

# Pore water geochemistry along continental slopes north of the East Siberian Sea: Inference of low methane concentrations

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**Abstract.** Continental slopes north of the Eastern Siberian Sea potentially hold large amounts of methane (CH<sub>4</sub>) in sediments as gas hydrate and free gas. Although release of this CH<sub>4</sub> to the ocean and atmosphere has become a topic of discussion, the region remains sparingly explored. Here we present pore water chemistry results from 32 sediment cores taken during Leg 2  
15 of the 2014 SWERUS-C3 expedition. The cores come from depth transects across the slope and rise extending between the Mendeleev and the Lomonosov ridges, north of Wrangel Island and the New Siberian Islands respectively. Upward CH<sub>4</sub> flux towards the seafloor, as inferred from profiles of dissolved sulfate (SO<sub>4</sub><sup>2-</sup>), alkalinity, and the δ<sup>13</sup>C of dissolved inorganic carbon (DIC), is negligible at all stations east of 143°E longitude. In the upper eight meters of these cores, downward SO<sub>4</sub><sup>2-</sup> flux never exceeds 6.2 mol/m<sup>2</sup>-kyr, the upward alkalinity flux never exceeds 6.8 mol/m<sup>2</sup>-kyr, and δ<sup>13</sup>C-DIC only moderately  
20 decreases with depth (-3.6‰/m on average). Moreover, upon addition of Zn acetate to pore water samples, ZnS did not precipitate, indicating a lack of dissolved H<sub>2</sub>S. Phosphate, ammonium, and metal profiles reveal that metal oxide reduction by organic carbon dominates the geochemical environment, and supports very low organic carbon turnover rates. A single core on Lomonosov Ridge differs, as diffusive fluxes for SO<sub>4</sub><sup>2-</sup> and alkalinity were 13.9 and 11.3 mol/m<sup>2</sup>-kyr, respectively, the δ<sup>13</sup>C-DIC gradient was 5.6‰/m, and Mn<sup>2+</sup> reduction terminated within 1.3 m of the seafloor. These are among the first pore  
25 water results generated from this vast climatically sensitive region, and they imply that abundant CH<sub>4</sub>, including gas hydrates, do not characterize the East Siberian Sea slope or rise along the investigated depth transects. This contradicts previous modelling and discussion, which due to the lack of data are almost entirely based on assumption.

## 1 Introduction

The Arctic is especially sensitive to climate change, and has experienced anomalous warming over the last century (Serreze et al., 2000; Peterson et al., 2002; Semiletov et al., 2004; Polyakov et al., 2012). Past and future increases in atmospheric and surface water temperatures should, with time, lead to significant warming of intermediate to deep waters (Dmitrenko et al.,

2008; Spielhagen et al., 2011), as well as sediment beneath the seafloor (Reagan and Moridis, 2009; Phrampus et al., 2014). Pore space within the upper few hundreds of meters of sediment along many continental slopes contains temperature-sensitive methane (CH<sub>4</sub>) in the form of gas hydrates, free gas, and dissolved gas (Kvenvolden, 1993, 2001; Beaudoin et al., 2014). Consequently, numerous papers have discussed the potential impact of future warming on CH<sub>4</sub> release from slope sequences  
5 of the Arctic Ocean (Paull et al., 1991; Reagan and Moridis, 2008; McGuire et al., 2009; Biastoch et al., 2011; Elliott et al., 2011; Ferré et al., 2012; Giustiniani et al., 2013; Thatcher et al., 2013; Stranne et al., 2016).

The amount and distribution of CH<sub>4</sub> in sediment along continental slopes remains poorly constrained (Beaudoin et al., 2014). This is particularly true for the Arctic Ocean, because sea-ice cover makes accessibility difficult. Nonetheless, numerous papers  
10 have inferred enormous quantities of gas hydrate surrounding the Arctic (Kvenvolden and Grantz, 1990; Max and Lowrie, 1993; Buffett and Archer, 2004; Klauda and Sandler, 2005; Max and Johnson, 2012; Wallmann et al., 2012; Piñero et al., 2013; Fig. 1 and 2). In some sectors, compelling evidence exists for abundant CH<sub>4</sub> and gas hydrate. Bottom simulating reflectors (BSRs) on seismic profiles generally mark the transition between overlying gas hydrate and underlying free gas (Holbrook et al., 1996; Pecher et al., 2001), and thereby imply high quantities of CH<sub>4</sub> in pore space (Dickens et al., 1997;  
15 Pecher et al., 2001). Such BSRs have been documented along the North Slope of Alaska (Collett et al., 2010), within the Beaufort Sea (Grantz et al., 1976; Grantz et al., 1982; Weaver and Stewart, 1982; Hart et al., 2011; Phrampus et al., 2014), around Canadian Arctic Islands (Hyndman and Dallimore, 2001; Majorowicz and Osadetz, 2001; Yamamoto and Dallimore, 2008), adjacent to Svalbard (Posewang and Mienert, 1999; Hustoft et al., 2009; Petersen et al., 2010), and within the Barents Sea (Løvø et al., 1990; Laberg and Andreassen, 1996; Laberg et al., 1998; Ostanin et al., 2013). Furthermore, Lorenson and  
20 Kvenvolden (1995) observed high CH<sub>4</sub> concentrations in shelf waters of the Beaufort Sea, and Shakhova (2010a, 2010b) have documented CH<sub>4</sub> escape to the water column above the East Siberian shelf. Sediment on slopes north of the East Siberian Sea potentially contains copious CH<sub>4</sub> and gas hydrate (Fig. 1), although little data supports or refutes this hypothesis.

Regional assessments for abundant CH<sub>4</sub> in marine sediment along continental slopes can be acquired through two general  
25 approaches. The first includes geophysical applications, primarily seismic reflection profiling and the recognition of BSRs (Kvenvolden, 1993; Carcione and Tinivella, 2000; Haacke et al., 2008), which are a common, but not ubiquitous feature, of hydrate bearing sediments. The second utilizes chemical analyses of pore waters obtained from sediment cores (Borowski et al., 1999; D'Hondt et al., 2003). In marine sediments with abundant CH<sub>4</sub>, a general process occurs near the seafloor. Microbes utilize upward migrating CH<sub>4</sub> and downward diffusing sulfate (SO<sub>4</sub><sup>2-</sup>) via anaerobic oxidation of methane (AOM; Barnes and  
30 Goldberg, 1976; Boetius et al., 2000): Eq. (1):



The reaction leads to characteristic pore water chemistry profiles, with a clearly recognizable sulfate-methane transition (SMT; Fig. 3). The depth of the SMT inversely relates to the flux of CH<sub>4</sub>, which in turns relates to the distribution of CH<sub>4</sub> beneath the

seafloor (Borowski et al., 1999; Dickens, 2001; Bhatnagar, 2011). Where CH<sub>4</sub> fluxes toward the seafloor are high, the SMT is located at shallow depth. For example, in cores from the continental shelf and slope of the Beaufort Sea, where seismic profiles indicate gas hydrate, Coffin et al. (2008, 2013) have documented SMTs in shallow sediment (< 10 mbsf).

5 The joint Swedish, Russian, U.S. Arctic Ocean Investigation of Climate-Cryosphere-Carbon interaction (SWERUS-C3) project is aimed at understanding spatial changes in carbon cycling across the continental margin north of Siberia. A central theme concerns the amount, distribution, and fluxes of CH<sub>4</sub>. The overall project included a two-leg expedition in the boreal summer of 2014 using the Swedish icebreaker IB Oden. Between August 21 and October 5, Leg 2 sailed between Barrow, Alaska and Tromsø, Norway, including surveys of the continental slope of the East Siberian Sea. SWERUS Leg 2 included  
10 geophysical mapping and retrieval of numerous sediment cores, of which 446 pore water samples from eight piston, seven gravity, and 17 multicores (Fig. 2) were studied to ascertain potential fluxes of CH<sub>4</sub> toward the seafloor.

## 2 Background

### 2.1 East Siberian margin geology

Extensive continental shelves and their associated slopes encircle the Arctic Ocean (Fig. 1). Although only 2.6% of the world's  
15 ocean by area (Jakobsson, 2002), the present Arctic Ocean receives ~10% of global freshwater input (Stein, 2008) as well as a massive discharge of terrigenous material (>249 Mt/yr; Holmes et al., 2002). Only Fram Strait (Fig. 1), with a modern sill depth of about 2540 m taken from the International Bathymetric Chart of the Oceans (IBCAO; Jakobsson et al., 2012), allows deep-water flow to and from the Arctic Ocean. It opened during the early to middle Miocene (Jakobsson et al., 2007; Engen et al., 2008; Hustoft et al., 2009). Prior to this, the Arctic Ocean was connected to other oceans only through shallow seaways  
20 (e.g., Turgay Strait), such that deep waters may have been anoxic for long intervals of the Cretaceous and Paleogene (Moran et al., 2006; Sluijs et al., 2006; Jakobsson et al., 2007; O'Regan et al., 2011).

The East Siberian Sea stretches between Wrangel Island to the east and the New Siberian Islands to the west (Fig. 2). The continental shelf within this region is the widest in the world, extending 1500 km north of the coast. North of this expansive  
25 shelf lies the continental slope, which connects to Mendeleev Ridge to the east and Lomonosov Ridge to the west (Jakobsson et al., 2012). As these slopes lie north of the East Siberian Sea proper, we hereafter refer to them as SNESS for convenience.

### 2.2 Regional oceanography

Bottom waters impinging SNESS generally can be divided into three masses: the Pacific Halocline (~50-200m), the Atlantic Layer (~200-800m), and Canada Basin Bottom Water (>800m; Rudels et al., 2000). The Pacific Halocline is a cold (-1.5-0°C),  
30 low salinity (32-33.5 psu) water mass that serves as a boundary between sea ice and Atlantic Layer water (Aagaard, 1981; Aagaard and Carmack, 1989). The underlying Atlantic Layer is warmer (>0°C) but more saline (33.5-34.5 psu; Rudels et al.,

2000). The Atlantic Layer originates from water arriving partly through Fram Strait and partly across the Barents Sea. Canada Basin Bottom Water is colder ( $\sim -0.5^{\circ}\text{C}$ ) and relatively saline ( $\sim 34.9$  psu), with a residence time exceeding 300 years (Stein, 2008). Importantly, inflow from the Atlantic varies over time, which can further influence temperature along slopes of the central Arctic Ocean (Dmitrenko et al., 2009).

### 5 2.3 Current speculation on gas hydrates in the Arctic

Even during summer months over the last decade, 2-3 m of sea ice covers much of SNESS (Stroeve et al., 2012). This necessitates the use of large ice breaking vessels to explore the region. Prior to SWERUS, only four icebreaker expeditions, the 1995 Polarstern Expedition ARK-XI/1 (Rachor, 1995), the 1996 Arctic Ocean Expedition ARK-XII/1 (Augstein et al., 1997), the 2008 Polarstern Expedition ARK-XXIII/3 (Jokat, 2010), and the 2009 Russian-American RUSALCA Expedition (Bakhmutov et al., 2009) have retrieved geophysical data and sediment on or adjacent to SNESS. So far, no deep drilling has occurred along SNESS. However, the 2004 Arctic Coring Expedition (Backman et al., 2009) drilled and cored the central Lomonosov Ridge (Fig. 1).

Despite the paucity of ground-truth data, many researchers have predicted widespread and abundant  $\text{CH}_4$  within SNESS, as clearly shown by maps of inferred Arctic gas hydrate distribution (Fig. 1). This inference has arisen for two main reasons. First, the integrated input of particulate organic carbon (POC) over time provides the ultimate source of  $\text{CH}_4$  in marine sediments (Kvenvolden and Grantz, 1990). Arctic slopes may contain high POC contents, which accumulated in a) shallow platform environments prior to the opening of the Amerasian Basin, (Spencer et al., 2011) b) during periods of high surface water productivity and oxygen poor bottom water conditions that persisted across much of the Arctic until the opening of the Fram Strait in the Neogene (Jakobsson et al., 2007; Stein, 2006; O'Regan et al., 2011; Jokat and Ickrath, 2015), or c) As terrigenous material carried to or deposited along the slopes during interglacial intervals of the Quaternary (Danyushevskaya et al., 1980; Darby, 1989; Archer, 2015). Certainly, organic rich Cretaceous and Eocene sediments have been documented on other Arctic margins and in the ACEX cores on Lomonosov Ridge (Moran et al., 2006; Backman and Moran, 2009; O'Regan et al., 2011). The second reason is that the thickness of the gas hydrate stability zone (GHSZ) depends on bottom water temperature and the geothermal gradient (Dickens, 2001). Because of very low bottom water temperatures along the slope, and generally low regional geothermal gradients (O'Regan et al., 2016), an extensive volume of sediment can host gas hydrate (Miles, 1995; Makogon, 2010).

### 2.4 Pore water chemistry above methane-charged sediment

Pore water chemistry provides powerful means to constrain  $\text{CH}_4$  abundance and fluxes in marine sediment (Borowski et al., 1996; Berg et al., 1998; Jørgensen et al., 2001; Torres and Kastner, 2009; Treude et al., 2014). At locations without significant fluid advection, pore water profiles relate to Fick's law of diffusion and chemical reactions (e.g., Berner, 1977; Froelich et al., 1979; Klump and Martens 1981; Boudreau, 1997; and Iverson and Jørgensen, 1993). The flux ( $J$ ) of a dissolved species through

porous marine sediment can be calculated from the concentration gradient by (Li & Gregory, 1974; Berner, 1975; Lerman, 1977):

$$J = -\phi D_s \frac{\partial C}{\partial Z}, \quad (2)$$

where  $\phi$  is porosity,  $D_s$  is the diffusivity of an ion in sediment at a specified temperature,  $C$  is concentration, and  $Z$  is depth.

5 Note that, as generally written,  $J$  is positive for upward fluxes and negative for downward fluxes relative to the seafloor.

At many locations,  $\phi$  and  $D_s$  change only moderately (<20%) in the upper tens of meters below the seafloor. However, abundant  $\text{CH}_4$  in sediment leads to a large concentration gradient toward the seafloor and, an upward flux of  $\text{CH}_4$ . The consequent reaction with  $\text{SO}_4^{2-}$  via AOM (Eqn. 1) leads to a series of flux changes in dissolved components (addition or  
10 removal), and predictable variations in concentration profiles across an SMT (Alperin, 1988; Borowski et al., 1996; Niewohner et al., 1998; Ussler and Paull, 2008; Dickens and Snyder, 2009; Chatterjee et al., 2011). Furthermore, the depth of the SMT directly relates to the flux of  $\text{CH}_4$  from below (Jørgensen et al., 1990; Dickens, 2001; D'Hondt et al., 2002; Hensen et al., 2003), largely because  $\text{SO}_4^{2-}$  concentrations at the seafloor are nearly constant throughout the oceans.

15 Large areas of continental slopes across the world host  $\text{CH}_4$  in sediment, and consequently have a prominent SMT (D'Hondt et al., 2002). This feature is generally within the upper 30 m beneath the seafloor, and is characterized as a thin (<3 m) horizon with major inflections in both  $\text{CH}_4$  and  $\text{SO}_4^{2-}$  profiles (Fig. 3). Sulfate concentrations decrease from seawater values at the seafloor to near zero at the SMT; by contrast,  $\text{CH}_4$  concentrations rise from zero at the SMT to elevated values at depth.

20 Importantly, though, as one can infer from Eqns. 1 and 2, AOM affects additional species dissolved in pore water (Alperin et al., 1988; Jørgensen et al., 1990; Dickens, 2001; Hensen et al., 2003; Snyder et al., 2007). Dissolved  $\text{HS}^-$  and  $\text{HCO}_3^-$  concentrations necessarily increase across the SMT, so an inflection occurs in their concentration profiles. These two species contribute to total alkalinity of marine waters (Gieskes and Rogers, 1973; Haraldsson et al., 1997), which can be defined as:

$$\text{Alk}_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HS}^-] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + [\text{NH}_3] + [\text{X}], \quad (3)$$

25 where  $X$  refers to several minor species. However, in shallow sediments found above almost all  $\text{CH}_4$  charged systems, this can be expressed as:

$$\text{Alk}_T \approx [\text{HCO}_3^-] + [\text{HS}^-]. \quad (4)$$

Therefore, because of the production of  $\text{HS}^-$  and  $\text{HCO}_3^-$ , an inflection in  $\text{Alk}_T$  occurs across the SMT (Luff and Wallmann 2003; Dickens and Snyder, 2009; Jørgensen and Parkes, 2010; Chatterjee et al., 2011; Smith and Coffin, 2014; Ye et al., 2016).

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Marked changes in pore water profiles of other components also typically occur across the SMT (Fig. 3). Because CH<sub>4</sub> is greatly depleted in <sup>13</sup>C, due to isotope fractionation during methanogenesis at depth (Whiticar, 1999; Paull et al., 2000), the conversion of CH<sub>4</sub> to HCO<sub>3</sub><sup>-</sup> (Eqn. 1) decreases the δ<sup>13</sup>C of DIC across the SMT (Torres et al., 2007; Holler et al., 2009; Chatterjee et al., 2011; Yoshinaga et al., 2014). However, the magnitude of this change in δ<sup>13</sup>C-DIC is complicated because  
5 excess <sup>13</sup>C-enriched HCO<sub>3</sub><sup>-</sup> (formed during methanogenesis and subsequent reactions) can also rise from below (Snyder et al., 2007; Chatterjee et al., 2011). Dissolved Ba<sup>2+</sup> concentrations generally increase significantly just above the SMT. This is because solid barite (BaSO<sub>4</sub>), a ubiquitous component of marine sediment on continental slopes (Dymond et al., 1992; Gingele and Dahmke, 1994), dissolves in the SO<sub>4</sub><sup>2-</sup>-depleted pore water and dissolved Ba<sup>2+</sup> then diffuses back across the SMT (Dickens, 2001; Riedinger et al., 2006; Nöthen and Kasten, 2011). Dissolved Ca<sup>2+</sup> concentrations usually decrease across the SMT. This  
10 is due to authigenic carbonate precipitation resulting from the production excess HCO<sub>3</sub><sup>-</sup> (Greinert et al., 2001; Luff and Wallmann 2003; Snyder et al., 2007). Conversely, dissolved NH<sub>4</sub><sup>+</sup> concentrations exhibit no inflection across the SMT. This is because while decomposition of particulate organic matter (POM) generates NH<sub>4</sub><sup>+</sup>, AOM does not (Borowski et al., 1996).

Studies at numerous locations demonstrate that characteristic pore water profiles delineate sediment sequences with significant  
15 CH<sub>4</sub>, including gas hydrate, in the upper few hundred meters below the seafloor (Fig. 3). Good examples include: Baltic Sea (Jørgensen et al, 1990), Black Sea (Jørgensen et al, 2004), Blake Ridge (Paull et al., 2000; Borowski et al., 2001), Cariaco Trench (Reeburgh, 1976), Cascadia Margin (Torres and Kastner, 2009), Gulf of Mexico (Kastner et al., 2008a; Hu et al., 2010; Smith and Coffin, 2014), Hydrate Ridge (Claypool et al., 2006), offshore Namibia (Niewohner et al., 1998), offshore Peru (Donohue et al., 2006), South China Sea (Luo et al., 2013; Hu et al., 2015), and Sea of Japan (Expedition Scientists, 2014).  
20 Moreover, in regions dominated by diffusion, fluxes of dissolved CH<sub>4</sub> can be estimated using Eqn. 2 from concentration profiles of multiple constituents (e.g., SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>) and knowledge of porosity and sedimentary diffusion constants (e.g., Niewohner et al., 1998; Snyder et al., 2007). At sites with abundant CH<sub>4</sub> in the upper few hundred meters below the seafloor, notably including sites with gas hydrate and sites in the Beaufort Sea, estimated values for *J*CH<sub>4</sub> and *-J*SO<sub>4</sub><sup>2-</sup> are universally high (> ~50 mol/m<sup>2</sup>-kyr).

25 It should be noted that, at seafloor locations with significant upward advection of fluids, such as at seeps and vents, the aforementioned reactions occur, but the pore water profiles become more complicated to model (Berner, 1980; Torres et al., 2002; Chatterjee et al., 2014). This is because the advecting fluids typically have different chemistry than surrounding sediment (even if charged with CH<sub>4</sub>), and because advection often involves multiphase fluid flow (free gas and liquid) that may be  
30 episodic. Nonetheless, at least on continental slopes, if the upward advecting fluids contain significant CH<sub>4</sub> (even as gas bubbles), a prominent SMT occurs, but is shoaled toward the seafloor with respect to predictions based on CH<sub>4</sub> diffusion alone (Luff and Wallmann, 2003; Kastner et al., 2008a). Indeed, at locations where CH<sub>4</sub> gas bubbles escape the seafloor, the SMT lies at the seafloor (e.g., Aharon and Fu, 2000; Joye et al., 2004; Hu et al., 2010).

### 3 Materials and Methods

#### 3.1 SWERUS-C3 Expedition, Leg 2

Leg 2 of SWERUS-C3 included four transects across the SNESS (Fig. 2). These transects were along Arlis Spur (TR-1), north of central East Siberia (TR-2), from close to Henrietta Island to the Makarov Basin (TR-3), and on the Amerasian side of Lomonosov Ridge (TR-4). Along each transect, scientific operations involved bathymetric mapping as well as sediment coring at stations. An additional coring station was located on Lomonosov Ridge, near its intersection with the Siberian margin.

An array of coring techniques were used along each transect. In total, 50 sediment cores were collected at 34 stations. These included: multicore sets (22), gravity cores (23), piston cores (11), and kasten cores (2). The multicorer was an 8-tube corer built by Oktopus GmbH. The polycarbonate liners were 60 cm long with a 10 cm diameter. The piston/gravity coring system was built by Stockholm University with an inner diameter of 10 cm. Trigger weight cores also were collected during piston coring. The different coring systems enabled sediment and pore water collection from the seafloor to upwards of 9 m below the seafloor (mbsf).

#### 3.2 Core material

For gravity and piston cores, physical properties were analysed on the ship using a Geotek Multi-Sensor Core Logger (MSCL). These included measurements of the gamma-ray derived bulk density, compressional wave velocity (p-wave), and magnetic susceptibility at 1 cm resolution. Discrete samples (2-3 per section) were taken for sediment index property measurements (bulk density, porosity, water content and grain density). Grain density was measured using a helium displacement pycnometer on oven-dried samples. Porosity profiles were generated using the smoothed (3-pt) MSCL-derived bulk density ( $\rho_b$ ) and the average grain density ( $\rho_g$ ) from each core, where:

$$\varphi = \frac{(\rho_g - \rho_b)}{(\rho_b - \rho_f)}, \quad (5)$$

and the pore fluid density ( $\rho_f$ ) was assumed to be 1.024 g/cm<sup>3</sup>.

#### 3.3 Interstitial water collection

Cores were cut into ~1.5 m long sections immediately on the ship deck, brought to the geochemistry laboratory, and placed on precut racks. Laboratory temperature was a near constant 22 °C. Pore waters were collected using Rhizon samplers (Seeberg-Elverfeldt et al., 2005; Dickens et al., 2007). Sampling involved drilling holes through the core liner, inserting Rhizons into the sediment core, and obtaining small volumes of pore water via vacuum and “microfiltration.” The Rhizons used were 5-cm porous flat tip male luer lock (19.21.23) with 12 cm tubing, purchased from Rhizosphere Research Products ([www.rhizosphere.com](http://www.rhizosphere.com)).

In total, 529 pore water samples were collected from 32 cores, which ranged from 0.16 to 8.43 m in length (Tbl. S2). Rhizons in gravity and piston cores typically were spaced every 20 to 30 cm. Because the use of rhizon sampling for collecting pore waters of deep-sea sediments remains a relatively novel and engaging topic (Dickens, 2007; ; Xu et al., 2012; Miller et al., 5 2014), we discuss the procedure in detail, as well as several experiments regarding our sampling, in Supplementary Information.

While in the shipboard laboratory, Rhizon samples were divided into six aliquots when sufficient water was available. This sample splitting led to 2465 aliquots of pore water in total, which then could be examined for different species at different 10 laboratories. Aliquots 1, 3, and 6 (below) were collected for all 32 cores.

### 3.4 Interstitial water analyses

The first aliquot was used to measure  $\text{Alk}_T$  using a Mettler Toledo titrator on *IB Oden*. Immediately after collection, pore water was diluted with milli-Q water and autotitrated. Fifteen spiked samples and eight duplicates were analyzed onboard for quality control. Spiked samples were created by pipetting certified reference material (Batch 135; 15 www.cdiac.ornl.gov/oceans/Dickson\_CRM) into milli-Q water. Results for spiked samples and duplicates are reported in Tbl. 1.

The second aliquot was used to measure the  $\delta^{13}\text{C}$  composition of DIC ( $\delta^{13}\text{C}$ -DIC). Septum sealed glass vials prepared with  $\text{H}_3\text{PO}_4$  and flushed with helium were prepared before the expedition. Samples were sealed in boxes and refrigerated for the 20 remainder of the cruise. Four field duplicates, two seawater standards, and a field blank were collected, stored, and analyzed with the samples. The  $\delta^{13}\text{C}$ -DIC analyses were performed on a Gasbench II coupled to a MAT 253 Mass Spectrometer (both Thermo Scientific) at Stockholm University. The  $\delta^{13}\text{C}$ -DIC is reported in conventional delta notation relative to Vienna PeeDee Belemnite (VPDB). Results for field duplicates and standards are reported in Tbl. 1. Standard deviation for the analyses of  $\delta^{13}\text{C}$ -DIC was less than 0.1 ‰.

25 The third aliquot was used to measure dissolved sulfur and metal concentrations. Samples were acid preserved with 10  $\mu\text{L}$  ultrapure  $\text{HNO}_3$ . Additionally, 11 blind field duplicates and 2 field blanks were collected and processed in the same manner. Concentrations of Ba, Ca, Fe, Mg, Mn, S, and Sr were determined on an Agilent Vista Pro Inductively Coupled Atomic Emission Spectrometer (ICP-AES) in the geochemistry facilities at Rice University. Known standard solutions and pore fluid 30 samples were diluted 1:20 with 18-M $\Omega$  water. Scandium was added to both standards and samples to correct for instrumental drift (emission line 361.383 nm). Wavelengths used for elemental analysis followed those indicated by Murray et al. (2000). Following initial analysis, an additional dilution, 1:80 with 18-M $\Omega$  water, was analyzed for Ca, Mg, and S. After every 10



analyses, an International Association of Physical Sciences (IAPSO) standard seawater spiked sample and a blank were examined for quality control. Relative standard deviations (RSD) from stock solutions are reported in Tbl. 1.

5 The fourth aliquot was used to measure dissolved ammonia ( $\text{NH}_4^+$ ) via a colorimetric method similar to that presented by Gieskes et al. (1991). Set volumes of pore water were pipetted into cuvettes and diluted with milli-Q water. Two reagents were then pipetted into the cuvettes. Reagent A was prepared by adding  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ,  $\text{C}_6\text{H}_5\text{OH}$ , and  $\text{Na}_2(\text{Fe}(\text{CN})_5\text{NO})$  to milli-Q water. Reagent B was prepared by dissolving  $\text{NaOH}$  in milli-Q water and adding  $\text{NaClO}$  solution. Solutions were mixed and allowed to react for at least six but not more than 24 hours. Solutions turned various shades of blue, which to relate to  $\text{NH}_4^+$  concentration, and were measured by absorbance at 630 nm on a Hitachi U-1100 spectrophotometer. Five point calibration  
10 curves were measured before each sample set and corrected using VKI standard (QC RW1; www.eurofins.dk; Tbl. 1).

The fifth aliquot was used to measure dissolved phosphate ( $\text{PO}_4^{3-}$ ) following the method given by Gieskes et al. (1991). Remaining pore water (generally between 1 and 3mL) was added to milli-Q water to a sum of 10 mL. Two reagents were added to the solution to react with  $\text{PO}_4^{3-}$ . Reagent A was prepared by making three solutions:  $(\text{NH}_4)_2\text{MoO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  
15  $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot \text{XH}_2\text{O}$  were added to milli-Q water, and the solutions were added dropwise. Reagent B was created with  $\text{C}_6\text{H}_8\text{O}_6$ . After samples were prepared, reagents A and B were added, mixed, and allowed to react 30 minutes. Solutions turned various shades of blue, relating to  $\text{PO}_4^{3-}$  concentration, and were measured at an absorbance of 880 nm. Five point calibration curves were measured before each sample set and corrected using VKI standard (QC www.eurofins.dk; Tbl. 1).

20 For 352 pore water samples, a sixth aliquot of approximately 2 mL was mixed with 200  $\mu\text{L}$  of a 2.5% Zn-acetate ( $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) solution. Given the extremely low solubility of  $\text{ZnS}$ , a white precipitate forms when such a solution is added to pore water samples with even trace  $\text{H}_2\text{S}$  concentrations (Cline, 1969; Goldhaber, 1974).

For the ICP-AES analyses, a method detection limit (MDL) can be determined as follows:

$$25 \quad MDL = \frac{(C_{High} - C_{Low})}{(I_{High} - I_{Low})} 3\sigma, \quad (6)$$

where C = concentration and I = intensity (counts per second on the ICP-AES). The MDLs were as follows: Ba = 0.01  $\mu\text{M}$ , Ca = 0.08  $\mu\text{M}$ , Fe = 5.9  $\mu\text{M}$ , Mg = 0.22  $\mu\text{M}$ , Mn = 0.24  $\mu\text{M}$ , S = 1.2  $\mu\text{M}$ , Sr = 0.01  $\mu\text{M}$ . On all plots, for reference, we place dashed lines for values of the IAPSO seawater standard (Alkalinity = 2.33 mM, Ba = 0.00 mM, Ca = 10.28 mM, Fe = 0.00 mM, Mg = 53.06 mM, Mn = 0.00 mM, S = 28.19 mM, Sr = 0.09 mM,  $\text{NH}_4^+$  = 0.00 mM,  $\text{HPO}_4^{2-}$  = 0.00 mM).

## 4 Results

### 4.1 General observations

With the large number of pore water measurements (Tbl. S1), we begin with some generalities regarding results. We plot pore water concentration profiles along each transect collectively (Fig. 4-8), irrespective of coring device or water depth, although clear variance in pore water chemistry exists between stations for some dissolved species (e.g., Fe).

Most species display “smooth” concentration profiles with respect to sediment depth (Fig. 4-8). That is, concentrations of successive samples do not display a high degree of scatter. This is expected for pore water profiles in sediment where diffusion dominates (Froelich et al., 1979; Klump and Martens 1981; Schulz, 2000; Torres and Kastner, 2009; Hu et al., 2015). However, for some dissolved species whose concentrations do not appreciably change over depth (e.g.,  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ ), scatter exists beyond that predicted from analytical precision. We discuss this in the Supplementary Information.

### 4.2 Alkalinity and $\delta^{13}\text{C}$ of DIC

Alkalinity concentrations increase with depth in all cores (Fig. 4-8). Moreover, in most cases, the rise is roughly linear. Across all stations on the four transects, alkalinity increases by an average of 0.51 mM/m, although variance exists between mean gradients for each transect ( $\text{Tr1} = 0.46$  mM/m,  $\text{Tr2} = 0.34$  mM/m,  $\text{Tr3} = 0.91$  mM/m, and  $\text{Tr4} = 0.44$  mM/m) and by station along each transect. The Lomonosov Ridge station differs (Fig. 8), as alkalinity increases much greater with depth (1.86 mM/m).

Concave-down  $\delta^{13}\text{C}$ -DIC profiles characterize pore waters at all stations (Fig. 4-8). The decrease in  $\delta^{13}\text{C}$ -DIC is most pronounced near the seafloor. Across all stations along the four transects, pore water  $\delta^{13}\text{C}$ -DIC values decrease from near zero close to the mudline at an average of -3.6 ‰/m. Again, variance in mean gradients occurs between stations and transects ( $\text{Tr1} = -3.3$  ‰/m,  $\text{Tr2} = -3.0$  ‰/m, and  $\text{Tr3} = -4.7$  ‰/m). As with alkalinity, the  $\delta^{13}\text{C}$ -DIC profile at the Lomonosov Ridge station differs, with values decreasing by 5.6 ‰/m, such that by eight mbsf,  $\delta^{13}\text{C}$ -DIC approaches -45 ‰. In summary, a basic relationship exists between higher alkalinity and lower  $\delta^{13}\text{C}$ -DIC across all stations.

### 4.3 Sulfur and sulfate

No sulfide was observed by smell and no ZnS precipitated in any pore water sample upon addition of Zn-acetate solution. Molar concentrations of total dissolved sulfur should, therefore, represent those of dissolved  $\text{SO}_4^{2-}$ . Along the four transects, dissolved sulfur concentrations decrease with depth at all stations (Fig. 4-7). The total dissolved sulfur concentrations in the shallowest samples varied from 27.3 to 30.6 mM and averaged 28.7 mM. From these “seafloor” values, concentrations decrease by an average 0.69 mM/m, again with variance according to stations and transect ( $\text{Tr1} = -0.58$  mM/m,  $\text{Tr2} = -0.57$  mM/m,  $\text{Tr3} = -1.09$  mM/m; and  $\text{Tr4} = -0.60$  mM/m). The dissolved sulfur gradients across all stations within SNESS range from -0.41 to

-1.13 mM/m. Dissolved sulfur at the Lomonosov Ridge station displays a significantly steeper decrease than any other station (-1.92 mM/m). Importantly, decreases in dissolved sulfur are similar in magnitude to increases in alkalinity at each station examined. Indeed, the molar ratio of alkalinity change to sulfur change ( $-\Delta\text{Alkalinity}/\Delta\text{S}$ ) is 0.98 (Fig. 9a).

#### 5 4.4 Ammonia and phosphate

The C:N:P molar ratio of typical marine organic matter is approximately 106:16:1 (Redfield, 1958; Takahashi, 1985). Although this ratio differs for terrestrial organic carbon (closer to 134:9:1, Tian et al., 2010), dissolved  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  concentrations in pore water can be used in a general sense to assess consumption of particulate organic carbon. This is because the degradation releases these species to pore water (Froelich et al., 1979). Notably, concentrations of  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  are near or below  
10 detection in samples immediately below the seafloor (Fig. 4-8).

Dissolved  $\text{NH}_4^+$  profiles increase almost linearly with depth, although with slight concave-down curvature. Similar to alkalinity profiles,  $\text{NH}_4^+$  concentrations rise with depth below the seafloor more at stations with shallower water depth (although we note an exception for Tr2). Across stations along the four transects, pore water  $\text{NH}_4^+$  concentrations increase with depth on average  
15 by 38.69  $\mu\text{M}/\text{m}$ , with a range from 11.3 to 76.1  $\mu\text{M}/\text{m}$ . Along each transect, the average  $\text{NH}_4^+$  gradients are as follows: Tr1 = 43.0  $\mu\text{M}/\text{m}$ , Tr2 = 17.4  $\mu\text{M}/\text{m}$ , Tr3 = 69.0  $\mu\text{M}/\text{m}$ , and Tr4 = 29.0  $\mu\text{M}/\text{m}$ .

By contrast, concentrations of dissolved  $\text{HPO}_4^{2-}$  in our cores typically increase to a subsurface maximum, and then decrease (Fig. 4-8). Based on the available data, a more pronounced maximum appears to occur at stations with relatively shallow water  
20 depth. For example, consider the peak in  $\text{HPO}_4^{2-}$  concentrations at four stations. At the two shallow stations, S12 (384 m) and S22 (367 m) the  $\text{HPO}_4^{2-}$  maxima are, 73  $\mu\text{M}$  (1.91 m) and 18  $\mu\text{M}$  (0.66 m), respectively, but at the two deeper stations, S17 (977 m) and S14 (733 m), the  $\text{HPO}_4^{2-}$  maxima are only 6.7  $\mu\text{M}$  (1.76 m) and 7.1  $\mu\text{M}$  (2.33 m) respectively. The station on Lomonosov Ridge (S31) has a high in  $\text{HPO}_4^{2-}$  concentration of 76  $\mu\text{M}$  at 1.02 m below the seafloor. In general, stations with more pronounced  $\text{HPO}_4^{2-}$  maxima also have greater increases in alkalinity with depth.

25 The  $\text{NH}_4^+$ ,  $\text{HPO}_4^{2-}$ , and alkalinity profiles relate to one another statistically, although with some distinctions. All stations have a C:N ratio in pore waters much higher than the canonical Redfield Ratio of 6.625 (Fig. 10). Rather, the concentration relationship of alkalinity and ammonium ion can be expressed by a second order polynomial ( $[\text{NH}_4^+] = -0.003[\text{Alk}]^2 + 0.105[\text{Alk}] - 0.253$ ; Fig. 9b) with an average molar ratio ( $\text{Alk}/\text{NH}_4^+$ ) of 14.7, close to that expected for degradation of terrestrial  
30 organic carbon. Interestingly, this ratio deviates somewhat across transects, increasing at sites from Tr1, Tr3, Tr2, to the Lomonosov Ridge station. Across all stations and above the subseafloor  $\text{HPO}_4^{2-}$  peak, the molar ratio of alkalinity to phosphate ion ( $\text{Alk}/\text{HPO}_4^{2-}$ ) averages 55.7 in pore water samples. This ratio also generally increases in cores from east to west.

## 4.5 Metals

At most stations, dissolved  $\text{Ba}^{2+}$  concentrations increase nonlinearly from values at or below detection limit ( $0.01 \mu\text{M}$ ) near the seafloor to generally constant values ( $0.6 - 0.7 \mu\text{M}$ ) within 0.8 m below the seafloor. However, at several stations, dissolved  $\text{Ba}^{2+}$  concentrations remain at or below the detection limit for all samples.

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Overall, dissolved  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Sr}^{2+}$  concentrations decrease with depth (Fig. 4-8). For the stations along the four transects,  $\text{Ca}^{2+}$  concentrations drop on average between  $-0.09$  and  $-0.12 \text{ mM/m}$  (Tr1), about  $-0.09 \text{ mM/m}$  (Tr2), between  $-0.09$  and  $-0.10$  (Tr3), and  $-0.075 \text{ mM/m}$  (Tr4). Magnesium concentrations also drop, the average change being between  $-0.43$  and  $-0.48 \text{ mM/m}$  (Tr1), between  $-0.27$  and  $-1.32$  (Tr2), between  $-0.86$  and  $-0.94 \text{ mM/m}$  (Tr3), and  $-0.467 \text{ mM/m}$  (Tr4). Strontium concentrations

10 decrease an average of  $0.3 \mu\text{M/m}$ , considering all stations along the four transects (Tr1 =  $0.5 \mu\text{M/m}$ , Tr2 =  $0.3 \mu\text{M/m}$ , Tr3 =  $0.1 \mu\text{M/m}$ , and Tr4 =  $0.1 \mu\text{M/m}$ ). The station on Lomonosov Ridge again stands apart. At this location, the decreases in dissolved  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Sr}^{2+}$  are  $0.27 \text{ mM/m}$ ,  $1.24 \text{ mM/m}$ , and  $0.50 \mu\text{M/m}$ , respectively.

The profiles of dissolved Mn and Fe are complicated in terms of location. Generally, profiles show a broad rise in

15 concentrations within the upper sediment and a subsequent drop in concentrations at deeper depth. Some stations have a maxima in dissolved Mn (Stations S12 ( $135 \mu\text{M}$  at 5 m), S28 ( $66 \mu\text{M}$  at 3.1 m), and Lomonosov Ridge ( $86 \mu\text{M}$  at 1.3 m), where concentrations decrease below. At other stations, however, Mn concentrations still appear to be increasing at the lowest depth. Iron concentrations are generally below the detection limit at or near the seafloor, and begin increasing around  $2.5 - 3.5$  m, reaching concentrations upward of  $20 \mu\text{M}$ .

## 20 5 Discussion

### 5.1 Fidelity of rhizon pore water measurements

Researchers have employed multiple methods to extract pore waters from marine sediments over the last few decades, but the rhizon technique remains relatively novel (e.g., Seeberg-Elverfeldt et al., 2005; Dickens et al., 2007; Pohlman et al., 2008). Several studies have questioned the accuracy and precision of analyses obtained through this approach (e.g., Schrum et al.,

25 2012; Miller et al., 2014). Two experiments conducted during the SWERUS-C3 Leg 2 Expedition using the Rhizons suggest that part of the problem concerns the timing and location of sampling (Supplementary Information). Notably, however, as clearly documented in previous works (Seeberg-Elverfeldt et al., 2005; Dickens et al., 2007; Pohlman et al., 2008), rhizon sampling can lead to “smooth” concentration profiles for multiple dissolved species, including alkalinity (Fig. 4-8).

30 Concerns about rhizon sampling may be valid for dissolved components when concentration gradients are very low. For example, Schrum et al. (2012) stressed alkalinity differences between samples collected at similar depth using rhizon sampling

and conventional squeezing. However, the total alkalinity range in this study was between 1.6 and 2.6 mM, and typical differences were 0.06 mM. A similar finding occurs in the dissolved  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  profiles of this study, where the range in values is small and adjacent samples deviate by more than analytical precision (Tbl. 1, Fig. S3). However, when the signal to noise ratio becomes high, as true with most dissolved components at most stations (Fig. 4-8), the rhizon sampling renders pore water profiles with well-defined concentration gradients that can be interpreted in terms of chemical reactions and fluxes.

## 5.2 General absence of methane

Direct measurements of dissolved  $\text{CH}_4$  in deep-sea sediment are complicated (Claypool and Kvenvolden 1983). During core retrieval and depressurization, major  $\text{CH}_4$  loss can occur from pore space (Dickens et al., 1997). Importantly, in sediments recovered through piston coring and where in situ  $\text{CH}_4$  concentrations significantly exceed solubility conditions at 1 Atm pressure, gas release typically generates sub-horizontal cracks (“gas voids”) that span the core between the liner. No such cracks were documented in any of the cores.

Excluding St31 on the Lomonosov Ridge, there is no indication of a shallow SMT in any of the cores. Interstitial water sulfur concentrations do not drop below 22.8 mM within the upper 8 m. In fact, calculated downward  $\text{SO}_4^{2-}$  fluxes, as inferred from sulfur concentration gradients (Tbl. 2) range from -1.8 to -6.2 mol/m<sup>2</sup>-kyr for all stations except Station S31. For comparison, a site with a near seafloor temperature of 2 °C (Fig. S2) and porosities similar to those measured (Fig. S1), an SMT at 6.0 mbsf would imply a  $\text{SO}_4^{2-}$  flux of -40 mol/m<sup>2</sup>-kyr.

Given the lack of  $\text{HS}^-$  and the measured pH (Fig. S2), alkalinity should closely approximate  $\text{HCO}_3^-$  concentrations (Eqn. 4). Estimated  $\text{HCO}_3^-$  fluxes ( $J_{\text{HCO}_3^-}$ ) do not exceed 6.8 mol/m<sup>2</sup>-kyr at any station east of the Lomonosov Ridge (Tbl. 2). For comparison, at sites with abundant  $\text{CH}_4$  at depth,  $J_{\text{HCO}_3^-}$  generally exceeds 30 mol/m<sup>2</sup>-kyr above the SMT (Tbl. 2). These extreme fluxes arise because methanogenesis in deeper sediment drives an upward flux of  $\text{HCO}_3^-$  (Fig. 3), and because AOM contributes additional  $\text{HCO}_3^-$  and  $\text{HS}^-$  to pore water at the SMT (Eqn. 1).

The  $\delta^{13}\text{C}$ -DIC values of pore water decrease with depth at all stations, almost in concert with the rise in alkalinity, implying no  $\text{CH}_4$  production because methanogenesis would increase  $\delta^{13}\text{C}$ -DIC values (Fig. 9c; Whiticar, 1999). Other than Station S31, the lowest value of  $\delta^{13}\text{C}$ -DIC is -25.23 ‰ at 5.5 m at Station S22 (Fig. 6). This is interesting because a series of microbial reactions utilizing POM can lead to higher alkalinity and lower  $\delta^{13}\text{C}$ -DIC values in pore water. The most important of these reactions is organoclastic sulfate reduction (OSR), which can be expressed as (Berner, 1980; Boudreau and Westrich, 1984):



As emphasized previously, methane-charged sediment sequences do occur on continental slopes in the Arctic. Of particular interest to this study are locations in the Beaufort Sea, where indications for gas hydrate manifest on seismic profiles (Grantz et al., 1976; Grantz et al., 1982; Weaver and Stewart, 1982; Hart et al., 2011; Phrampus et al., 2014), and pore water profiles have been generated using shallow piston cores (Coffin et al., 2013). Striking contrasts exist between pore water profiles of the Beaufort Sea and those of SNESS (Tbl. 2). In the Beaufort Sea, there are moderate to high downward  $\text{SO}_4^{2-}$  and upward  $\text{CH}_4$  fluxes (1.9 to 154.8 mol/m<sup>2</sup>-kyr), shallow SMTs (6.29 to 1.06 mbsf), high DIC fluxes between the SMT and the mudline (46.3 to 242.6), and negative  $\delta^{13}\text{C}$ -DIC values at SMT's ( $\approx -20\%$ ).

### 5.3 Special case: Lomonosov Ridge station

Station 31 on the Lomonosov Ridge (Fig. 8) differs from all other stations examined in this study. Here, pore water chemistry profiles hint at  $\text{CH}_4$  in pore space within shallow sediment. Extrapolation of the dissolved sulfur profile suggests an SMT at approximately 14 mbsf. This depth lies within the range common for locations with AOM (D'Hondt et al., 2002), notably including well studied sites on Blake Ridge (Borowski et al., 1999). Similar to some sites with  $\text{CH}_4$ , the  $\delta^{13}\text{C}$ -DIC values become very "light"; indeed, the value at the base of the core,  $-43.5\%$ , almost necessitates  $\text{CH}_4$  oxidation within shallow sediment. Comparably steep alkalinity (1.6 mM/m) and  $\text{NH}_4^+$  gradients (60.4  $\mu\text{M}/\text{m}$ ) also characterize most sites with  $\text{CH}_4$  near the seafloor. However, there is an issue concerning reduced sulfur, which is a product of AOM (Eqn. 1). If AOM was occurring at  $\sim 13.9$  mbsf, one might expect evidence for  $\text{HS}^-$  migrating from below (Fig. 3). No  $\text{ZnS}$  precipitated in pore waters of this core upon addition of  $\text{ZnAc}$ .

A comparison of published DIC fluxes,  $\text{SO}_4^{2-}$  fluxes, and SMT depths (Tbl. 2) reveals fluxes decrease exponentially with SMT depth (Fig. 11). In fact, a fundamental relationship exists when one considers that upward  $\text{CH}_4$  fluxes control the SMT depth (Eqn. 1; Fig. 3). The modest  $\text{SO}_4^{2-}$  flux ( $-13.9$  mol/m<sup>2</sup>-kyr) and alkalinity flux (11.3 mol/m<sup>2</sup>-kyr) estimated for the Lomonosov Ridge station conform to those expected for an SMT at about 14 mbsf. For example, Hensen et al. (2003) calculated a  $\text{SO}_4^{2-}$ -flux of  $-14.7$  mol/m<sup>2</sup>-kyr for a site with an SMT at 14 mbsf in the Argentine Basin, and Berg (2008) calculated a  $\text{SO}_4^{2-}$  flux of  $-8.05$  mol/m<sup>2</sup>-kyr for a site with an SMT at 16 mbsf along the Costa Rica Margin.

### 25 5.4 Other chemistry

Microbial communities preferentially utilize the most energetically favorable oxidant available leading to a characteristic reaction sequence in marine sediment (Froelich et al., 1979; Berner, 1980; D'Hondt et al., 2004). With increasing depth below the seafloor, these include: aerobic respiration, denitrification, manganese oxide reduction, iron oxide reduction,  $\text{SO}_4^{2-}$  reduction, and finally methanogenesis. Many of the cores collected across SNESS appear to terminate in the zone of metal oxide reduction. This is because, at most stations, Mn and Fe profiles are still increasing at the bottom of the sampled interval (Fig. 4-8), presumably due to dissimilatory Mn- and Fe-oxide reduction. However, Mn may be more complicated. März et al., (2011) find evidence from Mn profiles along the southern Mendeleev Ridge that suggest diagenetic remobilization of Mn at

depth and diffusion toward shallow sediments. The relatively deep depths of metal oxide reduction nevertheless, are consistent with a relatively low input of POM to the seafloor, and completely contrast with most sites where high CH<sub>4</sub> concentrations exist in shallow sediment. A simple interpretation is that there is insufficient input of POC over time to drive methanogenesis near the seafloor.

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The station on the Lomonosov Ridge again stands apart. Here, Mn and Fe concentrations reach maxima at 1.3 mbsf and 0.5 mbsf, respectively, and decrease below. This is likely due to Mn and Fe produced during dissimilatory oxide reduction, but where both metals precipitate below into carbonate (Mn and Fe) or sulfide phases (Fe; Jørgensen et al., 1990; März et al., 2011). This is common at locations with modest POC input, and the Lomonosov Ridge site appears to receive higher organic carbon burial over time than all the other locations examined. Given the relationship of alkalinity to ammonia (Fig. 10), much of the organic matter on the continental slope may derive from terrestrial rather than marine sources (Müller and Suess, 1979; Reimers et al., 1992), but a more detailed study of sedimentation rates and organic matter content and composition is required to elucidate these relationships further.

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### 5.5 Signatures of AOM and OSR

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Some authors have used changes in DIC and SO<sub>4</sub><sup>2-</sup> concentrations between the seafloor and the SMT to infer the relative importance of AOM and OSR in marine sediments (Kastner et al. 2008b; Luo et al. 2013; Hu et al. 2015). This idea can be expressed by comparing  $\Delta(\text{DIC} + \text{Ca}^{2+} + \text{Mg}^{2+})$  and  $\Delta\text{SO}_4^{2-}$ , where Ca<sup>2+</sup> and Mg<sup>2+</sup> are included to account for loss of DIC via carbonate precipitation (other authors, such as Snyder et al., 2007 and Wehrmann et al., (2011) use fluxes instead of concentrations). The rationale lies in the fact that the C:S ratio for AOM is 1:1 (Eqn. 1), whereas the C:S ratio for OSR is 2:1 (Eqn. 7). However, this approach neglects two considerations: (1) changes in concentration do not directly relate to fluxes, because of differences in diffusivities of various ionic species, and, (2) a flux of HCO<sub>3</sub><sup>-</sup> from below the SMT can augment the DIC produced from AOM or OSR at or above the SMT (Dickens and Snyder, 2009). Thus, changes in alkalinity relative to SO<sub>4</sub><sup>2-</sup> often exceed 1:1, even at locations completely dominated by AOM (Chatterjee et al., 2011).

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Rather than comparing changes in C:S molar ratios or going through detailed flux calculations to interrogate the importance of the two reactions in shallow sediment, one might also incorporate the  $\delta^{13}\text{C}$ -DIC values. This is because  $\delta^{13}\text{C}$ -DIC values and the depth of DIC production differ considerably across many sites where either AOM or OSR dominates. We generate a figure expressing these relationships at multiple sites (Fig. 12), where the y-axis is:

$$\frac{\Delta(\text{DIC} + \text{Ca}^{2+} + \text{Mg}^{2+})}{\Delta(\text{SO}_4^{2-})}, \quad (8)$$

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and the x-axis is:  $\text{DIC} \cdot \delta^{13}\text{C} - \text{DIC}$ . The C:S ratios of dissolved species lie above 1:1 at most locations, regardless of whether  $\text{CH}_4$  exists in shallow sediment and AOM dominates, as highlighted by Chatterjee et al. (2011). However, sites with significant  $\text{CH}_4$  have considerably more negative  $\text{DIC} \cdot \delta^{13}\text{C} - \text{DIC}$  values. Notably, pore waters from all stations examined here, except S31 on the Lomonosov Ridge, have modest  $\text{DIC} \cdot \delta^{13}\text{C} - \text{DIC}$  values consistent with a dominance of OSR in shallow sediment rather than AOM.

In summary, from general pore water considerations as well as from comparisons to pore water profiles at other locations, sediments across SNESS do not contain  $\text{CH}_4$  over extensive areas of shallow sediment. Implicit in this finding is that sediment sequences in this region lack widespread gas hydrate. As models for gas hydrate occurrence in the Arctic (Fig. 1) correctly predict gas hydrate in several regions (e.g., Kvenvolden and Grantz, 1990; Max and Lowrie, 1993; Max and Johnson, 2012), our findings prompt an interesting question: why are predictions so markedly wrong for the SNESS?

### 5.6 Possible explanations for widespread absence of gas hydrate and methane

To understand the likely absence of widespread gas hydrates across SNESS, one needs to consider the generalities of their occurrence in marine sediment. There are two basic conditions for gas hydrate on continental slopes (Kvenvolden, 1993; Dickens, 2001). The first consideration is the “potential volume”, or the pore space where physiochemical conditions (e.g., temperature, pressure, salinity, sediment porosity) are amenable to gas hydrate formation. As stressed in previous works, because of cold bottom water and a low geothermal gradient, the region has a relatively large volume of sediment with appropriate gas hydrate stability conditions (Stranne et al., 2016). The second consideration is the “occupancy”, or the fraction of sediment pore space with sufficient  $\text{CH}_4$  to precipitate gas hydrate. While environmental conditions across SNESS are highly conducive for gas hydrate formation, pore water profiles strongly indicate little to no  $\text{CH}_4$  exists in the upper hundred meters of sediment.

This inference strongly depends on recognition as to how diffusive systems operate in marine sediment. Hundreds of pore water profiles have been generated during scientific ocean drilling expeditions, including scores into  $\text{CH}_4$  charged sediment sequences. These profiles almost universally show vertical connectivity of pore water chemistry over hundreds of meters (Fig. 3). Moreover, away from local sites of advection, pore water profiles are generally similar over extensive areas. This occurs because, given sufficient permeability and time, diffusive fluxes transport species from intervals of high concentration to intervals of low concentration. Hence, unless some impermeable layer exists in the sediment sequence, even  $\text{CH}_4$  at depth impacts near seafloor concentrations. Indeed, work on the outer Blake Ridge wonderfully shows this phenomenon. The uppermost gas hydrate in sediment in this region lies at about 190 mbsf (Borowski et al., 1999). Nonetheless, its presence occurs over ~26,000 km<sup>2</sup> and affects shallow pore water profiles across this region, because the flux of  $\text{CH}_4$  from depth drives AOM near the seafloor (Borowski et al., 1999; Dickens, 2001).



No seafloor features indicative of seafloor CH<sub>4</sub> expulsion were found during the bathymetric mapping of SNESS. Nonetheless, it is possible that local CH<sub>4</sub> venting, perhaps related to and mediated by bubble transport, could occur away from transects and cores of SWERUS Leg 2. Certainly, the chemistry of advecting fluids toward seafloor features such as mud volcanoes and cold seeps typically differs from the much broader surrounding region (Luff and Wallmann, 2003; Coffin et al., 2007; Hiruta et al., 2009; Hu et al., 2010; Coffin et al., 2014; Hu et al., 2015). However, in such cases, even the encompassing area typically has shallow SMTs. Without invoking odd geology, such as an extensive impermeable layer, it is unlikely that significant CH<sub>4</sub> exists in shallow sediment across much of SNESS, including as gas hydrate or free gas. Here it is stressed that neither gas hydrate nor free gas can exist in sediment on continental slopes without high concentrations of dissolved gas in surrounding pore water (Dickens et al., 1997; Hiruta et al., 2009; Geprägs et al., 2016). The surprising lack of CH<sub>4</sub> across SNESS, as inferred from pore water profiles, suggests insufficient net input of POC over time, so that either methanogenesis has not occurred or the product has been lost.

The accumulation of POC within the SNESS region may be relatively low over the Plio-Pleistocene. With low POC inputs, other microbial reactions can exhaust the labile organic matter needed for methanogenesis. This may, in fact, explain why the pore water chemistry suggests that metal-oxide reduction dominates the geochemical environment at most of our stations. Without further investigation, we offer four possibilities (not mutually exclusive) as to why this might occur: (1) significant sea-ice concentrations, both at present-day and during past glacial intervals, greatly diminishes primary production of marine organic carbon within the water column; (2) the extremely broad continental shelf prevents large accumulations of terrestrial organic rich sediment from reaching the slope; (3) highly variable sediment accumulation, perhaps corresponding to glacial-interglacial oscillations, creates a situation where POC from either source is consumed during time intervals of low deposition; and although not directly related to POC accumulation (4) changes in sea level during the last glacial maximum caused much of the hydrate to outgas as the stability zone moved downslope (Stranne et al., 2016). With the third explanation, large land-based glaciers in the past may have physically scoured sediment (and organic matter) from the upper slope (Jakobsson et al., 2014). Importantly, the first three explanations distinguish the SNESS region from the Beaufort Sea, where abundant CH<sub>4</sub> in shallow sediment unquestionably occurs (Coffin et al., 2011, Treude et al., 2014).

In earlier times, particularly the Cretaceous through Early Eocene (Jenkyns et al., 2004; Sluijs et al., 2006; Backman et al., 2009), organic-rich sediment may have accumulated at high rates throughout the Arctic. Definitely on Lomonosov Ridge in the central Arctic, Lower Eocene sediments contain high organic carbon and potential indicators of past methanogenesis (e.g., barium mobilization). As these cores contain no CH<sub>4</sub> at present day, presumably if CH<sub>4</sub> was generated, it has been lost in the intervening time. Should these organic-rich horizons be buried across the SNESS region and presently generating CH<sub>4</sub> via thermogenesis, the gas is too deeply buried to affect shallow sediment.

## 6 Conclusions

Re Leg 2 of the SWERUS-C3 expedition recovered sediments and pore waters from numerous stations across the continental slopes North of the East Siberian Sea (SNESS). These stations extend from Wrangel Island to the New Siberian Islands, and provide information from a climatically sensitive but highly inaccessible area.

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In an effort to understand CH<sub>4</sub> cycling within the SNESS region, we generated detailed pore water profiles of multiple dissolved constituents. The pore water profiles are coherent and interpretable, and give a general view: most stations have low SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> fluxes (<6.2 and 6.8 mol/m<sup>2</sup>-kyr respectively), a moderate decrease in δ<sup>13</sup>C-DIC values with depth (-3.6‰/m average), no dissolved H<sub>2</sub>S, moderate rise in HPO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> concentrations, and slightly decreasing Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Sr<sup>2+</sup> concentrations. Except for one station on the Lomonosov Ridge, metal oxide reduction appears to be the dominant geochemical environment affecting shallow sediment, and there is no evidence for upward diffusing CH<sub>4</sub>. These results strongly suggest that gas hydrates do not occur on any of our depth transects spread across the continental slope in this region of the Arctic Ocean. This directly conflicts with ideas in multiple publications, which generally have assumed large quantities of CH<sub>4</sub> and gas hydrate. However, it remains possible that significant CH<sub>4</sub> occurs where the Lomonosov Ridge intersects the continental margin as well as westward on the Laptev Sea continental slope.

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### Figure Captions

20 **Figure 1:** Generalized Arctic map with background from GeoMapApp (<http://www.geomapapp.org>; Ryan et al., 2009). Observed sulfate-methane transitions during the MITAS 1 expedition shown in black diamonds (Coffin et al., 2013) and Arctic Coring Expedition (ACEX) shown as red squares (Backman et al., 2009).

**Figure2:** Bathymetric map of Eurasian Arctic showing the overall cruise track of Leg 2 along with the four transects and coring locations. Multicores shown as yellow triangles, gravity and piston cores as white stars, and the ship trackline as gray line from Barrow, Alaska.

25 **Figure 3:** Idealized pore water concentration profiles for high and low upward methane flux. Discrete data points for sites 722 (Arabian Sea; Seifert and Michaelis, 1991; D'Hondt et al., 2002) and 1230 (offshore Peru; Donohue et al., 2006) are given as reference.

**Figure 4:** Transect 1. results. IAPSO standard seawater (black dotted line) shown for comparison.

**Figure 5:** Transect 2. results. IAPSO standard seawater (black dotted line) shown for comparison.

**Figure 6:** Transect 3. results. IAPSO standard seawater (black dotted line) shown for comparison.

30 **Figure 7:** Transect 4. results. IAPSO standard seawater (black dotted line) shown for comparison.

**Figure 8:** Lomonosov Ridge Station results. IAPSO standard seawater (black dotted line), and representative stations from the four transects shown for comparison.

35 **Figure 9:** Relationship of (a) sulfate change (ΔSO<sub>4</sub><sup>2-</sup>) and carbonate corrected alkalinity change (ΔAlk+Ca<sup>2+</sup>+Mg<sup>2+</sup>); (b) the second order polynomial association of NH<sub>4</sub><sup>+</sup> to Alkalinity; and (c) decreasing δ<sup>13</sup>C-DIC values with alkalinity increase. Methane charged sites (1230, 1426, and 1427; 1230, Shipboard Scientific Party, 2003; 1426 and 1427, Expedition Scientists, 2014) given for comparison.

**Figure 20:** C:N:P ratio indirectly shown with  $\Delta\text{Alk}/\Delta\text{NH}_4^+$  and  $\Delta\text{Alk}/\Delta\text{HPO}_4^{2-}$ . Several global sites, 994, 995, 997, 1059, 1225, 1230, 1426, 1427, and 1319 (994-997, 1059, Borowski et al., 2000; 1225 and 1230, Shipboard Scientific Party, 2003; 1426 and 1427, Expedition Scientists, 2014) given for comparison. Blue marginal distribution curves show global distribution while red gives SNESS stations (this project). SNESS pore waters have higher C:N and lower C:P than comparative sites.

**Figure 31:** Bicarbonate ( $\text{HCO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) flux exponential relationship with SMT depth for all sites listed in Tbl. 2.

**Figure 42:** Ratio of carbonate corrected alkalinity change ( $\Delta\text{Alk}+\text{Ca}^{2+}+\text{Mg}^{2+}$ ) and sulfate change ( $\Delta\text{SO}_4^{2-}$ ) to the product of DIC and  $\delta^{13}\text{C}$ -DIC value (AT13-2 and KC151, Kastner et al., 2008a; PC02-PC14, Coffin et al., 2008; 994-997, 1059, Borowski et al., 2000; Paull et al., 2000; 1326 and 1329, Torres and Kastner, 2009; GC233 and GB425, Hu et al., 2010; D-5 – D-8 and D-F, Hu et al., 2015; C9-C19, Luo et al., 2013; PC-07, Smith and Coffin, 2014; 1230, Shipboard Scientific Party, 2003; 1244 and 1247, Claypool et al., 2006; 1305 and 1306, Party, 2005) including global sites for comparison) showing the paucity of methane charged sites actually reaching 1:1 C:S ratio. Error bars are one sigma. SNESS plotted pore waters substitute alkalinity for DIC. With the absence of sulfide, DIC and alkalinity should be roughly equivalent in these pore waters. SNESS locations use the same symbols as previous figures.

## Tables

Analysis	Sample Type	Number	Result
Alkalinity	Spiked	15	PE = 1.53%
Alkalinity	Duplicate	8	PD = 1.30%
$\delta^{13}\text{C}$ -DIC	Seawater Standard	2	0.23‰ and 0.32‰
$\delta^{13}\text{C}$ -DIC	Blind Field Duplicate	4	PD = 22.98%
$\delta^{13}\text{C}$ -DIC	Field Blank	1	No Result
$\delta^{13}\text{C}$ -DIC	Duplicate	10	PD = 14.70%
Metals	Spiked	51	RSD = 2.55% (Ba), 2.17% (Ca), 1.53% (Fe), 0.77% (Mg), 1.73% (Mn), 1.88% (S), and 1.42% (Sr)
Metals	Blind Field Duplicate	11	PD = 2.56% (Ba), 3.77% (Ca), 5.81% (Fe), 2.68% (Mg), 3.07% (Mn), 0.71% (S), and 3.79% (Sr)
Metals	Field Blank	2	BDL
Phosphate	VKI Standard	2	PE = 1.28% and 2.69%
Ammonia	VKI Standard	2	PE = 2.40% and 6.25%

Notes: PE = Percent Error  
 PD = Percent Difference  
 RSD = Relative Standard Deviation  
 BDL = Below Detection Limit

**Table 5:** QA/QC.

Ocean	Location	Water Depth (m)	SMT Depth (mbsf)	$\text{SO}_4^{2-}$ Flux (mol/m <sup>2</sup> kyr)	Alkalinity Flux (mol/m <sup>2</sup> kyr)	$\delta^{13}\text{C}$ at SMT (‰)
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Arctic	Beaufort Sea - Cape Halkett <sup>a,b</sup>	280	1.06	-154.8	242.6	-21.5
Arctic	Beaufort Sea - Cape Halkett <sup>a,b</sup>	342	1.47	-124.7	212.3	-20.2
Arctic	Beaufort Sea - Cape Halkett <sup>a,b</sup>	1005	3.73	-44.2	130.3	-18.2
Arctic	Beaufort Sea - Cape Halkett <sup>a,b</sup>	1458	6.29	-27.4	46.3	-19.7
Arctic	East Siberian Slope	349	61	-1.8	1.7	--
Arctic	East Siberian Slope	367	25	-6.9	6.3	--
Arctic	East Siberian Slope	384	64	-2.4	2.3	--
Arctic	East Siberian Slope	524	35	-5.6	2.8	--
Arctic	East Siberian Slope	733	58	-2.1	1.5	--
Arctic	East Siberian Slope	977	58	-2.1	1.6	--
Arctic	East Siberian Slope	964	23	-9.2	6.8	--
Arctic	East Siberian Slope	1000	52	-3.3	3.3	--
Arctic	East Siberian Slope	1143	44	-5.1	3.5	--
Arctic	East Siberian Slope	1120	14	-13.9	11.3	--
Atlantic	New Jersey Continental Slope <sup>q,i</sup>	912	28.9	-3.3	3.6 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,p</sup>	1293	50.3	-3.4	3.8 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,p</sup>	1798	26.9	-6.6	4.9 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,x</sup>	2567	42.0	-3.8	3.5 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,x</sup>	2641	24.5	-7.6	6.9 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,x</sup>	2777	21.7	-8.3	5.4 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,x</sup>	2770	22.5	-7.8	4.7 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,x</sup>	2798	21.5	-8.7	4.4 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,p</sup>	2985	9.3	-20.0	20.4 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,p</sup>	3481	12.3	-17.1	17.0 <sup>‡</sup>	--
Atlantic	Blake Ridge <sup>q,p</sup>	4040	16.8	-10.5	10.8 <sup>‡</sup>	--
Atlantic	Gulf of Mexico - Keathley Canyon <sup>w</sup>	1300	9	-33 <sup>‡</sup>	17 <sup>‡</sup>	-49.6
Atlantic	Gulf of Mexico - Atwater Valley <sup>w</sup>	1300	0.1	-2901	--	--
Atlantic	Gulf of Mexico - Atwater Valley <sup>w</sup>	1300	0.1	-2901	--	--
Atlantic	Gulf of Mexico - Atwater Valley <sup>w</sup>	1300	0.6	-437	--	--
Atlantic	Gulf of Mexico - Atwater Valley <sup>w</sup>	1300	7	-67	--	-46.3
Atlantic	Amazon Fan <sup>q,v,y</sup>	3191	37.2	-3.2	4.1 <sup>‡</sup>	-39.8
Atlantic	Amazon Fan <sup>q,v,y</sup>	3474	6.2	-24.6	22.7 <sup>‡</sup>	-47.5
Atlantic	Amazon Fan <sup>q,v,y</sup>	3704	3.7	-40.3	24.3 <sup>‡</sup>	-49.6
Atlantic	Western Africa <sup>q,z</sup>	426	12.8	-12.5	18.2 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	738	52.9	-3.1	2.9 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	1280	21.3	-12.0	15.6 <sup>‡</sup>	-19.8

Atlantic	Western Africa <sup>q,z</sup>	1402	18.3	-14.9	28.3 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	1713	38.5	-5.1	4.1 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	2179	26.7	-7.8	10.4 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	2382	21.1	-18.1	21.8 <sup>‡</sup>	--
Atlantic	Western Africa <sup>q,z</sup>	2995	29.7	-14.9	20.9 <sup>‡</sup>	--
Atlantic	Argentine Basin <sup>l</sup>	1228	10.5	-19.1	--	--
Atlantic	Argentine Basin <sup>l</sup>	1492	12	-20.2	--	--
Atlantic	Argentine Basin <sup>l</sup>	1568	4.9	-84.6	--	--
Atlantic	Argentine Basin <sup>l</sup>	1789	5.9	-55.6	--	--
Atlantic	Argentine Basin <sup>l</sup>	3247	10	-21.8	--	--
Atlantic	Argentine Basin <sup>l</sup>	3167	14	-14.7	--	--
Atlantic	Argentine Basin <sup>l</sup>	3542	3.7	-75.4	--	--
Atlantic	Argentine Basin <sup>l</sup>	3551	5.6	-39.9	--	--
Atlantic	Argentine Basin <sup>l</sup>	3551	4.1	-93.3	--	--
Atlantic	Argentine Basin <sup>l</sup>	3623	5	-43.1	--	--
Atlantic	Argentine Basin <sup>l</sup>	4280	5.1	-43.5	--	--
Atlantic	Argentine Basin <sup>l</sup>	4799	12	-17.9	--	--
Indian	Oman <sup>q,1</sup>	591	50.2	-2.2	1.1 <sup>‡</sup>	--
Indian	Oman <sup>q,1</sup>	804	46.5	-2.8	4.4 <sup>‡</sup>	--
Indian	Oman <sup>q,1</sup>	1423	82.4	-1.8	0.8 <sup>‡</sup>	--
Pacific	Bering Sea <sup>p,2</sup>	1008	6.3	-32.8	37.8	-25.1
Pacific	Cascadia <sup>q,u,2</sup>	959	9.0	-23.6	--	-23.8
Pacific	Cascadia <sup>q,u,2</sup>	1322	7.9	-21.3	--	-30.8
Pacific	Cascadia <sup>q,u,2</sup>	1828	2.5	-49.0	--	-33.9
Pacific	Cascadia - Hydrate Ridge <sup>o</sup>	834	8	-10.9	11.3	-19.6
Pacific	Cascadia - Hydrate Ridge <sup>o</sup>	850	7.65	-22.3	23.2	-30.2
Pacific	Cascadia - Hydrate Ridge <sup>o</sup>	871	7.4	-26.6	33.4	-24.9
Pacific	Cascadia - Hydrate Ridge <sup>g</sup>	896	7.8	-16	22	-22.5
Pacific	Umitaka Spur <sup>h</sup>	900	2.2	-71	114	--
Pacific	Umitaka Spur <sup>h</sup>	947	2.9	-58	80	--
Pacific	Umitaka Spur <sup>h</sup>	1034	2.0	-102	100	--
Pacific	Japan Sea <sup>s,4</sup>	901	10	-33.6	38.4 <sup>‡</sup>	--
Pacific	California Margin <sup>q,5</sup>	955	13.3	-17.3	19.6 <sup>‡</sup>	--
Pacific	California Margin <sup>q,5</sup>	1564	19.0	-9.3	12.8 <sup>‡</sup>	--
Pacific	California Margin <sup>q,5</sup>	1926	31.0	-4.3	3.1 <sup>‡</sup>	--
Pacific	Nankai Trough <sup>q,6</sup>	1741	32.2	-4.9	3 <sup>‡</sup>	--

Pacific	Nankai Trough <sup>s,6</sup>	2997	11.0	-5.6	8.7 <sup>‡</sup>	--
Pacific	Nankai Trough <sup>q,6</sup>	3020	18.2	-7.0	6.4 <sup>‡</sup>	--
Pacific	Santa Barbara <sup>k</sup>	587	1.3	-175.2	--	--
Pacific	Soledad <sup>k</sup>	542	1	-310.3	--	--
Pacific	Pescadero <sup>k</sup>	408	1.4	-164.3	--	--
Pacific	Magdalena <sup>k</sup>	600	1.5	-182.5	--	--
Pacific	Alfonso <sup>k</sup>	713	0.8	-474.5	--	--
Pacific	Costa Rica Margin <sup>q,7</sup>	3306	16.0	-8.1	9.6 <sup>‡</sup>	--
Pacific	Costa Rica Margin <sup>q,7</sup>	4177	19.8	-7.5	3.1 <sup>‡</sup>	--
Pacific	Costa Rica Margin <sup>q,7</sup>	4311	18.6	-12.3	12.4 <sup>‡</sup>	--
Pacific	Peru Margin <sup>s,8</sup>	161	30	-6.9	--	--
Pacific	Peru Margin <sup>t,9</sup>	427	40	-1.2	--	-25.4
Pacific	Peru Margin <sup>t,9</sup>	5086	9	-25.0	--	-13.2
Pacific	Chilean Coast <sup>c</sup>	586	5.55	-22.9	--	--
Pacific	Chilean Coast <sup>c</sup>	723	0.33	-362.0	--	--
Pacific	Chilean Coast <sup>c</sup>	980	2.92	-45.3	--	--
Pacific	Chilean Coast <sup>c</sup>	768	10.11	-13.3	--	--
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	12.8	-11.4	--	-31.4
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	4.4	-53.3	--	-31.6
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	3.6	-50.5	--	-31.4
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	2.1	-74.2	--	-33.4
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	3.8	-61.5	--	-35.0
Pacific	New Zealand - Porangahau Ridge <sup>f</sup>	1900-2150	1.8	-82.6	--	-48.8
Pacific	New Zealand - Hikurangi <sup>b,d</sup>	350	39.5	5 <sup>‡</sup>	7.3 <sup>‡</sup>	--
Pacific	New Zealand - Hikurangi <sup>b,d</sup>	332	12.9	19.3 <sup>‡</sup>	13.6 <sup>‡</sup>	--
Pacific	New Zealand - Hikurangi <sup>b,d</sup>	98	0.87	192.1 <sup>‡</sup>	160.9 <sup>‡</sup>	--
Pacific	New Zealand - Hikurangi <sup>b,d</sup>	285	3.64	65.2 <sup>‡</sup>	59.6 <sup>‡</sup>	--
Southern Ocean	Antarctic - Cumberland Bay <sup>n</sup>	237	5.03	-86	95	-25.4
Southern Ocean	Antarctic - Cumberland Bay <sup>n</sup>	260	0.80	-539	291	-23.5
Southern Ocean	Antarctic - Cumberland Bay <sup>n</sup>	275	2.80	-135	116	-15.5

**Table 2:** Published and Calculated Fluxes

a = Coffin et al., 2013; b = Personal Communication; c = Coffin et al., 2007; d = Coffin et al., 2006; e = Coffin et al., 2008; f = Hamdan et al., 2011 and Coffin et al., 2014; g = Dickens and Snyder, 2009; h= Snyder et al., 2007; i = Mountain et al., 1994; j = Lin et al., 2006; k = Berelson et al., 2005; l = Hensen et al., 2003; m = Dickens, 2001; n = Geprags et al., 2016; o = Claypool et al., 2006; p = Keigwin et al., 1998; q = Berg, 2008; r = Borowski et al., 2000; s = D'Hondt et al., 2002; t = D'Hondt et al., 2004; u = Torres et al., 2009; v = Burns, 1998; w = Kastner et al., 2008; x = Paull et al., 1996; y = Flood et al., 1995; z = Wefer et al., 1998; 1 = Prell et al., 1998; 2 = Takahashi et al., 2011; 3 = Riedel et al., 2006; 4 = Tamaki et al., 1990; 5 = Lyle et al., 1997; 6 = Moore et al., 2001; 7 = Kimura et al., 1997; 8 = Suess et al., 1988; 9 = D'Hondt et al., 2003. ‡ = Calculated from published material.

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