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Methane seepage at Vestnesa Ridge (NW Svalbard) since the Last Glacial Maximum

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A B S T R A C T

Multiple proxies in the geological record offshore NW Svalbard track shallow subseafloor diagenesis and seafloor methane seepage during the Last Glacial Maximum (LGM) extent and the disintegration of the Svalbard Barents Sea Ice Sheet (SBIS). Vestnesa Ridge, located at 79°N and in 1200 m water depth, is one of the northernmost known active methane seep sites and is characterised by a subseafloor fluid flow system, numerous seafloor pockmarks and gas flares in the water column. In this study, we develop a Late Pleistocene and Holocene stratigraphic framework, use stable oxygen and carbon isotope signatures ($\delta^{18}O$, $\delta^{13}C$) of benthic and planktic foraminifera, the mineralogical and carbon isotope composition of methane-derived authigenic carbonate (MDAC) and sediment geochemical data of ten sediment cores to assess methane seepage variability on Vestnesa Ridge.

The studied cores cover the age range between 31.9 and 10 cal ka BP and record 32 negative $\delta^{13}C$ excursions in benthic and planktic foraminifera with amplitudes down to −29 ‰ VPDB. These $\delta^{13}C$ excursions are often associated with elevated Ca/Ti and Sr/Ti elemental ratios in sediments and MDAC nodules. The precipitation of MDAC overgrowth on foraminiferal tests explains most of the negative $\delta^{13}C$ excursions. In this dataset, the oldest recorded methane emission episodes on Vestnesa Ridge occurred between the LGM (24–23.5 cal ka BP) and Heinrich Event 1 (HE 1; 17.7–16.8 cal ka BP).

Geological indicators for past subseafloor methane cycling and seafloor methane seepage, such as negative foraminiferal $\delta^{13}C$ excursions, MDAC nodules, and elevated Sr/Ti elemental ratios recorded in post-LGM sediments, possibly represent vertical migration of the sulphate-methane transition zone (SMTZ) and post-date sedimentation by up to 13.4 ka. However, it is important to note that indications of post-LGM seafloor methane seepage at Vestnesa Ridge also correspond to the established methane efflux chronology for the adjacent Barents Sea shelf, implying that glacio-isostatic adjustments and associated re-activation of pre-existing deep-seated faults after disintegration of the SBIS are likely important controlling factors on fluid migration towards the seafloor.

1. Introduction

Current global warming raises concern about the role of methane, a powerful greenhouse gas, in the Arctic as the circum-Arctic is expected to experience a larger temperature increase than any other region on the planet (Serreze and Barry, 2011; IPCC, 2013; AMAP Assesment, 2015). In the upcoming century, increasing

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Arctic bottom water temperatures are hypothesised as potential drivers for destabilisation of gas hydrates along continental margins that may cause unprecedented release of methane into the water column and the atmosphere (Reagan and Moridis, 2007; Westbrook et al., 2009; Biastoch et al., 2011; Giustiniani et al., 2013; Kretschmer et al., 2015; James et al., 2016). Although causal relationships between recent climate warming and increased methane release from Arctic Ocean sediments may seem likely, seepage observed today could have been initiated thousands of years ago. For example, methane release on the East Siberian Arctic Shelf that was attributed to current global warming (Shakhova et al., 2010) is more likely the result of submarine permafrost thaw after the inundation of terrestrial permafrost during the Holocene marine transgression (Bauch et al., 2001; Dmitrenko et al., 2011). Also, the persistent leakage of methane in the deep ocean offshore north-western Svalbard may not be related to climate warming (Knies et al., 2018).

To evaluate if climate warming or other Earth system processes affect the release of methane stored in Arctic Ocean sediments, a better understanding of the timing and drivers of past methane seepage variability in the Arctic is required. Since active methane seepage at Vestnesa Ridge, western Svalbard (Fig. 1), was first revealed by water column acoustic data, research in the area has provided key information for understanding the dynamics of seafloor methane release and seepage over geological time scales in the Arctic (Panieri et al., 2017b and references therein). Previous studies found evidence for seepage occurring during the past 17 cal ka (Panieri et al., 2014; Consolaro et al., 2015; Ambrose et al., 2015; Sztybor and Rasmussen, 2017a, 2017b; Schneider et al., 2017). However, these observations have limited regional coverage. The objective of this study is to identify episodes of past methane seepage along Vestnesa Ridge since the Last Glacial Maximum (LGM) and during the retreat of the Svalbard-Barents Sea Ice Sheet (SBIS). We develop a Late Pleistocene and Holocene stratigraphic framework for the investigated sediment cores from Vestnesa Ridge, and correlate our sedimentary record with established stratigraphic marker horizons along the western Svalbard continental margin. We use multiple proxies such as $\delta^{18}O$ and $\delta^{13}C$ records from benthic and planktic foraminifera, chemosynthetic bivalves, mineralogy and $\delta^{13}C$ of MDAC, and sediment geochemical data to identify shallow subseafloor diagenesis and seafloor methane seepage. This study provides the first comprehensive insight into timing and drivers of methane seepage activity or quiescence along Vestnesa Ridge since the LGM.

2. Background and processes in gas-charged sediments

Methane (CH_4) can be of microbial, thermogenic, or abiotic origin (Whiticar, 1999) and occurs in hydrocarbon reservoirs, stored in hydrate, or as dissolved and free gas in continental margin sediments worldwide (Kretschmer et al., 2015; Ruppel and Kessler, 2017). Methane seepage occurs where fluids enriched in methane migrate toward the sediment-water interface (e.g. Torres and Bohrmann, 2006; Etiope, 2015). Seepage is commonly understood as the release of fluids from the seafloor on continental margins and its location is named “seep” (Judd and Hovland, 2007 and references therein).

The geochemical conditions at methane seeps are characterised by opposing gradients of porewater sulphate (SO_4^{2-}) and methane. A biogeochemical boundary, the sulphate-methane transition zone (SMTZ), is established close or up to several metres below the seafloor, where microbial co-metabolism counterbalances the upward flux of methane and the downward flux of sulphate (Reeburgh, 1976; Whiticar and Faber, 1986; Valentine, 2002; Tryon et al., 1999). A changing methane flux can cause vertical migration of the SMTZ through the sediment (Borowski et al., 1996). A key geochemical process at the SMTZ (Eq. (1)) is the microbially mediated anaerobic oxidation of methane (AOM) involving syntrophic consortia of methane-oxidizing archaea and sulphate-reducing bacteria (Knittel and Boetius, 2009 and references therein):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (1)$$

Reducing conditions at the SMTZ can result in reductive dissolution of magnetic Fe-oxides (Canfield and Berner, 1987; Peckmann et al., 2001; Riedinger et al., 2005; Novosel et al., 2005; Dewangan et al., 2013) and alteration of the initial sediment composition and magnetic properties due to replacement of magnetic Fe-oxides by paramagnetic authigenic Fe-sulfides (Ferrell and Aharon, 1994; Bohrmann et al., 1998; Rodriguez et al., 2000; Greinert et al., 2001; März et al., 2008; Lin et al., 2016, 2017). Barium (Ba^{2+}) that is present dissolved in seep fluids (Hanor, 2000; Torres et al., 2003a) can react with porewater sulphate and can precipitate as authigenic barite ($BaSO_4$) at the upper boundary of the SMTZ (Torres et al., 1996; Dickens, 2001; Paytan et al., 2002; Riedinger et el., 2006; Kasten et al., 2012; Sauer et al., 2017). As porewater sulphate is depleted underneath the SMTZ, buried barite dissolves and barium diffuses upward to the SMTZ where it re-precipitates as authigenic barite (Torres et al., 1996; Dickens, 2001). Barite fronts are commonly found immediately above the present-day depth of porewater sulphate depletion and serve as a geochemical tracer for the SMTZ (Dickens, 2001; Riedinger et al., 2006).

The SMTZ is also the sedimentary interval where MDAC precipitates. The AOM (Eq. (1)) elevates the porewater alkalinity (Ritger et al., 1986; Paull et al., 1992), and thus promotes the precipitation of $Ca(Mg/Sr)CO_3$ (Eq. (2)):

$$2\ HCO_3^- + Ca^{2+}\ (Mg^{2+}/Sr^{2+}) \rightarrow Ca(Mg/Sr)CO_3 + CO_2 + H_2O \quad (2)$$

Carbonates with $\delta^{13}C$ values more negative than −30 ‰ VPDB are consistent with carbon sourced from AOM (Whiticar, 1999; Aloisi et al., 2000; Bohrmann et al., 2001; Greinert et al., 2001; Naehr et al., 2007). MDAC is often composed of aragonite, high-Mg calcite (5–20 mol% $MgCO_3$, Burton, 1993), or dolomite (Bohrmann et al., 1998, 2001; Aloisi et al., 2000; Greinert et al., 2001; Naehr et al., 2007) and occur as early diagenetic micrite-cemented nodules, cavity fills, coatings, or crusts on the seafloor (Bohrmann et al., 1998, 2001; Mazzini et al., 2004; Bayon et al., 2009; Crémière et al., 2016a; Sauer et al., 2017). Aragonite and high-Mg calcite precipitate near the seafloor and indicate that the SMTZ was located in the shallow subsurface (cm or dm scale) during episodes of high CH_4-flux (Aloisi et al., 2000; Greinert et al., 2001; Naehr et al., 2007). It was suggested that large MDAC crusts require time spans of hundreds to thousands of years to form and often yield different ages compared to their host sediment (Teichert et al., 2003; Bayon et al., 2009; Luff et al., 2004, 2005).

Together with fossil remains of seep fauna, MDAC provides direct geological evidence of AOM and methane seepage in the sedimentary record. Panieri et al. (2017a) showed that foraminifera serve as preferred nucleation templates for authigenic Mg-calcite precipitation at methane seeps. Negative $\delta^{13}C$ excursions from benthic foraminifera in sedimentary records have been used to identify periodic release of methane stored in gas hydrates at various times in earth history (Dickens et al., 1997; Kennet et al., 2000; Thomas et al., 2002; Jenkyns, 2003; Tripati and Elderfield, 2005; Zachos et al., 2007). Several studies have shown that MDAC precipitates form coatings around foraminiferal tests and may overprint the primary shell mineralogy and stable isotope composition, which complicates the use of foraminiferal $\delta^{13}C$