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

L.M. Wehrmann^{1, 2*}, C. Ockert^{3a}, A. Mix⁴, N. Gussone³, B.M.A. Teichert⁵, and P. Meister²

¹Department of Earth Sciences, University of California, Riverside, Riverside, USA,
laura.wehrmann@ucr.edu

²Department of Biogeochemistry, Max Planck Institute for Marine Microbiology,
Celsiusstrasse 1, D-28359 Bremen, Germany, pmeister@mpi-bremen.de

³Institut für Mineralogie, Universität Münster, Corrensstrasse 24, D-48149 Münster,
Germany, c.ockert@fz-juelich.de, nikolaus.gussone@uni-muenster.de

⁴College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR,
USA, amix@coas.oregonstate.edu

⁵Institut für Geologie und Paläontologie, Universität Münster, Corrensstrasse 24, D-48149
Münster, Germany, barbara.teichert@uni-muenster.de

^aPresent address: IBG-3/Agrosphere, Forschungszentrum Jülich GmbH, D-52425 Jülich,
Germany

*Corresponding author. Department of Earth Sciences, University of California Riverside,
900 University Ave., Riverside, CA 92521-0423, USA, laura.wehrmann@ucr.edu
Phone: (951)827-3728, Fax: (951)827-4324

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 methane oxidation (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; Parkes et al., 2005; Schippers et al., 2005; 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 (Schrage et al., 2013).

Organic carbon reaching the seafloor is degraded via fermentation and hydrolysis and organic intermediates are oxidized by terminal electron accepting 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, 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 and during AOM takes part in carbonate precipitation (Aloisi et al., 2002; Luff and Wallmann, 2003; Ussler and Paull, 2008).

Dolomite [$\text{CaMg}(\text{CO}_3)_2$] beds, nodules, or overgrowth coatings have often been observed to occur in organic carbon-rich ocean margin deposits, such as in the Miocene Monterey Formation, California (Murata et al., 1969; Garrison and Graham, 1984; Compton and Siever, 1986; Burns et al., 1988). They were also discovered in recent marine sediments at several Deep-Sea Drilling Program (DSDP) sites (Pisciotta and Mahoney, 1981; Kelts and McKenzie, 1982, Baker and Burns, 1985). Dolomite found in hemipelagic sediments has a wide range of carbon isotopic values; $\delta^{13}\text{C}$ links their formation to a particular diagenetic setting, i.e., the sulfate reduction or methanogenic zone (Kelts and McKenzie, 1984; 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 subseafloor 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 subseafloor 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 unlithified 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 paleo-productivity 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 seafloor biogeochemical activity and paleoceanographic conditions.

During the past 4.3 Ma the accumulation rate of organic matter and biogenic opal at Site U1341 has generally decreased, and is inferred to reflect a long-term reduction of primary productivity (Aiello and Ravelo, 2012; März et al., 2013). This trend was 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 10^5 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 to 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 meters 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 ridges' 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 et al., 1999, 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 and for short time periods thereafter indicate that short high productivity events also occurred during the Pleistocene (März et al., 2013). Higher opal deposition during the Pliocene may have been the result of enhanced vertical mixing of nutrients promoted by weaker ocean stratification and stronger upwelling (Aiello and Ravelo, 2012). März et al. (2013) proposed that the pronounced high productivity event that caused elevated opal deposition at around 2.58-2.51 Ma was 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 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 grey, reddish grey or light grey and occur as distinct thin layers or intermixed with

biogenic and silicilastic sediment as a result of bioturbation (Expedition 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 0.1 ± 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 Shipbord porewater geochemistry

Sulfate concentrations at Site U1341 decrease from seawater-like values at the sediment surface to values around 23.4 mM in the top 25 mbsf. At greater depths, sulfate concentration values remain almost constant to a depth of 150 mbsf before they 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 meters 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 meters 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 μ M at 1.3 mbsf to a value of 131 μ M 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 400-500mbsf. 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 seafloor (CCSF-B) reported in meters below seafloor (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 Figure 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. CuK α radiation was used and the samples were scanned from 3 to 85° (2 θ) (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, 2011) 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 an automated acidification device (type “Kiel”) at the Geological Institute, University of Bremen. The analytical precision of the mass spectrometer is $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$, and $\pm 0.07\text{‰}$ for $\delta^{18}\text{O}$ measurements. Powdered Solnhofner Plattenkalk calibrated against the NBS-19 standard, was used as in-house standard and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carbonates are reported relative to Vienna Pee Dee Belemnite Standard (VPDB). All $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values were used to calculate formation temperatures for dolomite based on the oxygen isotope fractionation factor by Vasconcelos et al. (2005) [$1000 \ln \alpha_{\text{Dolomite-H}_2\text{O}} = 2.730 \cdot 10^6/T^2 + 0.26$] and assuming that porewater $\delta^{18}\text{O}$ values were similar to modern seawater. There are likely limitations to this assumption since seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}$. 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 (Tab. 3). Ground samples were treated with 1 N acetic acid (suprapur) at 70°C for three hours 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 100µl 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 $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Total procedural blanks for strontium were less than 0.1 ng. Repeated runs of NBS

standard 987 yielded average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.710208 ± 0.000007 (2σ , $n = 8$). The sample data were normalized to a NBS standard 987 value of 0.710248.

3.3.4 Calcium isotope composition of porewater calcium

For calcium isotope analyses, porewater samples were mixed with a ^{42}Ca - ^{43}Ca 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; Teichert et al., submitted). Of the purified solution, about 300 ng calcium recovered in 2.5N HCl were loaded on an outgassed Re-single filament with a Ta-activator in sandwich technique. Calcium isotope ratios were determined using a Thermo Fisher Triton T1 Thermal Ionisation 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 $\delta^{44/40}\text{Ca}$ values ($\delta^{44/40}\text{Ca}$ [‰SRM915a] = $((^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1) \times 1000$) 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‰ ($n=2$). This value lies within the range of previously published values for IAPSO seawater standard (c.f., Hippler et al., 2003; Teichert et al., 2009; Teichert et al., submitted). 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; Tab. 1). Hard, lithified diagenetic carbonate fragments at Site U1341 are composed of varying mixtures of calcite and dolomite (Fig. 2a, Tab. 1). The petrographic texture shows only micrite with large amounts of diatoms. A few planktonic foraminifer 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 2θ 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; Tab. 1). Oxygen isotope values of the same samples range from 1.7 to 5.3‰ (Fig. 5c; Tab. 1). Carbon and

oxygen isotope values are not correlated ($R^2 < 0.1$). The oxygen isotope values of carbonate concretions indicate paleo-temperature values of 3.6-16.3°C (Fig. 5e).

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, $\delta^{13}\text{C}$ values of DIC average -10.8‰ (Fig. 3d).

4.2.3 Strontium isotope composition of dissolved porewater strontium and diagenetic dolomite

The $^{87}\text{Sr}/^{86}\text{Sr}$ 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; Tab. 2).

The $^{87}\text{Sr}/^{86}\text{Sr}$ 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; Tab. 3).

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; Tab. 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; Tab. 2).

5. Discussion

5.1 Diagenetic carbonate formation in U1341 seafloor sediments

Diagenetic carbonate layers occur in several intervals between 150 mbsf and 600 mbsf at Site U1341 (Fig. 2a; Tab. 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 435 mbsf (Ba-depletion zone; Fig. 2) 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 Breyman 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 (Tab. 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 (cf., 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 (Tab. 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., 2005; Veizer, 1999) and show little imprint of enhanced ash alteration and a deep minimum in the porewater strontium isotope profile (see 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 to 16°C, with dolomite concretions in the range of 3.6 to 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 (c.f., 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 composition of all analyzed carbonate phases falls into a narrow range of -16 to -14‰ (Fig. 5a; Tab. 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 $\delta^{13}\text{C}$ values of as low as -66‰ (Ritger et al., 1987) because they record ^{13}C -depleted DIC produced during the anaerobic oxidation of ^{13}C -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 ^{13}C -enriched DIC sources on the total DIC and associated carbonate carbon 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 ^{13}C 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‰ to the total DIC pool.

The carbon isotope values of the diagenetic carbonates, however, are much lighter than values previously reported from ODP sites where methanogenesis plays an important role, e.g., ODP Leg 201 Site 1227 (maximum $\delta^{13}\text{C}$ -value + 11.5‰; Meister et al., 2007) and ODP Leg 175 Site 1081 (+ 7.7‰; Pufahl and Wefer, 2001). At these sites, strong ^{13}C -enrichment was explained by the downward movement of the SMTZ and associated dolomite formation interface, which consequently traced the mixing of ^{13}C -depleted DIC formed during lower rates of AOM and a large pool of ^{13}C -enriched DIC, previously formed in the methanogenic zone (Meister et al., 2008). Alternatively, these relatively heavy $\delta^{13}\text{C}$ -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; Wehrmann et al., 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 280-440 mbsf may therefore indicate that they have a) formed during short formation periods and did not record pronounced shifts in the depth of the SMTZ, and b) were imprinted by DIC of mixed origin with a contribution from organoclastic sulfate reduction, AOM and methanogenesis but likely did not form in the methanogenic zone. At Site U1341 the present-day carbon isotope composition of DIC in the top 80 m, derived from the mineralization of organic carbon by sulfate reduction in the absence of methanogenesis, shows a minimum value of -11‰ (Fig. 3d). This value indicates that the mineralization of organic matter alone at Site U1341 at present does not drive the carbon isotope values of DIC light enough to form carbonates with a carbon isotope composition of the carbonate layers found in the deeper sediment, particularly when further carbon isotope fractionation during the formation of dolomite is taken into account (Sheppard and Schwarcz, 1970; Ohmoto and Rye, 1979).

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 magnesium concentration profile follows the distribution of sulfate concentrations (Figs. 3a and 3b). 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 found at 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 concentrations 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 highest values in the top 30 meters. It thus has 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, 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 pattern 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 to 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, 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 basement-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 ^{34}S -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 seafloor 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; Aagaard 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 (Expedition 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 $^{87}\text{Sr}/^{86}\text{Sr}$ therefore suggests a combination of carbonate dissolution and additional release of un-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 recrystallization 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 volcanogenic material (Perry et al., 1977; Gieskes and Lawrence, 1981; Aagaard et al., 1989; Egeberg, 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 (Aagaard et al., 1989; Egeberg, 1990; Tribble and Wilkens, 1994). Calcium is released from the ashes as it does not become incorporated into diagenetic 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 (Figs. 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 phase 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; Teichert et al., submitted).

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 aluminium 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., 2006). A signal of volcanic ash alteration which commonly results in magnesium uptake into smectite (Aagaard et al., 1989; Egeberg, 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, 1981; 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 ongoing carbonate formation. In the depth interval between 100 and 300 mbsf past precipitation of carbonate phases is indicated by decreasing calcium concentration and relatively heavy calcium isotope values (Fig. 3c). The previous precipitation of carbonate associated with the past occurrence of the SMTZs probably led to preferential uptake of light calcium depending on mineralogy, temperature and the rate of carbonate formation (cf., Marriott et al., 2004; Lemarchand et al. 2004, Gussone et al., 2003, 2005, Tang et al., 2008, Teichert et al. submitted). The increase in calcium concentrations and decrease of calcium isotope values below 300 mbsf suggests the release of calcium from ash alteration and the dissolution of calcium carbonate minerals (e.g., Fantle and DePaolo, 2007) which may occur at Site U1341 at similar depth as evidenced in a strontium concentration increase (Fig. 3e). The decrease in

concentrations 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 below 300 mbsf 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, 1979; Boatman 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, 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 (Figs. 3c, g), a process that was also suggested for sediments from the Cascadia margin (Teichert et al. 2009).

This process likely 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 Pliocene and Pleistocene deposition history of the southwestern Bowers Ridge margin. These 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

subseafloor biogeochemical activity has been shown in a deeper slope setting rather than on a shallow shelf. Hence, such 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. 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 subseafloor 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.

- 770 - The distribution of porewater calcium and magnesium concentrations is effected by
771 carbonate formation, recrystallization and dissolution as well as additional geochemical
772 processes such as the alteration of volcanic ash and deep fluid sources. These signals can
773 be preserved in deeply buried porewaters.
- 774 - Besides concentration profiles, deeply buried porewaters also may preserve isotope
775 signatures. Porewater strontium and calcium isotope values can provide valuable
776 information on diagenetic processes such as the alteration of reactive silicates in the
777 methanogenic zone, carbonate dissolution and the imprint of deep fluids.

778

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

787

788 **Acknowledgments**

789 This research used samples and data provided by the Integrated Ocean Drilling
790 Program. We acknowledge the great support of the IODP Expedition 323 shipboard scientists
791 and staff, especially the co-chief scientists C. Ravelo and K. Takahashi. We would like to
792 thank M. Segl and G. Lavik for isotope analyses of diagenetic carbonate phases. Thanks to C.
793 Vogt, J. Birkenstock, and M. Dankworth for assistance during XRD analyses and S. Flotow
794 for providing high quality petrographic thin sections. We would like to thank T.G. Ferdelman

for supporting this participation in IODP. L.M. Wehrmann acknowledges funding by the German Max Planck Society and the German Research Foundation (DFG grand We 5015/1-1). C. Ockert, B.M.A. Teichert and N. Gussone acknowledge funding by DFG grand GU 1035/1. A. Mix thanks A. Ross for assistance with isotopic analyses, and USSSP and the US National Science Foundation NSF (grant OCE0962949) for funding. P. Meister acknowledges funding by the Swiss National Science Foundation (SNF). We would like to thank M. Malone and an anonymous reviewer for their insightful comments, and K. Takahashi for editorial handling of the manuscript.

References

- Aagard, P., Egeberg, P. K., Smalley, P. C., 1989. Diagenetic reactions in Leg 104 sediments inferred from isotope and major element chemistry of interstitial waters. In: Eldholm, O., Thiede, J., Taylor, E., et al., (Eds.). *Proc. Ocean Drilling Sci. Results*, 104, 273-280.
- Adler, M., Hensen, C., Kasten, S., Schulz, H. D., 2000. Computer simulation of deep sulfate reduction in sediments of the Amazon Fan. *Int. J. Earth Sciences* 88, 641-654.
- Aiello, I. W., Ravelo, A. C., 2012. Evolution of marine sedimentation in the Bering Sea since the Pliocene. *Geosphere*, in press.
- Aloisi, G., Pierre C., Rouchy, J.-M., Foucher, J.-P., Woodside, J., and the MEDINAUT Scientific Party, 2000. Methane-related authigenic carbonates of eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilization. *EPSL* 184, 321-338.
- Aloisi, G., Bouloubassi, I., Heijs, S. K., Pancost, R.D., Pierre, C., Damsté, J. S. S., Gottschal, J. C., Forney, L. J., Rouchy, J. M., 2002. CH₄-consuming microorganisms and the formation of carbonate crusts at cold seeps. *Earth Planet. Sci. Lett.* 203, 195-203.
- Aguilar-Islas, A. M., Hurst, M. P., Buck, K. N., Sohst, B., Smith, G. J., Lohan, M. C., Bruland, K. W., 2007. Micro- and macronutrients in the southeastern Bering Sea: Insight into iron-replete and iron-depleted regimes. *Prog. Oceanogr.* 73, 99-126.
- Arndt, S., Brumsack, H.-J., and Wirtz, K. W., 2006. Cretaceous black shales as active bioreactors: A biogeochemical model for the deep biosphere encountered during ODP Leg 207 (Demerara Rise). *Geochim. Cosmochim. Acta* 70, 408-425.
- Arndt, S., Hetzel, A., and Brumsack, H.-J., 2009. Evolution of organic matter degradation in Cretaceous black shales inferred from authigenic barite: A reaction-transport model. *Geochim. Cosmochim. Acta* 73, 2000-2022.
- Arning, E.T., Lückge, A., Breuer, C., Gussone, N., Birgel, D., Peckmann, J., 2009. Genesis of phosphorite crusts off Peru. *Marine Geology* 262, 68-81.
- Baker, P. A., Burns, S. J., 1985. Occurrence and Formation of Dolomite in Organic-Rich Continental-Margin Sediments. *AAPG Bull.* 69, 1917-1930.
- Baker, P. A., Kastner M., 1981. Constraints on the formation of sedimentary dolomite. *Science*, 213, 214-216.
- Banse, K., English, D. C., 1999. Comparing phytoplankton seasonality in the eastern and western subarctic Pacific and the western Bering Sea. *Prog. Oceanogr.* 43, 235-288.
- Barker, J. F., Fritz, P., 1981. Carbon isotopic fractionation during microbial methane oxidation. *Nature* 293, 289-291.

- Ben-Avraham, Z., Cooper A. K., 1981. Early evolution of the Bering Sea collision of oceanic rises and North Pacific subduction zones. *Geol. Soc. Am. Bullet.* 92, 485-495.
- Bian, L., Hinrichs, K.-U., Xie, T., Brassell, S. C., Iversen, N., Fossing, H., Jørgensen, B. B., 2001. Algal and archaeal polyisoprenoids in a recent marine sediment: Molecular isotopic evidence for anaerobic oxidation of methane. *Geochemistry Geophysics Geosystems* 2, 1-22.
- Bickert, T., 2006. Influence of geochemical processes on stable isotope distribution in marine sediments. In: Schulz, H. D., Zabel, M., (Eds.), *Marine Geochemistry*. Springer, Berlin Heidelberg.
- Birgel, D., Peckmann, J., 2008. Aerobic methanotrophy at ancient marine methane-seeps: A synthesis. *Organic Geochemistry* 39, 1659-1667.
- Blanc, G., Vitali, F., Stille, P., 1995. Unusual diagenetic alteration of volcanoclastic sediments in the Tonga fore-arc: Evidence from chemical and strontium isotopic composition of interstitial waters. *Geochem. Cosmochim. Acta* 22, 4633-4644.
- Boatman, C.D. and Murray, J.W., 1982. Modeling exchangeable NH_4^+ adsorption in marine sediments: Process and controls of adsorption. *Limnol. Oceanogr.* 27, 99-110.
- Boetius, A., Ravensschlag, K., Schubert, C. J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B. B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature* 407, 623-626.
- Boudreau, B. P., Canfield, D. E., 1988. A Provisional Diagenetic Model for pH in Anoxic Porewaters - Application to the Foam Site. *J. Mar. Res.* 46, 429-455.
- Boudreau, B. P., Canfield, D. E., 1993. A comparison of closed- and open system models for porewater pH and calcite-saturation state. *Geochim. Cosmochim. Acta* 57, 317-334.
- Brown, Z. W., van Dijken, G. L., Arrigo, K. R., 2011. A reassessment of primary production and environmental change in the Bering Sea. *J. Geophys. Res.* 116, C08014.
- Brumsack, H.-J., and Gieskes J., 1983. Interstitial water trace metal chemistry of laminated sediments from the Gulf of California Mexico. *Marine Chemistry* 14, 86-106.
- Burns, S. J., Baker, P. A., Showers, W. J., 1988. The factors controlling the formation and chemistry of dolomite in organic-rich sediments: Miocene Drakes Bay Formation, California. In: Shukla, V. Baker, P. A. (Eds.), *Sedimentology and Geochemistry of Dolostone*. SEPM Spec. Pub., Tulsa, vol. 43, pp. 3-10.
- Compton, J. S., Siever, R., 1986. Diffusion and mass balance of Mg during early dolomite formation, Monterey Formation. *Geochem. Cosmochim. Acta* 50, 125-135.
- Cooper, A. K., Marlow, M. S., Ben-Avraham, Z., 1981. Multichannel seismic evidence bearing on the origin of Bowers Ridge, Bering Sea. *Geol. Soc. Am. Bullet.* 92, 474-484.
- Cooper, A. K., Marlow, M. S., Scholl, D. W., Stevenson, A. J., 1992. Evidence for Cenozoic crustal extension in the Bering Sea region. *Tectonics* 11(4), 719-731.
- Crowley, T.J., 1991. Modeling Pliocene warmth. *Quat. Sci. Rev.* 10, 275-282.
- Degens, E. T., Guillard, R. R. L., Sackett, W. M., Hellebust, J. A., 1968. Metabolic fractionation of carbon isotopes in marine plankton. I. Temperature and respiration experiments. *Deep Sea Research* 15: 1-9.
- Dickens, G. R., 2001. Sulfate profiles and barium fronts in sediment on the Blake Ridge: present and past methane fluxes through a large gas hydrate reservoir. *Geochim. Cosmochim. Acta* 65, 529-543.
- Dickson, J. A. D., 1966. Carbonate identification and genesis as revealed by staining. *J. Sed. Petrol* 35, 643-655.
- D'Hondt S., Rutherford S., and Spivack A. J. 2002. Metabolic activity of subsurface life in deep-sea sediments. *Science* 295(5562), 2067-2070.
- D'Hondt, S., Jørgensen, B. B., Miller, D. J., Batzke, A., Blake, R., Cragg, B. A., Cypionka, H., Dickens, G. R., Ferdelman, T., Hinrichs, K. U., Holm, N. G., Mitterer, R., Spivack, A., Wang, G. Z., Bekins, B., Engelen, B., Ford, K., Gettemy, G., Rutherford, S. D., Sass, H., Skilbeck, C. G., Aiello, I. W., Guerin, G., House, C. H., Inagaki, F., Meister, P., Naehr, T., Niitsuma, S., Parkes, R. J., Schippers, A., Smith, D. C., Teske, A., Wiegand, J., Padilla, C. N., Acosta, J. L. S., 2004. Distributions of microbial activities in deep subseafloor sediments. *Science* 306, 2216-2221.

- 891 Elderfield, H., Gieskes, J. M., 1982. Sr isotopes in interstitial waters of marine sediments from Deep
892 Sea Drilling Project cores, *Nature* 300, 493–497.
- 893 Elderfield, H., 1986. Strontium isotope stratigraphy, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 57, 71–
894 90.
- 895 Egeberg, P. K., the Leg 126 Shipboard Scientific Party, 1990. Unusual composition of pore waters
896 found in the Izu-onin fore-arc sedimentary basin. *Nature* 344, 215–218.
- 897 Emerson, S., Jahnke, R., Bender, M., Froelich, P., Klinkhammer, G., Bowser, C., Setlock, G., 1980.
898 Early Diagenesis in Sediments from the Eastern Equatorial Pacific.1. Pore Water Nutrient and
899 Carbonate Results. *Earth Planet. Sci. Lett.* 49(1), 57–80.
- 900 Expedition 323 Scientists, 2010. Bering Sea paleoceanography: Pliocene–Pleistocene
901 paleoceanography and climate history of the Bering Sea. Integrated Ocean Drilling Program,
902 Preliminary Report 323. doi:10.2204/iodp.pr.323.2010
- 903 Expedition 323 Scientists, 2011a. Methods. In Proc. IODP, 323 (eds. Takahashi K., Ravelo A. C.,
904 Alvarez Zarikian C. A., and the Expedition 323 Scientists). Integrated Ocean Drilling Program
905 Management International, Inc, Tokyo. doi:10.2204/iodp.proc.323.102.2011
- 906 Expedition 323 Scientists, 2011b. Site U1341. In Proc. IODP, 323 (eds. Takahashi K., Ravelo A. C.,
907 Alvarez Zarikian C. A., and the Expedition 323 Scientists). Integrated Ocean Drilling Program
908 Management International, Inc, Tokyo. doi:10.2204/iodp.proc.323.105.2011
- 909 Fantle M. S. and DePaolo D. J., 2007. Ca isotopes in carbonate sediment and pore fluid from ODP Site
910 807A: The $\text{Ca}^{2+}(\text{aq})$ -calcite equilibrium fractionation factor and calcite recrystallization rates
911 in Pleistocene sediments. *Geochim. Cosmochim. Acta*, 71, 2524–2546.
- 912 Farrell, J.W., Clemens, S.C., and Gromet, L.P., 1995. Improved chronostratigraphic reference curve of
913 late Neogene seawater $^{87}\text{Sr}/^{86}\text{Sr}$. *Geol.* 23, 403–406.
- 914 Fenchel, T. M. and Jørgensen, B. B., 1977. Detritus food chains of aquatic ecosystems: The role of
915 bacteria. In: Alexander, M. (ed), *Advances in Microbial Ecology*, 1, Plenum Press, NY, pp. 1–
916 58.
- 917 Ferry, J. G., 1992. Methane from acetate. *J. Bacteriol.* 174, 5489–5495.
- 918 Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D.,
919 Dauphin, P., Hammond, D., Hartman, B., Maynard V., 1979. Early oxidation of organic
920 matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim.*
921 *Cosmochim. Acta* 43(7), 1075–1090.
- 922 Garrison, R. E., Graham, S. A., 1984. Early diagenetic dolomites and the origin of dolomite-bearing
923 breccias, lower Monterey Formation, Arroyo Seco, Monterey County, California. In: Garrison,
924 R. E., Kastner, M., Zenger, D. H. (Eds.), *Dolomites of the Monterey Formation and Other*
925 *Organic-rich Units*. Pacific Sect. SEPM 41, 87–101.
- 926 Gieskes, J. M., Lawrence, J. R., 1981. Alteration of volcanic matter in deep sea sediments: evidence
927 from chemical composition of interstitial waters from deep sea drilling cores. *Geochim.*
928 *Cosmochim. Acta* 45, 1687–1703.
- 929 Gieskes, J. M., Gamo, T., Brumsack, H., 1991, Chemical methods for interstitial water analysis aboard
930 JOIDES Resolution. ODP Tech. Note, 15. doi:10.2973/odp.tn.15.1991
- 931 Gussone, N., Eisenhauer, A., Heuser, A., Dietzel, M., Bock, B., Böhm, F., Spero, H. J., Lea, D.W.,
932 Bijma, J., and Nägler, T. F., 2003. Model for Kinetic Effects on Calcium Isotope Fractionation
933 ($\delta^{44}\text{Ca}$) in Inorganic Aragonite and Cultured Planktonic Foraminifera. *Geochim. Cosmochim.*
934 *Acta* 67 (7), 1375–1382.
- 935 Gussone, N., Böhm, F., Eisenhauer, A., Dietzel, M., Heuser, A., Teichert, B. M. A., Reitner, J.,
936 Wörheide, G., Dullo, W.-C., 2005. Calcium isotope fractionation in calcite and aragonite.
937 *Geochim. Cosmochim. Acta* 69, 4485–4494.
- 938 Gussone, N., Nehrke, G. and Teichert, B.M.A., 2011. Calcium isotope fractionation in ikaite and
939 vaterite. *Chem. Geol.* 285, 194–202.
- 940 Haug, G. H., Ganopolski, A., Sigman, D. M., Rosell-Mele, A., Swann, G. E. A., Tiedemann, R.,
941 Jaccard, S. L., Bollmann, J., Maslin, M. A., Leng M. J., Eglinton, G., 2005. North Pacific
942 seasonality and the glaciation of North America 2.7 million years ago, *Nature* 433, 821–825.
- 943 Haywood, A. M., Valdes, P. J., 2004. Modelling Pliocene warmth: Contribution of atmosphere, ocean
944 and cryosphere. *Earth Planet. Sci. Lett.* 218, 363–377.

- Hawkesworth, C. J., Elderfield, H., 1978. The strontium isotopic composition of interstitial waters from Sites 245 and 336 of the Deep Sea Drilling Project. *EPSL* 40, 423-432.
- Hensen, C., Zabel, M., Pfeifer, K., Schwenk, T., Kasten, S., Riedinger, N., Schulz, H. D., Boetius, A., 2003. Control of sulfate pore-water profiles by sedimentary events and the significance of anaerobic oxidation of methane for the burial of sulfur in marine sediments. *Geochim. Cosmochim. Acta* 67, 2631-2647.
- Heuser, A., Eisenhauer, A., Gussone, N., Bock, B., Hansen, B. T., and Nägler, T. F., 2002. Measurement of Calcium Isotopes ($\delta^{44}\text{Ca}$) Using a Multicollector TIMS Technique. *International Journal of Mass Spectrometry* 220, 387-399.
- Hippler, D., Schmitt, A.-D., Gussone, N., Heuser, A., Stille, P., Eisenhauer, A., and Nägler, T. F., 2003. Ca isotopic composition of various standards and seawater. *Geostandards Newsletter The Journal of Geostandards and Geoanalysis*, 27 (1), 13-19.
- Hoehler, T. M., Alperin, M. J., Albert, D. B., Martens, C. S., 1994. Field and laboratory studies of methane oxidation in an anoxic marine sediment — evidence for a methanogensulfate reducer consortium. *Glob. Biogeochem. Cycles* 8, 451-463.
- Jicha, B. R., Scholl, D. W., Singer, B. S., Yogodzinski, G. M., Kay, S. M., 2006. Revised age of Aleutian Island Arc formation implies high rate of magma production. *Geology* 34, 661-664. doi:10.1130/G22433.1.
- Jørgensen, B. B., 1982. Mineralization of organic matter in the sea bed-the role of sulphate reduction. *Nature* 296, 643-645.
- Jørgensen, B.B., 2006. Bacteria and Marine Biogeochemistry. In: Schulz H.D., Zabel, M., *Marine Geochemistry*, 2nd edition, Springer, pp. 169-206.
- Hoehler, T. M., Alperin, M. J., Albert, D. B., Martens, C. S., 1994. Field and Laboratory Studies of Methane Oxidation in an Anoxic Marine Sediment - Evidence for a Methanogen-Sulfate Reducer Consortium. *Global. Biogeochem. Cy.* 8, 451-463.
- Kastner M., 1984. Control of dolomite formation. *Nature*, 311, 410-411.
- Kawabata, H., Sato, K., Tatsumi, Y., Scholl, D. W., Takahashi, K., the Expedition 323 Scientists, 2011. Description of basement volcanic sequences in Holes U1342A and U1342D on Bowers Ridge in the Bering Sea. In *Proc. IODP, 323* (eds. Takahashi K., Ravelo A. C., Alvarez Zarikian C. A., and the Expedition 323 Scientists). Integrated Ocean Drilling Program Management International, Inc, Tokyo. doi:10.2204/iodp.proc.323.110.2011
- Kelts, K., McKenzie, J. A., 1982. Diagenetic Dolomite Formation in Quaternary Anoxic Diatomaceous Muds of Deep-Sea Drilling Project Leg-64, Gulf of California. *Initial Reports of the Deep Sea Drilling Project* 64, 553-569. doi:10.2973/dsdp.proc.64.110.1982
- Kim, S.-T. and O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, *Geochim. Cosmochim. Acta* 61, 3461-3475.
- Kinder, T. H., Coachman, L. K., 1978. Front Overlaying Continental Slope in Eastern Bering Sea. *J. Geophys. Res.-Oceans*. 83, 4551-4559.
- König, I., Haeckel, M., Lougear, A., Suess, E., Trautwein, A. X., 2001. A geochemical model of the Peru Basin deep-sea floor –and the response of the system to technical impacts. *Deep-Sea Res. II* 48, 3737-3756.
- Lawrence, J. R., Drever, J. I., Anderson, T. F., Brueckner, H. K., 1979. Importance of volcanic alteration in the sediments of site 323: chemistry, $\text{O}^{18}/\text{O}^{16}$, $\text{Sr}^{87}/\text{Sr}^{86}$. *Geochim. Cosmochim. Acta* 43, 573-588.
- Lemarchand D., Wasserburg G. J., and Papanastassiou D. A., 2004. Rate-controlled Calcium Isotope Fractionation in Synthetic Calcite. *Geochim. Cosmochim. Acta* 68(22), 4665-4678.
- Lumsden, D. N., 1979. Discrepancy between thin-section and X-ray estimates of dolomite in limestone. *J. Sed. Petrol.* 49, 429-435.
- Luff, R., Wallmann, K., 2003. Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: Numerical modeling and mass balances. *Geochim. Cosmochim. Acta* 67, 3403-3421.
- Magalhães, V.H., Pinheiro, L.M., Ivanov, M.K., Kozlova, E., Blinova, V., Kolganova, J., Vasconcelos, C., McKenzie, J.A., Bernasconi, S.M., Kopf, A.J., Díaz-del-Río, V., González, F.J., Somoza, L., 2012. Formation processes of methane-derived authigenic carbonates from

999 the Gulf of Cadiz. *Sed. Geol.* 243-244, 155-168.

1000 Malone, M. J., Claypool, G., Martin, J. B., Dickens, G. R., 2002. Variable methane fluxes in shallow
1001 marine systems over geologic time: The composition and origin of pore waters and authigenic
1002 carbonates on the New Jersey shelf. *Marine Geology* 189, 175-196.

1003 McManus, J., Berelson, W. M., Klinkhammer, G. P., Johnson, K. S., Coale, K. H., Anderson, R. F.,
1004 Kumar, N., Burdige, D. J., Hammond, D. E., Brumsack, H.-J., McCorkle, D. C., and Rushdi
1005 A., 1998. Geochemistry of barium in marine sediments: Implications for its use as a
1006 paleoproxy. *Geochim. Cosmochim. Acta* 62, 3453–3473.

1007 Manheim, F. T., Brooks, E. G., Winters, W. J., 1994. Description of a hydraulic sediment squeezer:
1008 U.S. Geological Survey Open-File Report 94–584, 39 p.

1009 Marriott, C. S., Henderson, G. M., Belshaw, N. S., Tudhope, A. W., 2004. Temperature dependence of
1010 $\delta^7\text{Li}$, $\delta^{44}\text{Ca}$ and Li/Ca during growth of calcium carbonate. *Earth Planet. Sci. Lett.* 222, 615–
1011 624.

1012 Martens, C. S., Berner, R. A., 1974. Methane production in interstitial waters of Sulfate-depleted
1013 marine sediments. *Science* 185, 1167-1169.

1014 Martin, J. B., 1994. Diagenesis and hydrology at the New Hebrides Forearc and intra-arc Aoba Basin.
1015 In: Greene, H. G., Collot, J.-Y., Stokking, L. B., et al., (Eds.), *Proc. Ocean Drilling Prog. Sci*
1016 *Results*, 134, 109-130.

1017 März, C., Hoffmann, J., Bleil, U., de Lange, G. J., Kasten, S., 2008. Diagenetic changes of magnetic
1018 and geochemical signals by anaerobic methane oxidation in sediments of the Zambezi deep-
1019 sea fan (SW Indian Ocean). *Mar. Geol.* 255, 118-130.

1020 März, C., Schnetger, B., Brumsack H.-J., 2013. Nutrient leakage from the North Pacific to the Bering
1021 Sea (IODP Site U1341) following the onset of Northern Hemispheric Glaciation ?
1022 *Paleoceanography*, 28(1), 68-78.

1023 Mazzullo, S.J., 2000. Organogenic dolomitization in peritidal to deep-sea sediments. *Journal of*
1024 *Sedimentary Research* 70(1), 10-23.

1025 Meister, P., McKenzie, J. A., Warthmann, R., Vasconcelos, C., 2006. Mineralogy and petrography of
1026 diagenetic dolomite from the ODP Leg 201 Peru Margin drill sites. In: Jørgensen, B.B.,
1027 D'Hondt, S., Miller, J. (Eds.), *College Station, TX (Ocean Drilling Program). Proc. ODP, Sci.*
1028 *Results*, vol. 201.

1029 Meister, P., McKenzie, J. A., Vasconcelos, C., Bernasconi, S., Frank, M., Gutjahr, M., Schrag, D. P.,
1030 2007. Dolomite formation in the dynamic deep biosphere: results from the Peru Margin.
1031 *Sedimentology* 54, 1007-1031.

1032 Meister, P., Bernasconi, S. M., Vasconcelos, C., McKenzie, J. A., 2008. Sealevel changes control
1033 diagenetic dolomite formation in hemipelagic sediments of the Peru Margin. *Marine Geology*
1034 252, 166-173.

1035 Meister, P., Gutjahr, M., Frank, M., Bernasconi, S., McKenzie, J. A., Vasconcelos, C., 2011a.
1036 Dolomite formation within the methanogenic zone induced by tectonically-driven fluids in the
1037 Peru accretionary prism. *Geology* 39, 563-566.

1038 Meister, P., Reyes, C., Beaumont, W., Rincon, M., Collins, L., Berelson, W., Stott, L., Corsetti, F.,
1039 Nealson, K.H., 2011b. Calcium and magnesium-limited dolomite precipitation at Deep
1040 Springs Lake, California. *Sedimentology* 58(7), 1810-1830.

1041 Meister, P., 2013. Two opposing effects of sulfate reduction on carbonate precipitation in normal
1042 marine, hypersaline, and alkaline environments. 41(4), 499-502.

1043 Mix, A. C., Tiedemann, R., Blum, P., et al., 2003. *Proceedings of the Ocean Drilling Program, Initial*
1044 *Reports* 202. doi:10.2973/odp.proc.ir.202.2003

1045 Moore, T. S., Murray, R. W., Kurtz, A.C., Schrag, D.P., 2004. Anaerobic methane oxidation and the
1046 formation of dolomite. *Earth Planet. Sci. Lett.* 229, 141-154.

1047 Mudelsee, M., Raymo, M. E., 2005. Slow dynamics of the Northern Hemisphere glaciation.
1048 *Paleoceanography* 20, PA 4022.

1049 Murata, K. J., Friedman, I., Madsen, B. A., 1969. Isotopic Composition of Diagenetic Carbonates in
1050 Marine Miocene Formations of California and Oregon. *USGS Prof. Paper*, Vol. 614-B, p. 24.

1051 Leblanc, K., Hare, C. E., Boyd, P. W., Bruland, K. W., Sohst, B., Pickmere, S., Lohan, M. C., Buck,
1052 K., Ellwood, M., Hutchins, D. A., 2005. Fe and Zn effects on the Si cycle and diatom

- community structure in two contrasting high and low-silicate HNLC areas. *Deep-Sea Research Part I-Oceanographic Research Papers* 52(10), 1842-1864.
- Luff, R., Wallmann, K., 2003. Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: Numerical modeling and mass balances. *Geochim. Cosmochim. Acta* 67, 3403-3421.
- Ockert, C., Gussone, N., Kaufhold, S., Teichert, B. M. A., 2013. Isotope fractionation during Ca exchange on clay minerals in a marine environment. *Geochem. Cosmochim. Acta* 112, 374-388.
- Ockert, C., Wehrmann L.M., Kaufhold S., Ferdelman T.G., Teichert B.M.A., Calcium-ammonium exchange on standard clay minerals and natural marine sediments in seawater. *Isotopes in Environmental and Health Studies*, in press.
- Ohmoto, H., and Rye, R.O., 1979. Isotope of sulfur and carbon, in Barnes, H. L. Ed., *Geochemistry of Hydrothermal deposits*, John Wiley & Sons, p. 509-567.
- Okkonen, S. R., Schmidt, G. M., Cokelet, E. D., Stabeno, P. J., 2004. Satellite and hydrographic observations of the Bering Sea 'Green Belt'. *Deep-Sea Res. Pt. II* 51, 1033-1051.
- Onodera J., Takahashi K. and Nagatomo R.. Diatoms, silicoflagellates, and ebridians at Site U1341 on the western slope of Bowers Ridge, IODP Expedition 323. *Deep-Sea Res. Pt. II*, this issue.
- Parkes, R. J., Webster, G., Cragg, B. A., Weightman, A. J., Newberry, C. J., Ferdelman, T. G., Kallmeyer, J., Jørgensen, B.B., Aiello, I.W., Fry, J.C., 2005. Deep sub-seafloor prokaryotes stimulated at interfaces over geological time. *Nature* 436, 390-394.
- Perry, E. A., Gieskes, J. M., Lawrence, J. R., 1976. Mg, Ca and O¹⁸/O¹⁶ exchange in the sediment-pore water system, Hole 149, DSDP. *Geochim. Cosmochim. Acta* 40, 413-423.
- Pimmel, A., and G. Claypool, 2001. Introduction to shipboard organic geochemistry on the JOIDES Resolution. ODP Tech. Note, 30. doi:10.2973/odp.tn.30.2001
- Pisciotta, K. A., Mahoney, J. J., 1981. Isotopic survey of diagenetic carbonates. In: Yeats, R. S., Haq, B. U. et al. (Eds.), *Init. Repts. DSDP US Govt. Printing office*. Washington, D.C., vol. 63, pp. 595-609.
- Pufahl, P. K., and Wefer, G., 2001. Data report: Petrographic, cathodoluminescent, and compositional characteristics of organogenic dolomites from the southwest African margin. In Wefer, G., Berger, W.H., and Richter, C. (Eds.), *Proc. ODP, Sci. Results*, 175, 1-17
- Raiswell, R., (1988). Chemical model for the origin of minor limestone-shale cycles by anaerobic methane oxidation. *Geol.* 16, 641-644.
- Riedinger, N., Pfeifer, K., Kasten, S., Garman, J. F. L., Vogt, C., Hensen, C., 2005. Diagenetic alteration of magnetic signals by anaerobic oxidation of methane related to a change in sedimentation rate. *Geochim. Cosmochim. Acta* 69, 4117-4126.
- Ritger, S., Carson, B., Suess, E., 1987. Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. *Geological Society of America Bulletin*, 98, 147-156.
- Rodriguez, N. M., Paull, C. K., and Borowski, W. S., 2000, Zonation of authigenic carbonates within gas hydrate-bearing sedimentary sections on the Blake ridge: Offshore southeastern North America, in Paull, C.K., et al., eds., *Proceedings of the Ocean Drilling Program, Scientific results*, Volume 164: College Station, Texas, Ocean Drilling Program, p. 301-312.
- Rosenbaum, J., Sheppard, S. M. F., 1986. An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochim. Cosmochim. Acta* 50, 1147-1150.
- Rosenfeld, J.K., 1978. Ammonium adsorption in nearshore anoxic sediments. *Limnol. Oceanogr.* 24, 356-364.
- Sambrotto, R. N., Mordy, C., Zeeman, S. I., Stabeno, P. J., Macklin, S. A., 2008. Physical forcing and nutrient conditions associated with patterns of Chl a and phytoplankton productivity in the southeastern Bering Sea during summer. *Deep-Sea Res. Pt. II* 55, 1745-1760.
- Sánchez-Román, M., McKenzie, J.A., de Luca Rebello Wagener, A., Rivadeneyrac, M. A., and Vasconcelos, C., 2009. Presence of sulfate does not inhibit low-temperature dolomite precipitation. *Earth Planet. Sci. Lett.* 285, 131-139.

- 1106 Sansone, F. J., Martens, C. S., 1981. Methane Production from Acetate and Associated Methane
1107 Fluxes from Anoxic Coastal Sediments. *Science* 211, 707-709.
- 1108 Schippers, A., Neretin, L. N., Kallmeyer, J., Ferdelman, T. G., Cragg, B. A., Parkes, R. J., Jørgensen,
1109 B. B., 2005. Prokaryotic cells of the deep sub-seafloor biosphere identified as living bacteria.
1110 *Nature* 433, 861-864.
- 1111 Scholz, F., Hensen, C., Schmidt, M., Geersen, J., 2013. Submarine weathering of silicate minerals and
1112 the extent of pore water freshening at active continental margins. *Geochim. Cosmochim. Acta*
1113 100, 200-216.
- 1114 Schrag, D.P., Higgins, J.A., Macdonald, F.A., Johnston, D.T., 2013. Authigenic Carbonate and the
1115 History of the Global Carbon Cycle. *Science* 339, 540-543.
- 1116 Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., Kölling M., 2005. Rhizon sampling of porewaters
1117 near the sediment-water interface of aquatic systems. *Limnol. Oceanogr.: Methods* 3, 361-371.
- 1118 Shackleton, N. J., Hall, M.A., 1984. Oxygen and carbon isotope stratigraphy of Deep Sea Drilling
1119 Project hole 552A: Plio-Pleistocene glacial history. *Initial Rep. Deep Sea Drill. Proj.* 81, 599–
1120 609.
- 1121 Sheppard, S.M.F., and Schwarcz, H.P., 1970. Fractionation of carbon and oxygen isotopes and
1122 magnesium between coexisting metamorphic calcite and dolomite. *Contrib. Mineral. Petrol.*
1123 26, 161-198.
- 1124 Soetaert, K., Hofmann, A. F., Middelburg, J. J., Meysman, F. J. R., Greenwood, J., 2007. The effect of
1125 biogeochemical processes on pH. *Mar. Chem.* 106, 380-401.
- 1126 Springer, A. M., McRoy, C. P., Flint, M. V., 1996. The Bering Sea Green Belt: shelf-edge processes
1127 and ecosystem production. *Fish. Oceanogr.* 5, 205–223.
- 1128 Takahashi, K., 1999. Paleooceanographic changes and present environment of the Bering Sea, in:
1129 Loughlin, T.R., Ohtani, K. (Eds.), *Dynamics of the Bering Sea*. North Pacific Marine Science
1130 Organization (PICES), Fairbanks, pp. 365-385.
- 1131 Takahashi, K., 2002. Long term monitoring of particle fluxes in the Bering Sea and the central
1132 subarctic Pacific Ocean, 1990-2000. *Prog. Ocean.* 55, 95-112.
- 1133 Takahashi, K., 2005. The Bering Sea and paleoceanography. *Deep-Sea Res. II* 52, 2080-2091.
- 1134 Takahashi, K., Ravelo, A. C., Alvarez Zarikian, C. A., 2009. Pliocene–Pleistocene paleoceanography
1135 and climate history of the Bering Sea. *IODP Sci. Prosp.*, 323. doi:10.2204/iodp.sp.323.2009
- 1136 Tang J., Dietzel M., Böhm F., Köhler S. J., Eisenhauer A., 2008. Sr²⁺/Ca²⁺ and 44Ca/40Ca
1137 fractionation during inorganic calcite formation: II. Ca isotopes. *Geochim. Cosmochim. Acta*,
1138 72, 3733-3745.
- 1139 Teichert, B. M. A., Torres, M. E., Bohrmann, G., Eisenhauer, A., 2005. Fluid sources, fluid pathways
1140 and diagenetic reactions across an accretionary prism revealed by Sr and B geochemistry.
1141 *Earth Planet. Sci. Lett.* 239, 106-121.
- 1142 Teichert, B. M. A., Gussone, N. and Torres, M. E., 2009. Controls on Calcium Isotope Fractionation in
1143 Sedimentary Porewaters. *Earth Planet. Sci. Lett.* 279, 373-382.
- 1144 Teichert, B.M.A., Meister, P., Mavromatis, V., Ockert, C., Gussone, N., Early diagenetic, primary
1145 dolomite formation on the Peru Margin - Insights from Ca and Mg isotopes. *Earth Planet. Sci.*
1146 *Lett.*, submitted.
- 1147 Teske A., Sørensen K. B., 2008. Uncultured archaea in deep marine subsurface sediments: have we
1148 caught them all? *ISME J.* 2, 3-18.
- 1149 Thornburg, T. M., Suess, E., 1990. Carbonate cementation of granular and fracture porosity;
1150 implications for the Cenozoic hydrologic development of the Peru Continental Margin. In:
1151 *Proc. ODP. Sci. Results* 112, 95-109. Ocean Drilling Program. College Station, TX.
- 1152 Torres, M. E., Brumsack, H. J., Bohrmann, G., Emeis, K. C., 1996. Barite fronts in continental margin
1153 sediments: a new look at barium remobilization in the zone of sulfate reduction and formation
1154 of heavy barites in diagenetic fronts. *Chem. Geol.* 127, 125-139.
- 1155 Torres, M. E., Mix, A., Rugh, W. D., 2005. Precise $\delta^{13}\text{C}$ analysis of dissolved inorganic carbon in
1156 natural waters using automated headspace sampling and continuous-flow mass spectrometry.
1157 *Limnol. Oceanogr.: Methods* 3, 2005, 349–360.
- 1158 Tribble, J. S., Wilkens, R. H., 1994. Microfabric of altered ash layers, ODP Leg 131, Nankai
1159 Trough. *Clays and Clay Minerals* 42(4), 428-436.

- Tyrrell, T., Merico, A., Waniek, J. J., Wong, C.S., Metzl, N., Whitney, F., 2005. Effect of seafloor depth on phytoplankton blooms in high-nitrate, low-chlorophyll (HNLC) regions. *J. Geophys. Res.-Biogeo.* 110, G02007.
- Ussler, W., Paull, C. K., 2008. Rates of anaerobic oxidation of methane and authigenic carbonate mineralization in methane-rich deep-sea sediments inferred from models and geochemical profiles. *Earth Planet. Sci. Lett.* 266, 271-287.
- Valentine, D. L., Reeburgh, W. S., 2000. New perspectives on anaerobic methane oxidation. *Environ. Microbiol.* 2, 477-484.
- Vasconcelos, C., McKenzie, J. A., Warthmann, R., Bernasconi, S., 2005. Calibration of the $\delta^{18}\text{O}$ paleo-thermometer with dolomite formed in microbial cultures and natural environments. *Geology* 33, 317-320.
- Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebner, S., Godderis, Y., Jasper, T., Korte, G., Pawellek, F., Podlaha, O.G. and Strauss, H. (1999) $^{87}\text{Sr}/^{86}\text{Sr}$, d^{13}C and d^{18}O evolution of Phanerozoic seawater. *Chem. Geol.*, 161, 59-88.
- von Breyman, M. T., Collier, R., Suess, E., 1990. Magnesium adsorption and ion exchange in marine sediments: A multi-component model. *Geochim. Cosmochim. Acta* 54, 3295-3313.
- Von Breyman, M. T., Brumsack, H.-J., and Emeis K.-C., 1992. Depositional and diagenetic behaviour of barium in the Japan Sea. *Proc. ODP, Sci. Results* 127/128, 651-663.
- Wallmann, K., Aloisi, G., Haeckel, M., Tishchenko, P., Pavlova, G., Greinert, J., Kutterolf, S., and Eisenhauer, A., 2008. Silicate weathering in anoxic marine sediments. *Geochim. Cosmochim. Acta* 72, 3067-3090.
- Wanke, M., Portnyagin, M., Hoernle, K., Werner, R., Hauff, F., van den Bogaard, P., Garbe-Schönberg, D., 2012. Bowers Ridge (Bering Sea): An Oligocene-Early Miocene island arc. *Geology* 40, 687-690. doi: 10.1130/G33058.1
- Wehrmann, L. M., Risgaard-Petersen, N., Schrum, H. N., Walsh, E. A., Huh, Y., Ikehara, M., Pierre, C., D'Hondt, S., Ferdelman, T. G., Ravelo A. C., Takahashi K., Alvarez Zarikian C., the IOPD Exp. 323 Scientific Party, 2011. Coupled organic and inorganic carbon cycling in the deep seafloor sediment of the northeastern Bering Sea slope (IODP Exp. 323). *Chem. Geol.* 284, 251-261.
- Wehrmann, L. M., Arndt, S., März, C., Ferdelman, T. G., Brunner B., 2013. The evolution of early diagenetic signals in Bering Sea seafloor sediments in response to varying organic carbon deposition over the last 4.3 Ma. *Geochim. Cosmochim. Acta* 109, 175-196. .
- Whiticar, M. J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 161, 291-314.
- Whiticar, M. J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments – CO_2 reduction vs. acetate fermentation-Isotope evidence. *Geochim. Cosmochim. Acta* 50, 693-709.

1208 **Tables**

1209 Table 1. Depth and composition of diagenetic carbonate concretions and disseminated
1210 carbonate phases at Site U1341.

Sample ID	Depth [mbsf]	Calcite [%]	Dolomite [%]	$\delta^{13}\text{C}$ [‰PDB]	$\delta^{18}\text{O}$ [‰PDB]
Dolomite concretions					
323-U1341A-22H-3, 80-98 cm	200.5	2.3	70.1	-16.2	5.0
	200.5	2.5	86.6	-16.6	5.3
323-U1341A-22H-3, 98-112 cm	200.7	1.2	81.1	-15.7	4.9
323-U1341A-24H-7, 0-17 cm	221.1	0.0	96.3	-16.6	5.1
323-U1341A-25H-4, 36-41 cm	225.1	0.0	93.7	-16.6	5.1
323-U1341A-25H-4, 104-106 cm	225.7	0.0	92.7	-16.3	5.1
323-U1341A-34H-2, 87-97 cm	301.2	0.0	95.3	-16.0	4.0
323-U1341A-35H-1, 0-10 cm	308.3	2.8	75.4	-16.3	4.6
323-U1341B-42H-3, 100-109 cm	371.5	2.1	53.9	-14.9	3.6
	371.5	0.0	97.0		
323-U1341B-58X-3, 38-42 cm	471.1	0.0	84.8	-15.6	4.2
	471.1	0.0	92.9	-15.7	4.7
323-U1341B-58X-3, 73-75 cm	471.4	0.0	68.5	-16.4	3.2
323-U1341B-58X-5, 120-140 cm	474.9	0.0	97.1	-15.9	4.3
323-U1341B-64X-2, 90-140 cm	527.6	0.0	80.7	-16.0	2.4
323-U1341B-69X-CC, 11-16 cm	573.4	0.0	94.6		
	573.4	0.0	95.2	-16.6	3.2
Mixed calcite-dolomite concretions					
323-U1341A-16H-5, 40-55 cm	142.9	45.1	13.9	-15.5	3.7
323-U1341B-17H-2, 135-150 cm	152.4	53.8	21.5	-16.0	3.8
323-U1341B-17H-3, 0-10 cm	152.5	44.7	26.9	-14.4	3.7
323-U1341A-18H-5, 36-72 cm	161.4	41.6	39.7	-16.2	4.6
323-U1341B-51H-4, 81-87 cm	436.5	46.8	4.3	-15.8	3.1
	436.5	35.3	56.1	-16.0	2.5
Disseminated carbonate phases					
323-U1341A-17H-2, 135-150 cm	148.3				
323-U1341A-17H-3, 0-10 cm	148.5				
323-U1341B-23H-1, 106-150 cm	199.5				
323-U1341B-23H-2, 106-113 cm	200.9				
323-U1341B-23H-2, 137-139 cm	201.2				
323-U1341B-24H-1, 129-139 cm	209.7				
323-U1341B-24H-1, 143-150 cm	209.8		dolomite		
323-U1341B-24H-2, 0-3 cm	209.9				
323-U1341B-24H-2, 9-12 cm	210.0		dolomite		
323-U1341B-26H-7, 0-43 cm	236.1				
323-U1341B-32H-3, 0-12 cm	286.8				
323-U1341A-32H-3, 106-130 cm	287.1				
323-U1341A-32H-5, 138-140 cm	290.3				
323-U1341A-34H-4, 40-42 cm	303.7				
323-U1341A-34H-6, 140-150 cm	307.6				
323-U1341A-34H-7, 0-4 cm	307.7				
323-U1341B-39H-4, 3-10 cm	350.0				
323-U1341B-41H-1, 0-150 cm	358.5				
323-U1341B-60X-6,	495.6		Low TIC content	-13.6	1.9
323-U1341B-60X-7, 96 cm	496.2				
323-U1341B-62X-5, 20-57 cm	512.1				
323-U1341B-62X-6, 92-150 cm	514.3		dolomite	-14.0	1.8
323-U1341B-62X-7, 0-4 cm	514.9				

1211

1212 Table 2. Porewater strontium and calcium isotope composition.

Sample ID	Depth [mbsf]	Normalized $^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{44/40}\text{Ca}$ [‰SRM915a]
U1341A-2H-1	4.4	0.709177	1.56
U1341A-5H-6	39.6	0.709181	1.49
U1341A-12H-6	105.2	0.709141	1.60
U1341A-22H-6	205.2	0.708964	1.66
U1341A-30H-6	271.0	0.708930	1.42
U1341B-41H-5	365.2	0.708770	0.85
U1341B-50H-5	430.5	0.708706	n.d.
U1341B-59X-6	485.9	0.708651	0.84
U1341B-63X-6	524.5	0.708733	0.93
U1341B-68X-6	572.5	0.708787	1.02
U1341B-71X-6	600.9	0.708824	1.25

1213

1214 Table 3. Strontium isotope composition of diagenetic dolomites.

Sample ID	Depth [mbsf]	Normalized $^{87}\text{Sr}/^{86}\text{Sr}$
U1341A-22H-3	200.38	0.708836
U1341A-25H-4	225.47	0.709002
U1341A-34H-2	301.03	0.708968
U1341A-38H-1	332.49	0.708936
U1341B-42H-3	371.83	0.709016
U1341B-58X-3	471.32	0.708259
U1341B-58X-3	471.33	0.708854
U1341B-58X-5	474.96	0.708861
U1341B-69X-cc	573.43	0.708906

1215

1216

1217 Figure captions

1218 **Fig. 1.** Map of the Bering Sea including location of Integrated Ocean Drilling Program
1219 (IODP) Expedition 323 Site U1341 on Bowers Ridge (black dot).

1220

1221 **Fig. 2. a)** Sediment lithology based on Aiello and Ravelo (2012), occurrences of diagenetic
1222 carbonate phases (Expedition 323 Scientists, 2010) and barium-depletion zone
1223 (interval of low Ba/Al ratios based on März et al. (2013)). Diagenetic concretions that
1224 were not analysed or where no sample was available are indicated by a dashed line. **b)**
1225 Sedimentation rates over the last 4.3 Ma based on Onodera et al. (this issue) and **c)**
1226 background total inorganic carbon (TIC) and total organic carbon (TOC) contents.

1227

1228 **Fig. 3.** Porewater **a)** sulfate and chloride concentrations, **b)** magnesium concentration, **c)**
1229 calcium concentration ([Ca]) and calcium isotope composition ($\delta^{44/40}\text{Ca}$), **d)** dissolved
1230 inorganic carbon ([DIC]) concentration (from Expedition 323 Scientists, 2011b) and

carbon isotope composition ($\delta^{13}\text{C-DIC}$), **e**) strontium concentration ($[\text{Sr}]$) and strontium isotope composition ($^{87}\text{Sr}/^{86}\text{Sr}$), **f**) potassium concentration, and **g**) ammonium concentration with depth at Site U1341 (concentrations from Expedition 323 Scientists, 2011b).

Fig. 4. X-ray diffractograms of hard lithified diagenetic carbonate samples from IODP Site U1341. **a**) Entirely dolmitic sample U1341B-70X-CCW, 15-17 cm (592.4 mbsf) (Tab. S1), **b**) partially dolomitic and calcitic sample U1341B-51H-4W, 84-86 cm (436.5 mbsf) (Tab. 1), and **c**) comparison of three samples U1341B-70X-CCW, 15-17 cm, U1341A-22H-3W, 88-88.5 cm, and U1341B-51H-4W, 84-86 cm showing increasing calcite content. Increasing CaCO_3 content in the dolomite phase is evidenced by a shift of the 104 peak towards lower 2Θ angles.

Fig. 5. **a**) Downcore distribution of diagenetic carbonate phases, **b**) carbon isotope composition ($\delta^{13}\text{C}$) of diagenetic carbonate phases and porewater dissolved inorganic carbon (DIC), **c**) strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of strontium in porewater and diagenetic carbonates and **d**) carbonate formation temperatures ($^{\circ}\text{C}$) calculated from $\delta^{18}\text{O}$ values in diagenetic carbonates. Temperature values for disseminated carbonate phases are not included.

Fig. 6. Summary of present (recent) and past (paleo) biogeochemical processes and their effects on porewater concentrations and isotope values with depth at Site U1341. Brackets denote concentration, a delta sign the isotopic ratio. Up- and downward arrows indicate that the concentration or isotope ratio is increasing or decreasing at this depth.

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6: