as the main driver of higher sulfate reduction rates and the onset of methanogenesis (Fig. S1; März et al., 2013; Wehrmann et al., 2013). The diagenetic carbonate layers likely formed as a result of the enhanced production of DIC and alkalinity during AOM in these SMTZs (e.g., Moore et al., 2004; Meister et al., 2007; Ussler and Paull, 2008).

Several of the remaining diagenetic carbonate phases at Site U1341 can also be correlated with time periods of elevated biogenic accumulation rates (März et al., 2013) and higher modeled organic carbon fluxes in the Pliocene and during short time periods in the Pleistocene (Wehrmann et al., 2013; Fig. S1). In the Pliocene, organic carbon fluxes are inferred to have been generally higher than during most of the Pleistocene as indicated by higher opaline silica accumulation (Fig. S1; Aiello and Ravelo, 2012; März et al., 2013). The dolomite layers located in Pliocene sediments at depths > 400 mbsf are also embedded in relatively pure diatom ooze, which contained organic matter with a higher reactivity (Fig. S1). During the Pleistocene at 2.14–2.08 Ma (212–230 mbsf), organic carbon fluxes were elevated, albeit not as high as during the 2.58 Ma event (Fig. S1). Diagenetic dolomite layers were found throughout this interval, including dolomite concretions at 221 and 225 mbsf (Table 1).

It is likely that during these time intervals organic carbon mineralization rates were higher than at present. Higher rates of organic carbon degradation would have led to the enhanced production of DIC, low porewater sulfate concentrations, and the onset of carbonate precipitation. The formation of dolomite in the sulfate zone, i.e., the zone where organoclastic sulfate reduction prevails and sulfate is not depleted, has previously been described for organic-rich sediment sites, for example, for the Miocene Drake Formation (Burns et al., 1988). Thus these carbonate layers may have formed in the absence of methanogenesis and AOM.

Sulfate reduction initially results in carbonate dissolution rather than precipitation (Boudreau and Canfield, 1993; Meister, 2013). Sulfate concentrations during the time of dolomite formation were thus likely low, e.g., during formation of the dolomite layers presently located at 200–225 mbsf. This setting, however, was susceptible for the onset of short periods of methanogenesis and AOM due to the low sulfate concentrations, and these processes may have occurred intermittently. Several studies also suggest that the presence of sulfate in marine porewaters may inhibit dolomite precipitation (Baker and Kastner, 1981; Kastner, 1984; Magalhães et al., 2012). Although this hypothesis remains controversial (Sánchez-Román et al., 2009; Meister et al., 2011b), it offers an explanation for the occurrence of layers primarily composed of calcite and minor amounts of dolomite found at 140–160 mbsf (Table 1). These layers may have formed in the sulfate zone without the occurrence of AOM.

We infer that diagenetic carbonate layers found in the U1341 sediments formed during early stages of diagenesis at shallow sediment depths. This inference is supported by the strontium isotope ratios of the diagenetic carbonate phases (Fig. 5D), which are only slightly below Pliocene/Pleistocene seawater strontium isotope values (Farrell et al., 1995; Veizer et al., 1999) and show little imprint of enhanced ash alteration and a deep minimum in the porewater strontium isotope profile (see Section 5.2.2). The calculated carbonate formation temperatures based on oxygen isotopic values for the diagenetic carbonates, which are mostly in the range of 4–16 °C, with dolomite concretions in the range of 3.6–10.9 °C (Fig. 5E), match the temperature gradient in the uppermost 100 m of the sediment column (Expedition 323 Scientists, 2010), also suggesting relatively shallow depths of diagenetic carbonate precipitation. Outliers from these temperature estimates can be assigned to mixed dolomite–calcite phases, which are associated with a different oxygen isotope fractionation factor (Kim and O’Neil, 1997) than the one we applied for pure dolomite based on Vasconcelos et al. (2005). The oxygen isotope value of disseminated dolomite in the deepest sediment section (514.3 mbsf) is slightly lower than for the concretions in the rest of the sediment column, resulting in higher calculated paleo-temperatures (18.8 °C). Given the uncertainty of paleo-oxygen isotope values of the seawater in this region, however, these values are still in the expected range of isotopic and temperature values of carbonate formed at shallow depth during the Pliocene.

The carbon isotopic compositions of all analyzed carbonate phases fall into a narrow range of −16 to −14‰ (Fig. 5A and Table 1). This remarkably close range of carbon isotope values of carbonates at Site U1341 (Fig. 5A) spanning 620 m and 4.3 Ma, distinguishes this site from other ODP sites where carbonates were analyzed. These samples are less 13C-depleted than diagenetic carbonate phases that have previously been attributed to AOM coupled to sulfate reduction at a SMTZ, which can display δ13C values of as low as −66‰ (Ritger et al., 1987) because they record 13C-depleted DIC produced during the anaerobic oxidation of 13C-depleted methane (e.g., Ritger et al., 1987; Raiswell, 1988; Aloisi et al., 2000). The comparably heavy carbon isotope values of the diagenetic carbonate layers at Site U1341 indicate the influence of other more 13C-enriched DIC sources on the total DIC and associated carbonate isotope composition during the time of carbonate formation. These sources are likely DIC derived from (a) the mineralization of marine organic matter, which yields carbon isotope values of −30 to −10‰ (Degens et al., 1968; Bickert, 2006), and (b) at depth where the occurrence of AOM was inferred from the distribution of porewater sulfate concentrations and low Ba/Al ratios (Wehrmann et al., 2013), methanogenesis, which leads to an enrichment of 13C in the porewater DIC pool (Barker and Fritz, 1981). The contribution of DIC from overlying...
seawater may additionally have added carbon with an isotopic composition of ~1%o to the total DIC pool.

The carbon isotope values of the diagenetic carbonates, however, are much lighter than values previously reported from ODP sites were methanogenesis plays an important role, e.g., ODP Leg 201 Site 1227 (maximum △13C-value = +11.5‰; Meister et al., 2007) and ODP Leg 175 Site 1081 (+7.7‰; Pufahl and Wefer, 2001). At these sites, strong 13C-enrichment was explained by the downward movement of the SMTZ and associated dolomite formation interface, which consequently traced the mixing of 13C-depleted DIC formed during lower rates of AOM and a large pool of 13C-enriched DIC, previously formed in the methanogenic zone (Meister et al., 2008). Alternatively, these relatively heavy 13C-values at those sites were explained by the formation of carbonate in the methanogenic zone. To balance the negative pH effect of methanogenesis (Soetaert et al., 2007) processes such as the weathering of biogenic silicate (Wallmann et al., 2008, 2011) or an inflow of alkaline fluids, e.g., formed during silicate alteration in underlying rocks (Meister et al., 2011a) must occur in this scenario. The narrow range of carbon isotope values of the SMTZ-associated diagenetic carbonates at Site U1341 between 280 and 440 mbsf may therefore indicate that they have (a) formed during short formation periods and did not record pronounced shifts in the carbon isotope values at those sites were explained by the formation of carbonate in the methanogenic zone.

5.2. Reconstruction of past and present biogeochemical processes based on porewater concentration and isotopic signatures

The porewater element concentration and associated isotope profiles with depth at Site U1341 are the result of ongoing biogeochemical activity superimposed on a residual porewater pool reflecting biogeochemical activity in the past (Fig. 6). The high productivity event at 2.58–2.51 Ma that led to the development of a large methanogenic zone framed by two SMTZs was a main driver for secondary geochemical processes that can still be traced in the porewater at present (Wehrmann et al., 2013). The solid-phase Ba-depletion zone, which outlines the maximum extent of the former methanogenic zone, is imprinted at sediment depths of 304–435 mbsf while the linked porewater signatures, e.g., low sulfate concentrations, have shifted downward in the sediment column by diffusion and are now mostly observed at 400–500 mbsf (Fig. 6). In the following we discuss how the biogeochemical processes evolving through time have affected the signatures in modern porewater.

5.2.1. Signals of past and present diagenetic carbonate formation

The porewater magnesium concentration profile follows the distribution of sulfate concentrations (Fig. 3A and B). The correlation of the sulfate and magnesium concentration profiles can be explained by the past formation of the diagenetic dolomite layers, which are currently located at around 300 mbsf and 350 mbsf, during the 2.58–2.51 Ma high productivity event. Similar to the sulfate concentration profile, the magnesium profile does not show evidence for its consumption at shallower depth, albeit disseminated and lithified dolomite layers were formed around 200 and 221 mbsf (Fig. 2A). This finding supports the notion that any event of elevated sulfate consumption that occurred after 2.51 Ma and led to the formation of diagenetic dolomite was probably only short lived. A surprising observation is the extent of the present-day magnesium decrease, which shows a minimum value of 29 mM (Fig. 3B). Assuming that this profile was affected at 2.51 Ma and has largely been influenced by diffusion thereafter, the magnesium concentrations were probably even lower in the past. Such a strong loss of magnesium is usually not observed at dolomite formation zones of SMTZs or in the sulfate zone since it cannot be balanced by a similar calcium removal due to the much lower calcium concentrations in marine porewater, except when large amounts of calcite are available for dolomitization. However, biogenic calcite precipitations in Bering Sea sediments are low (Fig. 2C). Often, magnesium concentrations even increase in sediments characterized by high rates of organic matter turnover due to magnesium desorption from clay minerals and replacement by ammonium (von Breymann et al., 1990). Thus, additional processes that remove magnesium from marine porewaters have to be considered.

In contrast to the magnesium and sulfate profiles, the calcium profile does not show a minimum between 400 and 500 mbsf but local minima at around 80 mbsf, 200 mbsf and 290 mbsf, and a pronounced increase in concentrations below this depth (Fig. 3C). A comparison of these minima with the depth of diagenetic carbonate layers reveal that the carbonate layers at around 200 mbsf and 290 mbsf may still affect the calcium profile at present (Fig. 2A). Likely, such a signal is less visible in the magnesium concentration profile due to the different concentration ranges of these constituents (i.e., the much higher Mg concentrations), which make excursions of 2–4 mM difficult to trace in the magnesium concentration profile compared to the calcium profile. The increase in calcium concentrations towards the depth where sulfate and magnesium concentrations show concentration minima may suggest that during burial of the carbonate layers, at present located between 470 and 570 mbsf,
calcium was or is still being released from carbonate phases. This may be driven by the replacement of calcite by dolomite or carbonate dissolution. However, diagenetic dolomites in this interval show no petrographic evidence for recrystallization. At the base of the sediment core, the porewater profiles are overprinted by another fluid source, which has presumably a seawater-like composition, as all profiles show a trend to seawater values towards depth. The deep source may be associated with the lateral inflow of seawater into a lithological conduit below or upward fluid advection from the basement (Wehrmann et al., 2013).

In contrast to the other profiles, the DIC concentration profile shows the highest values in the top 30 m. It has thus lost the transient signals of the previous high-productivity events and associated elevated organic carbon turnover rates. This suggests that the removal of DIC by carbonate formation was faster in equilibrating the DIC profile than the diffusion of sulfate, which leads to the rebound of the sulfate profile. Furthermore, the DIC profile does not show any excursions towards the diagenetic carbonate phases, which suggests that these layers do not imprint on the DIC profile at present.

Overall the porewater sulfate, magnesium, calcium, and DIC profiles at Site U1341 show very dissimilar distributions that indicate different sensitivities and reaction time scales of the constituents with respect to the occurrence and decline of methanogenesis, AOM, and carbonate formation and dissolution (Figs. 3 and 6). The sulfate and magnesium profiles seem to reflect major and prolonged changes in the paleo-diagenetic processes at Site U1341 while the DIC profile reflects the present depth of organic carbon mineralization. The calcium concentration profile also lost some of the signals of past biogeochemical changes but is currently sensitive to small scale diagenetic alteration of carbonate phases.

5.2.2. Isotopic evidence for enhanced ash alteration during time periods of methanogenesis

Isotope values of porewater strontium from Site U1341 follow the distribution patterns of porewater magnesium and sulfate concentrations (Fig. 3E) with a trend towards less radiogenic isotope values at the same depth as the observed minimum magnesium concentrations at 300–500 mbsf. This suggests that secondary geochemical processes, linked to the occurrence of the methanogenic zone and/or sulfate reduction coupled to AOM, took place that affected the porewater strontium isotope composition. In marine sediments a non-radiogenic imprint of porewater strontium can result from (a) the dissolution of biogenic carbonates with an isotope composition between 0.7092 and 0.7075 reflecting the composition of contemporaneous seawater (Elderfield and Gieskes, 1982; Elderfield, 1986), (b) the intrusion of non-radiogenic fluids from the underlying oceanic basement (e.g., Elderfield, 1986; Teichert et al., 2005), and/or (c) the alteration of volcanic ash (Hawkesworth and Elderfield, 1978; Lawrence et al., 1979; Gieskes and Lawrence, 1981).

The first hypothesis can be excluded since it would require the presence of carbonates with an age of at least 15 Ma which is by far exceeding the age of the entire sedimentary sequence at this site and no lithological evidence for the input of “old carbonate”, e.g., by mass wasting, was found. The lateral inflow of fluids that have reacted with the underlying basaltic basement, e.g., facilitated by normal faulting in a passive margin setting, into the 400–500 mbsf depth interval, or the episodic inflow of base-level derived fluids from deeper layers, could facilitate a non-radiogenic strontium isotopic composition of local porewater strontium. Such scenarios would also represent alternative explanations for the observed low sulfate and magnesium concentrations in the same depth interval. However, the strong 34S-enrichment of the sulfate in this interval (Wehrmann et al., 2013) and the occurrence of a zone of pronounced solid-phase barium depletion (Fig. 2A) support the hypothesis that sulfate reduction coupled to AOM was the cause for the sulfate minimum. Furthermore, the influx of basement fluids into sediments is usually apparent in other proxies, such as a depletion in chloride concentrations, which, however, only marginally decrease with depth from values around 570 mM in the uppermost sediment section to values around 550 mM in the deepest sediment section (Fig. 3A).

Strontium isotope signals imprinted by the alteration of volcanic ash have been described at multiple deep subseaﬂoor sediment sites, e.g., at the Bellinghausen Abyssal Plain (Deep Sea Drilling Program (DSDP) Site 323; Lawrence et al., 1979), at the Norwegian Continental Margin (Ocean Drilling Program (ODP) Leg 104; Aagard et al., 1989) and at the Tonga fore-arc (ODP Site 841; Blanc et al., 1995). Ash layers were found frequently at Site U1341 throughout the sediment from 3 to 602 mbsf without any clear trend to more frequent or paused occurrences at specific depth intervals (Expediton 323 Scientists, 2010). Thus, the pronounced peak in non-radiogenic strontium in the 400–500 mbsf interval can be attributed to the enhanced alteration of volcanic ash in a specific diagenetic zone compared to the rest of the sediment column where ashes are also present. Porewater strontium concentrations show a steady increase with depth, probably due to the dissolution of biogenic calcite or the recrystallization of biogenic or diagenetic carbonate phases (Fig. 3E). The strontium concentration increase in combination with a decrease in 87Sr/86Sr therefore suggests a combination of carbonate dissolution and additional release of non-radiogenic strontium during ash alteration. The intriguing correlation between the strontium isotope and porewater sulfate profiles suggests that enhanced ash alteration occurred during the presence of the pronounced methanogenic zone in the sediment at around 2.58–2.51 Ma.

The inverse calcium and magnesium concentration patterns that were observed at a similar depth may support the hypothesis that ash alteration played a role in shaping the diagenetic signals at Site U1341. This overprint accompanies the effect of past formation of dolomite on the magnesium and carbonate crystallization on the calcium profiles (Section 5.2.1). Inverse calcium and magnesium patterns have previously been observed in deep marine sediments as a result of alteration of volcanicogenic material (Perry et al., 1976; Gieskes and Lawrence, 1981; Aagard et al., 1989; Egeberg and the Leg 126 Shipboard Scientific Party, 1990; Martin, 1994). The uptake of magnesium results from the formation of Mg-rich smectite as one of the major alteration products of ash diagenesis (Aagard et al., 1989; Egeberg and the Leg 126 Shipboard Scientific Party, 1990; Tribble and Wilkins, 1994). Calcium is released from the ashes as it does not become incorporated into diageneric clay mineral phases such as smectite and many zeolites. However, while previous studies have described approximately equal increases and decreases of calcium and magnesium, respectively, during ash alteration (Perry et al., 1976; Martin, 1994), in our study the decrease of magnesium (~20 mM) and increase of calcium (~6 mM) in this depth interval are not balanced (Fig. 3B and C). A fraction of calcium released during ash alteration to smectite may thus have been consumed during other processes, i.e., the formation of carbonate phases in the sediment. It is likely that the calcium released during ash alteration represented an isotopically light source of calcium to the porewater in line with the observed decrease in porewater calcium isotope ratios reaching values as low as 0.8‰ (Fig. 3C) compared to a present-day seawater value of 1.87‰ (Teichert et al., 2009).

Wallmann et al. (2008), based on cores from the Sea of Okhotsk, discussed the enhanced alteration of reactive silicate phases such as olivine, pyroxenes and ashes in the methanogenic zone of marine sediments. The authors suggest that dissolved organic carbon (DOC) in the form of humic and fulvic acids,
present in high concentrations in methanogenic zones, functions as strong ligand and forms complexes with aluminum and iron. This promotes the dissolution of Fe- and Al-rich silicate phases. However, at the sites in the Sea of Okhotsk the most prominent weathering process is the incongruent dissolution of the reactive silicate phases to kaolinite and gibbsite, rather than the formation of smectite. Consequently, the pronounced weathering of terrigenous cation-rich silicates such as olivine and pyroxenes at these sites results in an increase in magnesium concentrations in the methanogenic zone (Wallmann et al., 2008). A signal of volcanic ash alteration which commonly results in magnesium uptake into smectite (Aagard et al., 1989; Eggerb and the Leg 126 Shipboard Scientific Party, 1990; Tribble and Wilkens, 1994) at the Sea of Okhotsk sites may thus be overprinted.

Scholz et al. (2013) describe a spatial separation of incongruent weathering of reactive silicate phases, which occurs in the top few meters of the sediment and smectite formation, which takes place at greater burial depth in sediments off Central Chile. The incongruent weathering of silicate phases releases bicarbonate, calcium, and magnesium into the porewater (Scholz et al., 2013). The authors attribute the spatially confined occurrence of incongruent silicate weathering to the availability of CO₂ from methanogenesis. In contrast to these studies, the inverse magnesium and calcium profiles and the decreases in calcium and strontium isotope values at Site U1341 suggest that ash alteration to smectite, driven by high DOC concentrations produced during organic matter degradation, may have been more pronounced than incongruent silicate weathering of reactive silicate phases, driven by elevated CO₂ concentration in former methanogenic zones. This can be attributed to a much smaller input of reactive silicate phases such as olivine and pyroxenes from land due to the more distal location of Bowers Ridge in the southern Bering Sea compared to the sites on Sakhalin slope and off Chile studied by Wallmann et al. (2008) and Scholz et al. (2013). However, the porewater potassium profile which often also shows excursions due to the alteration of ash (e.g., Gieskes et al., 1991; Gieskes and Lawrence, 1981) does not show a distinct trend with depth at this site.

5.2.3. Isotopic evidence for enhanced ammonium-calcium ion exchange during time periods of higher organic carbon turnover rates

The porewater calcium concentration and isotope profiles show the most dynamic distributions amongst the investigated porewater constituents, which is a result of the sensitivity of the porewater calcium system to multiple geochemical processes. As outlined above, calcium concentration minima at 200 mbsf and 290 mbsf are likely evidence of on-going carbonate precipitation of carbonate associated with the past occurrence of carbonate phases is indicated by decreasing calcium concentration in the deepest sediment section results from the inflow of a seawater-like fluid from below (Fig. 3C). The porewater calcium isotope profile together with the present-day ammonium profile suggest that the release of light calcium from clay minerals due to ammonium–calcium ion exchange may additionally have played a role at this site at present and during past periods of elevated organic carbon mineralization, especially at around 2.58–2.51 Ma. In sediment layers experiencing high organic matter degradation, high concentrations of ammonium are produced which substitutes for all cations attached to clay mineral exchange sites (Rosenfeld, 1978; Boorman and Murray, 1982). Magnesium–ammonium and calcium–ammonium exchange with clay minerals have been studied by von Breymann et al. (1990) and Ockert et al. (in press). Clay–mineral attached calcium has a lighter isotope signature than the surrounding porewater, thus leading to a shift in the porewater calcium isotope composition of up to ~2.5‰ during exchange of calcium with ammonium (Ockert et al., 2013).

In the uppermost 20 mbsf at Site U1341 increasing ammonium and decreasing sulfate concentrations indicate current organic matter remineralization (Figs. 3A, G and 6). Calcium concentrations, however, increase slightly with depth before showing a decrease in this interval. Similarly, the porewater calcium isotopic value is lowered to 1.49‰ before it increases again (to a maximum of 1.66‰ at 205 mbsf). It is likely, that calcium desorption from clay minerals is responsible for light calcium isotope values in the porewater in this depth interval at present (Fig. 3C and G), a process that was also suggested for sediments from the Cascadia margin (Teichert et al., 2009).

This process likely also played a role in the 300–500 mbsf depth interval since the former methanogenic zone was established as a result of the increased supply of easily degradable organic matter, which led to higher ammonium concentrations in the porewater. At present this zone still shows the highest ammonium concentration in the sediment column with values of up to 5 mM at 400 mbsf (Fig. 3G). Based on the present data set, the effect of ammonium-calcium exchange, carbonate dissolution/recrystallization and volcanic ash alteration may thus all play a role in shaping the porewater calcium isotope profile at Site U1341 (Fig. 6).

5.3. Implications of repeated events of diagenetic carbonate formation for a global assessment of organic carbon burial and remineralization

Site U1341 shows distinct differences compared to other studies in which dolomite layers were used as indicators for past biogeochemical processes, such as AOM coupled to sulfate reduction in SMTZs. For example, ODP Site 1229 on the Peru Margin shows a higher resolution record of dolomite layers formed during AOM that was possibly triggered by glacial interglacial oceanographic changes through variations in sedimentation rate. However, the latter variations occurred on the shelf in rather shallow water. In contrast, IODP Site 1341, located at more than 2000 m water depth, has remained permanently in deep water over the last 4.3 Ma while changes in sediment deposition rates were mainly driven by variation in surface water productivity (März et al., 2013; Wehrmann et al., 2013). Our study shows evidence that multiple, episodic events of high organic matter degradation, increased sulfate reduction, and likely the onset of methanogenic zones may have occurred throughout the Plio- and Pleistocene deposition history of the southwestern Bowers Ridge. The Pleistocene events were probably caused by increased sedimentation rate, as they fall into the time with strongly variable deposition rates between 2.5 and 1 Ma ago (Fig. 2B). These intervals of high sedimentation rate were likely connected to increased primary production in the Southern Bering Sea (März et al., 2013; Wehrmann et al., 2013). Our findings highlight the sensitivity of the diagenetic system to oceanographic changes. To our knowledge, this is one of the first studies (e.g., König et al., 2001), where a direct coupling between oceanographic changes and subsurface biogeochemical activity has been shown in a deeper slope setting rather than on a shallow shelf.
Hence, such a high-frequency oceanographic–diagenetic coupling may not only affect coastal and shelf areas but much larger parts of the ocean, and may occur more widespread in deeper ocean margin and open ocean environments. This finding implies that subsurface redox zones are more dynamic than previously assumed and may represent a major feedback in organic carbon burial fluxes that have to be taken into account for a global assessment of these fluxes. The study of biogeochemical signatures preserved in diagenetic precipitates may strongly improve such assessments, perhaps most efficiently by complementing reactive transport modeling, to resolve short-term variations in subseaflow biogeochemical conditions.

### 6. Conclusions

Varying organic carbon deposition is the main driver for frequent changes in the prevailing biogeochemical processes at Site U1341 over time, which resulted in non-steady state signals in a variety of porewater profiles such as those of sulfate, calcium, and magnesium. Several diagenetic carbonate layers are additional evidence of short time periods of higher organic carbon deposition, sulfate reduction rates, and potentially the onset of methanogenesis and AOM that are not imprinted in the present-day porewater signals or traced by inverse-reaction transport modeling approaches. Our study on the porewater and solid-phase signals related to the formation of diagenetic carbonates at Site U1341 has important implications for the interpretation of these signals as paleo-diagenetic tracers for deep biosphere biogeochemical processes:

- The carbon isotopic composition of diagenetic carbonates such as dolomite traces several sources of DIC, most importantly from organoclastic sulfate reduction and AOM at past SMTZs. The distributions of porewater calcium and magnesium concentrations are effected by carbonate formation, recrystallization and dissolution as well as additional geochemical processes such as the alteration of volcanic ash and deep fluid sources. These signals can be preserved in deeply buried porewaters.
- Besides concentration profiles, deeply buried porewaters also may preserve isotope signatures. Porewater strontium and calcium isotope values can provide valuable information on diagenetic processes such as the alteration of relictic silicates in the methagenic zone, carbonate dissolution and the imprint of deep fluids.

This combined approach using geochemical signals in diagenetic dolomite and residual porewater pools revealed a record of multiple events of elevated organic carbon turnover rates likely via sulfate reduction, at least one period characterized by the onset and decline of a methanogenic zone, and potentially shorter time intervals during which this process also occurred. These variations in the prevailing biogeochemical processes suggest a response of the subseaflow biosphere to oceanographic conditions in a deep water ocean setting. This feedback needs to be taken into account in future global assessments of carbon burial and remineralization.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dsr2.2013.09.008.

### References


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