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Williscroft, K, Grasby, SE, Beauchamp, B et al. (5 more authors) (2017) Extensive Lower Cretaceous (Albian) methane seepage on Ellef Ringnes Island, Canadian High Arctic. Geological Society of America Bulletin, 129 (7-8). pp. 788-805. ISSN 0016-7606

https://doi.org/10.1130/B31601.1

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Extensive Lower Cretaceous (Albian) methane seepage on Ellef Ringnes Island, Canadian High Arctic

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ABSTRACT

During field mapping of Ellef Ringnes Island, Canadian Arctic Archipelago, 139 isolated Lower Cretaceous methane seep deposits were found from 75 field sites. Stable isotopes of the carbonates have values of $\delta^{13}C$= -47‰ to -35‰ and $\delta^{18}O$= -4.0‰ to +0.7‰. Isoprenoids in organics from one of the seeps are significantly depleted in ^{13}C, with the most negative $\delta^{13}C$ of = -118 ‰ and -113 ‰ for PMI and phytane/crocetane, respectively. These values indicate an origin through methane oxidation, consistent with biomarkers that are characteristic for anaerobic methanotrophic archaea within the seep deposits, accompanied by terminally-branched fatty acids sourced by sulphate-reducing bacteria, showing similar ^{13}C values (-92‰). The seep deposits contain a moderate diversity macrofaunal assemblage containing ammonites, bivalves, gastropods, scaphopods, 'vestimentiferan' worm tubes and brachiopods. The assemblage is dominated numerically by species that probably had chemosymbionts. The seep deposits formed in the subsurface with strong redox zones, in an otherwise normal marine setting, characterised by oxic waters at high paleolatitudes.

While geographically widespread, over an area of ~10,000 km^2, seep deposits on Ellef Ringnes Island occur in a narrow stratigraphic horizon, suggesting a large release of biogenic methane occurred over a brief period of time. This gas release was coincident with a transition from a cold to warm climate during the latest Early Albian, and we hypothetize that this may relate to gas hydrate release.

1.0 INTRODUCTION

Methane seepage into modern marine environment was first recognized at the foot of the Florida Escarpment (Paull et al., 1984). Since then, the seepage of methane-enriched fluids from the seabed into the water column has been found to be a common feature along continental margins, forming in many cases distinctive seafloor feature such as pockmarks and mud volcanoes, and ranging from isolated occurrences to high density fields on the sea floor (e.g. Judd and Hovland, 2007; Kulm et al., 1986; Suess, 2014). At seep sites, a major proportion of the methane is consumed in sub-surface sediments by sulfate-dependent anaerobic oxidation of methane (AOM) biogeochemical process (Hoehler et al., 1994), mediated by anaerobic methane oxidizing archaea (ANMEs) and sulfate-reducing bacteria (SRB) (Boetius et al., 2000; Hinrichs et al., 1999; Milucka et al., 2012; Orphan et al., 2001). AOM produces an excess of dissolved inorganic carbon (DIC), promoting the rapid precipitation of authigenic carbonates depleted in ^{13}C as a by-product (Paull et al., 1984; Ritger et al., 1987). These carbonates have complex cement fabrics (e.g. Aloisi et al., 2000; Haas et al., 2010; Naehr et al., 2007; Ritger et al., 1987), and a wide variety of morphologies (e.g. nodules, tubular/tabular concretions, cemented breccias and pavements) and sizes (e.g. Campbell, 2006). The seep carbonates are often exhumed onto the seafloor by sediment erosion and can then act as hard substrates for attached epifaunal animals (e.g. serpulid tubeworms). Active methane seeps support diverse and high-biomass communities of macrofauna, which are dominated by animals having symbiotic relationships with chemotrophic bacteria (principally methanotrophs and thiotrophs). These taxa include bivalves (e.g. solemyid, vesicomyid, lucinid and thyasirid clams, and bathymodiolin mussels) and siboglinid (vestimentiferan) tubeworms (e.g. Dubilier et al., 2008; Levin, 2005; Paull et al., 1984; Sibuet and Olu, 1998).

One of the first identifications of methane seeps in the geological record was from Lower Cretaceous strata in the Sverdrup Basin (Fig. 1) (Beauchamp et al., 1989). In that study, four methane seep deposits were described, two each on Ellef Ringnes and Prince Patrick islands in the remote Canadian High Arctic, and the first linkage with modern cold methane seeps was made. Subsequent detailed petrographic studies of samples from these deposits (Beauchamp and Savard, 1992; Savard et al., 1996) identified a suite of early phase carbonate cements (calcite microspar, fibrous botryoidal and splayed calcite and anhedral yellow calcite) with very negative $\delta^{13}C$ isotope values derived from methane and, on Ellef Ringnes Island only, late phase carbonate cements (saddle dolomite, bladed calcite and coarse anhedral calcite) with less negative $\delta^{13}C$ values formed during burial diagenesis. Savard et al. (1996) showed that original aragonite is present in the early phase cements from the seep deposits from both islands; this constituted the first recognition of aragonite precipitation at ancient methane seeps deposited under ‘calcite sea’ conditions. Beauchamp et al. (1989) and Beauchamp and Savard (1992) recorded a biota of molluscs (abundant bivalves, smaller numbers of ammonites and gastropods), worm tubes (larger diameter serpulids and smaller diameter possible serpulids), foraminifera, fish teeth and wood fragments from all four seep deposits, and, in addition, terebratulid brachiopods (later described as Modestella jeletzkyi (Sandy, 1990)) and coiled spirorbid tubes in the southern deposit of Prince Patrick Island.

Since recognition of the Cretaceous Sverdrup Basin examples, many ancient fossil-rich seep deposits have been recognised in the rock record throughout the world, from as old as the Devonian, or even Silurian, with similar paragenetic cement phases and stable isotopic compositions (see Campbell, 2006 and references therein). In addition, organic biomarkers for AOM have been discovered in seep deposits back to the Carboniferous (Birgel et al., 2008a).

Like modern examples, ancient seep deposits have a wide variety of morphologies, but lens shapes at various scales (metres to 10s metres in diameter and centimetres to metres high) are common (Campbell, 2006). These are often exposed on the land surface as indurated mound-shaped structures, due to the erosion of enclosing fine grained sediments. Ancient seep carbonates can occur as isolated deposits, but are usually found with other examples in the same sedimentary sequence, sometimes at high density. For example, in Late Cretaceous sediments of the Western Interior Seaway, USA, up to 13 ‘Tepee Buttes’ seep deposits crop out over 25 km^2 area (Cochran et al., 2015), 15 Late Jurassic to Early Cretaceous seep deposits crop out along 10 km of exposure in Spitsbergen (Hammer et al. 2011), and numerous Paleocene seep deposits are exposed over 5 km in the Panoche Hills, California (Schwartz et al., 2003).

The original studies of the Sverdrup Basin seep deposits (Beauchamp et al., 1989; Beauchamp and Savard, 1992; Savard et al., 1996). were based on only a few hand samples collected as part of a regional mapping expedition in the mid 1970s (Nassichuk and Roy, 1975). While this allowed recognition of methane seeps in the geologic record, the overall context of the sites was poorly constrained. For three decades no additional field work had been conducted on Ellef Ringnes Island given the remoteness, and the seep deposits there were thought to be isolated occurrences. However, a series of expeditions by the Geological Survey of Canada between 2009 and 2011 led to the discovery of 137 new methane seep deposits across the island, a remarkable density that rivals any other occurrence of seepage in the geologic record (Campbell, 2006). Here we give an integrated morphological, geochemical and paleontological description of these newly discovered seep deposits, analyse their geographic and stratigraphic context, and constrain the style, duration and distribution of seafloor seepage in the Sverdrup Basin in context of Lower Cretaceous climate change.

2.0 GEOLOGIC SETTING

Ellef Ringnes Island is part of the Canadian High Arctic, Nunavut, Canada (Fig. 1). It comprises Jurassic through Paleogene sediments of the Sverdrup Basin, a major Carboniferous to Paleocene depocentre (Embry and Beauchamp, 2008). The basin is a ~1000 km long, north-easterly trending depression filled with up to 13 km of marine and non-marine sediments, as well as Cretaceous (predominantly Aptian) basaltic flows and mafic dykes and sills (Balkwill, 1978) (Fig. 2). The Sverdrup Basin originated during Carboniferous-Early Permian rifting (Balkwill, 1978). Deepening and enlargement of the basin resulted in marine transgression and the deposition of over 400 m of evaporites of the Upper Carboniferous Otto Fiord Formation (Nassichuk and Davies, 1980; Thorsteinsson, 1974). Later lithostatic loading, related to the high clastic sediment flux in the Triassic, initiated diapirism of Otto Fiord Formation evaporites in the central part of the Sverdrup Basin (Gould and DeMille, 1964; Macauley et al., 2000; Thorsteinsson, 1974). Stratigraphic evidence shows that diapirs were still mobile during the Cretaceous (Dewing et al., 2016), during the time when seep deposits described here were formed.

Subsidence and sedimentation increased in the basin during renewed rifting and extension in the Upper Jurassic to Lower Cretaceous (Embry and Beauchamp, 2008). Sediment supply rates greatly increased and normal faults were active. Thick, coarse-grained fluvial sediments (Isachsen Formation) and offshore muds and silts (Christopher Formation) were deposited from the Hauterivian to the Late Albian. Marginal uplift in the mid-Aptian occurred in the northeast Sverdrup Basin, where common volcanic units (sills and basalt flows) were emplaced between 130 and 90 Ma (Embry and Beauchamp, 2008; Saumur et al., 2016).

Methane seep deposits in this study are found within the Upper Aptian to Upper Albian Christopher Formation that is composed of medium-grey to black silty mudstone and fine siltstone, and is divided into the lower Invincible Point and upper MacDougall Point members. The two members are separated by a resistant reddish-brown volcanogenic sandstone and hyalotuff (marker bed in Fig. 3) (Embry, 1985), that was dated at 105.4 +/-0.22 Ma (Evenchick et al., 2015). During Christopher Formation deposition, the Sverdrup Basin was located at ~72° N, relatively close to its current latitude of ~78° N (Wynne et al., 1988),

The Sverdrup Basin rock units on Ellef Ringnes Island are characterized by a general southward dip, which exposes Lower Jurassic rocks in the northwest regions of the island and uppermost Cretaceous rocks in the southeast (Evenchick and Embry, 2012a; Evenchick and Embry, 2012b; Stott, 1969). Large scale, northwest-trending open folds are present over most of the island and deform Cretaceous and older sediments (Evenchick and Embry, 2012a; Evenchick and Embry, 2012b) (Fig. 2). Salt diapirism caused localized deformation and tilting of overlying sediments (Boutelier et al., 2011; Dewing et al., 2016). Steep faults associated with salt diapirs are radially positioned in relation to individual diapirs, displaying strikes 30° to 60° relative to the diapir boundary (Evenchick and Embry, 2012a; Evenchick and Embry, 2012b), and offsetting Cretaceous strata. Diapirs exposed at the surface on Ellef Ringnes Island include the Contour, Dumbells, Hakkon, Helicopter, Hoodoo, Isachsen, and Malloch domes (Fig. 2).

3.0 METHODS

3.1 Field Sampling

As part of the Geological Survey of Canada's Geo-Mapping for Energy and Minerals (GEM) Program, a geological mapping campaign to Ellef Ringnes Island was undertaken from 2009 to

2011, which included a focussed search for methane seep deposits in addition to those previously discovered by Beauchamp et al. (1989). The seep deposits were readily identified in the field as they form resistive, positive relief mounds of carbonate, projecting from the otherwise mudstone-dominated strata that forms a rolling landscape of Arctic tundra (Figs. 4a,b). The two seep sites originally reported by Beauchamp et al. (1989) were visited and sampled as well. All seep sites were located with a high-yield GPS receiver relative to NAD-83 (Fig. 2; Table 1). Some seep sites constituted a single carbonate body, while others had several (up to 8) individual deposits, and are listed in Table 1 as a single site. We defined an individual carbonate mound with defined edges as a ‘seep deposit’ and a ‘seep site’ as a location with one or more seep deposits in close proximity (< 5 m). The size of the seep deposits was measured as length and width parallel to bedding and height perpendicular to bedding. Multiple hand samples ranging in size from a few cm up to 30 cm in diameter were collected from different areas of 80 seep deposits. Macrofossils were collected from 35 deposits, with numbers ranging from three to 80 specimens from each site (Table 1).

3.2 Petrography

A subset of hand samples collected in the field were prepared for 30 μm thick uncovered and unpolished thin sections. Observation of these thin sections was conducted with a Nikon Eclipse E600W Polarizing Microscope at the Geological Survey of Canada in Calgary, to identify sediment type and carbonate cements.

3.3 Geochemistry

One hundred and eleven samples from the Ellef Ringnes seep deposits were analyzed for $\delta^{13}C$ and $\delta^{18}O$ values of distinct carbonate phases (micrite, yellow calcite, boytroidal calcite, and blocky calcite), carbonate infilling articulated fossils (‘fossil fill’), calcified wood, and carbonate cemented sandstones underlying the seep deposits (Table 2). Powdered samples were obtained by drilling cut rock faces, and then analysed at the Isotope Science Laboratory at the University of Calgary (ISL-UofC). Approximately 2 mg of powdered material was reacted with anhydrous phosphoric acid in a Y tube reaction vessel at 25 °C. The evolved CO_2 was cryogenically distilled from the reaction vessel into a 6 mm Pyrex tube and flame sealed. The CO_2 gas was then inlet to the ion source of a VG 903, stable isotope ratio mass spectrometer and analyzed for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. Selected internal standards ($\delta^{13}C$ values of -40.31 and -2.51 ‰) were run at the beginning and end of the sample set and were used to normalize the data as well as to correct for any instrument drift. The results are expressed as conventional δ-values relative to the Vienna Peedee Belemnite standard (V-PDB). The precision and accuracy of the analysis was 0.2‰ for both $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$.

Carbon isotopes of organic matter were measured in four seep deposit samples from site 10KRW001. To characterise background host shale chemistry, an additional, 38 samples of Christopher Formation mudstone were collected at approximately every 10 m in section 11KRW0045, from 25 m above the zone of seep deposits (which is 34 m thick; see section 4.1) to the base of the formation, 400 m below the seep zone (Table 3). The mudstone and seep carbonate samples were washed with hydrochloric acid, and rinsed with hot distilled water to remove any carbonate before determination of $\delta^{13}C$ of organic carbon using the same methods as above.

Molybdenum (Mo) concentrations in mudstones are frequently used as an indicator of paleo-redox conditions. Under anoxic/euxinic conditions molybdate ions are converted to oxythiomolybdate ions, which react with, and are sequestered by sulphide minerals or organic matter, becoming enriched in sediments (Emerson and Huested, 1991; Voegelin et al., 2009), relative to values for marine carbonates of 0.4 ppm and Post Archean Average Shale (PAAS) concentration of 1.0 ppm (Taylor and McLennan, 1985; Turekian and Wedepohl, 1961). We made elemental determinations for Mo concentration on the Christopher Formation shale samples detailed above (Table 3) and 62 seep carbonate samples (Table 2). All samples for Mo determination were powdered in an agate mortar and pestle, digested in a 2:2:1:1 acid solution of H_2O-HF-$HClO_4$-HNO_3, and subsequently analyzed using a PerkinElmer Elan 9000 mass spectrometer, with ± 2% analytical error.

3.4 Biomarkers for AOM

Four carbonate samples from a seep deposit at Hoodoo Dome (field station 10KRW001 in Table 1) were prepared and decalcified after methods described in Birgel et al. (2006a). After a saponification procedure with 6% KOH in methanol, the samples were extracted with a microwave extraction system (CEM Discovery) at 80 °C and 250 W with a dichloromethane-methanol (3:1) mixture. The total extracts were pre-cleaned by a separation into an n-hexane soluble and dichloromethane-soluble fraction. The n-hexane fraction was further separated by column chromatography into four fractions of increasing polarity (Birgel et al., 2008b). Only the hydrocarbon and the carboxylic acid fractions were found to contain compounds to constrain carbonate precipitation. Other than the hydrocarbon and carboxylic acid fractions, the alcohol fraction, was affected by thermal maturation and biodegradation and did not contain genuine lipid biomarker signatures. This peculiarity is observed also in other ancient methane seep carbonates experiencing low to intermediate maturity (e.g. Birgel et al., 2006b; Birgel et al., 2006a; Little et al., 2015; Natalicchio et al., 2015). The carboxylic acids were found to contain two octadecenoic acids, which are rather unlikely to be preserved, especially when looking at the low to intermediate mature hydrocarbons (see also section 4.5). Both the hydrocarbons and the carboxylic acids were analyzed by coupled gas chromatography–mass spectrometry (GC-MS) with an Agilent 7890 A GC system, coupled to an Agilent 5975 C inert MSD mass spectrometer at the Department for Geodynamics and Sedimentology, University of Vienna. The carrier gas was helium. The GC temperature program used was as follows: 60 °C (1 min); from 60 °C to 150 °C at 10 °C/min; from 150 °C to 320 °C at 4 °C/min, 25 min isothermal. This temperature program was used for both fractions. Identification of individual compounds was based on retention times and published mass spectral data in comparison with other samples. Compound-specific carbon isotope analysis of molecular fossils was performed with a Thermo Fisher Trace GC Ultra connected via a Thermo Fisher GC Isolink interface to a Thermo Fisher Delta V Advantage spectrometer at the Department of Terrestrial Ecosystem Research, University of Vienna. Conditions chosen for the gas chromatograph were identical to those described above. Carbon isotopes are given as δ values in per mil relative to the Vienna Peedee belemnite (V-PDB) standard. Each measurement was calibrated using several pulses of CO_2 with known isotopic composition at the beginning and end of the run. Instrument precision was checked with a mixture of n-alkanes (C_{14} to C_{38}) of known isotopic composition. Analytical standard deviation was below 0.7‰.

4.0 RESULTS

4.1 Seep deposit distribution

One hundred and thirty-seven new seep deposits were discovered during the 2009 to 2011 field campaign. The addition of the two previously reported sites by Beauchamp et al. (1989) makes an extensive occurrence of 139 seep deposits on Ellef Ringnes Island. These occurred in 75 sites exclusively within the Christopher Formation. The majority were exposed along the periphery of the salt diapirs: around Hoodoo Dome (104), Dumbells Dome (17), Helicopter Dome (6), Haakon Dome (2), and Isachsen Dome (2). No seep deposits were found associated with Contour or Malloch domes (Fig. 2). Eight seep deposits were not spatially associated with an exposed salt diapir. Of these, seven were found near the centre of the island, 11.5 km or more away from the edge of the closest diapir (Fig. 2). These seep deposits were not associated with any mapped faults or fractures. One additional seep deposit was found 7.5 km southwest of Hakkon Dome, where the Christopher Formation is truncated by three large normal faults. All the seep deposits were located within the upper portion of the Invincible Point Member, below the regional volcanogenic marker unit dated at 105.4 +/-0.22 Ma (Evenchick et al., 2015) (Fig. 3). At any one site, seep deposits occur at the same defined stratigraphic level. Exposure made it difficult to trace this level between sites, but where it was possible seep mounds all appeared on the same stratigraphic horizon indicated by a siltstone bed. The stratigraphic position of the seep sites, measured relative to the regional marker unit, varied from a maximum of 42 m at Helicopter Dome to a minimum of 8 m at Dumbells Dome, a 34 m stratigraphic range. Geopetal fabrics, and bedding of a few larger deposits, have the same dip as the bedding of Christopher Formation strata that hosts them.

4.2 Seep deposit morphology

Based on their appearance in outcrop, we classified the seep deposits on Ellef Ringnes Island into three morphological categories: 1) carbonate mounds, 2) carbonate beds, and 3) carbonate crusts. These categories do not necessarily reflect the original morphology of the carbonates during formation. The carbonate mounds (Fig. 4b) were the most common observed morphology (125 individual mounds). However, this may have been partly a function of the ease of their observation from aerial helicopter survey. The carbonate mounds ranged in size from 0.2 to 6.7 m in width, 0.3 to 39.0 m in length, and 0.2 to 3.1 m in height (Table 1). The mounds were always greater in length than height, having an average length:height ratio of 4:1. They comprised large cohesive blocks of carbonate rocks up to ~1 m^3, to mounds completely composed of carbonate rubble.

The five carbonate beds were distinguished from the mounds based on their broad lateral extent and limited relief. They ranged in size from 0.1 to 4.2 m in width, 12.4 to 62.0 m in length, and 0.1 to 0.3 m in height (Table 1), with a length:height ratio greater than 15:1 (Fig. 4C). The carbonate beds were composed of carbonate rubble, rarely containing pieces of carbonate rocks larger than 10 cm^3. Three of the beds contained highly cemented calcareous siltstone, giving these beds slightly more relief than those without any siliciclastic content.

The three carbonate crusts had no relief, being composed of a thin layer (<0.2 m) of carbonate rubble. They ranged in size from 0.5 to 1.7 m in width, and 0.6 to 2.2 m in length (Table 1).

4.3 Carbonate cements

All the morphological variants of the seep deposits contained a number of distinct carbonate cement phases (Fig. 4D), including 1) dark grey to grey-brown micrite, 2) banded calcite, 3) botryoidal calcite, 4) yellow calcite, and 5) blocky calcite. The micrite formed circular to elongated band-shaped areas that range from millimeters to 10s of cms in thickness. In thin section, the micrite was beige to dark brown and contained grains including peloids, opaque minerals, wood debris, and mollusc shells; it was also burrowed and fractured (Fig. 4E). Micrite and associated peloids showed dissolution along corrosion surfaces.

The banded calcite was composed of beige (botryoidal calcite) and brown (yellow calcite) layers that alternated in bands from 1 to 6 cm in thickness. The botryoidal calcite was composed of well-developed, radiating, fibrous clusters of prismatic crystals separated into growth bands indicated by opaque, submillimeter cement horizons (Fig. 4F,G). Petrographically, the botryoidal calcite comprised clean and dirty phases. Clean botryoidal calcite was composed of clear sweeping bands of prismatic calcite devoid of any inclusions or organic material. Individual calcite crystals could only be distinguished in cross-polarised light and reached over 1mm in length but were usually shorter than crystals of the other two botryoidal phases. Dirty botryoidal calcite was similar to clean calcite except that it contained microcrystalline grey to brown ‘debris’ within the calcite. The dark material was dispersed throughout the whole botryoids, or concentrated in horizons 70 to 200 µm apart. The submillimeter horizons were either very smooth or had wavy ‘V’ shaped tips. Both the clean and dirty botryoidal calcite contained clear, square-tipped needles that were over 2.3 mm in length and ~3.5 to 14 µm in width, observed both petrographically and with SEM. Previous work has interpreted these as remnant acicular aragonite needles (Savard et al., 1996). Corrosion surfaces within the botryoidal calcite layers were typically associated with 10 to 50 µm dark bands of impurities.

The yellow calcite had a clotted, euhedral texture and did not display distinct crystal boundaries. In thin section, yellow calcite was yellow to orange in colour and anhedral to clotted in appearance. Individual layers of yellow calcite ranged in thickness from 150 µm to over 3 mm and alternated with botryoidal calcite. The yellow calcite contained many opaque fragments, between 10 to 500 µm in diameter. The amount of opaque debris within the yellow calcite was variable among seep deposits, with some areas of yellow calcite containing no visible opaque material. Corrosion surfaces were common at the basal contact between the yellow calcite and the underlying cements it overgrew.

The blocky calcite was yellow to white and had a sparry texture with excellent crystal development, and filled voids up to 8 cm (Fig. 4H). Petrographically, the blocky calcite crystals ranged in size from < 30 µm to over 2 mm, with crystal boundaries that were typically sharp and linear, but at times had a slight curve. The blocky calcite always nucleated from what was once a free surface, with crystals that grew progressively larger as the void space filled in towards the center. The blocky calcite did not contain organic matter or opaque grains, and was homogenous in appearance. Microfractures as well as large void spaces, including centers of worm tubes, were filled with blocky calcite that typically, but not always completely, filled the once-open void.

4.4 Carbon and oxygen isotopes

Carbon and oxygen stable isotope data from the seep deposits fell into two distinct clusters (Fig. 5). Group 1 represented fossil fill, calcified wood, carbonate cement in calcareous sandstones, and all of the cement phases (with the exception of the blocky calcite) and was characterised by very negative $\delta^{13}C$ values ($\delta^{13}C$= -52.6‰ to -32.3‰) and $\delta^{18}O$ values around zero ($\delta^{18}O$= -7.1‰ to +1.3‰) (Fig. 5).

The blocky calcite cement formed a second sample cluster (Group 2) characterised by less negative $\delta^{13}C$ values ($\delta^{13}C$ = -24.8‰ to -7.5‰) and more negative $\delta^{18}O$ values ($\delta^{18}O$= -21.3‰ to -11.0‰) compared to Group 1. This included blocky cement that occurs as fill of a worm tube, sample C-540385-1 in Table 2 and indicated as 'fossil fill' within the Group 2 cluster on Figure 5.

The $\delta^{13}C_{org}$ values of organic matter from the four carbonate deposit samples from site 10KRW001 had values of -47.9, -41.1, -38.1, and -31.7‰. In comparison, those of the Christopher Formation mudstone samples ranged from -25.9 to -17.1‰ $\delta^{13}C_{org}$ (Table 3; Fig. 6). There was no vertical trend in $\delta^{13}C_{org}$ values going up section towards the zone of seep deposits.

4.5 Lipid biomarkers

Biomarker analysis showed that the predominant compounds in the hydrocarbon fraction were isoprenoidal hydrocarbons indicative of AOM, including head-to-tail linked phytane, tail-to-tail linked crocetane and 2, 6, 10, 15, 19-pentamethylicosane (PMI), and three head-to-head linked biphytanes comprising no, one, or two cyclopentane rings (Fig. 7A). Further, minor amounts of pseudohomologue series of head-to-tail linked isoprenoids with 18 to 24 carbons were found. Apart from the predominant isoprenoids, only minor n-alkanes with 16 to 23 carbon atoms and terminally-branched alkanes with 16 to 19 carbon atoms were found in the hydrocarbons, possibly derived from biodegraded organic matter or oil (e.g. Peters and Moldowan, 1993), and entombed within the carbonate matrix. However, when comparing the high amounts of isoprenoids with the only minor biodegraded lipid biomarkers, oil migration and the presence of oil-derived lipid biomarkers was of minor importance for the studied samples.

All isoprenoids were significantly ^{13}C depleted, with the lowest $\delta^{13}C$ value of = -118 ‰ and -113 ‰ for PMI and phytane/crocetane, respectively. Somewhat less ^{13}C depleted values were found for biphytanes (-109 ‰), and pristine (the least ^{13}C depleted compound). Most n-alkane and branched alkane contents were too low to determine compound-specific isotopes, but n-C_{23} was found, as well with a very low $\delta^{13}C$ value of -101 ‰, as reported in other methane seep deposits (e.g. Chevalier et al., 2013; Peckmann et al., 2009; Thiel et al., 2001). The fatty acids results (Fig. 7B) need to be used carefully, since pristine signatures were amalgamated with secondary signatures, which most likely were introduced after the carbonate precipitation and the entombment of the original signature of the microbial seep community. The most reliable biomarkers of SRB, partners in AOM, are terminally-branched iso- and anteiso-C15 fatty acids, which are prominent and also displayed the characteristic isotopic fingerprint of SRB of modern sites, with $\delta^{13}C$ values of -92 ‰ and -87 ‰, respectively. Interestingly, the short-chain fatty acids n-C_{14} and n-C_{16} still seem to represent original signals as well, since they were only slightly less ^{13}C depleted than the branched fatty acids. This finding is rather unusual for Mesozoic samples, where most often only the terminally-branched fatty acids carried the AOM signature (e.g. Birgel et al., 2006b). In contrast, the two prominent octadecenoic acids probably represent contaminants, since the pattern preserved in this sample is not like any patterns recorded in modern seep sites (Elvert et al., 2003).

4.6 Paleontology

Of the 137 Ellef Ringnes Island seep deposits mapped in this study, 62 had macrofossils, 75 did not contain visible macrofossils, and two were not recorded for fossil content (Table 1). The carbonate mound morphologies typically had the highest density of macrofossils, but mounds with abundant calcareous siltstone contained few or no macrofossils. Four of the carbonate beds and two of the crusts contained macrofossils (Table 1). Fossil abundances were related to the amount of siliciclastics and size of each deposit, with high siliciclastic content and small deposits containing fewer fossils (Table 1).

The invertebrate macrofossil assemblage comprised molluscs, brachiopods and worm tubes belonging to at least 20 species (Table 4; Fig. 8). Only the nuculid bivalves and wood were previously identified from the two original Ellef Ringnes seep deposits (Beauchamp et al. 1989). The molluscs and brachiopods were preserved in the micrite cements, typically with their original shell material still present, such as nacre of nuculid bivalve and ammonite fossils. There was little evidence for transportation of shells on the seafloor, as few shells were fragmented and most of the bivalves and brachiopods were still articulated. The mollusc fauna was dominated by bivalves (n = 396; belonging to eight species; Fig. 8A-I), with smaller numbers of gastropods (n = 62; at least four species; Fig. 8K), ammonites (n = 32; at least four species; Fig. 8J) and scaphopods (n = 14). Brachiopods were rare, with only four specimens being found. The bivalve fauna included taxa with a variety of inferred paleoecologies (Table 4), the majority of which potentially had chemoautotrophic bacterial symbionts (n = 353; four species), together with small numbers of infaunal deposit feeders (n = 27; three species) and epifaunal filter feeders (n = 16; one species).

The ammonite fossils were frequently incomplete and were found only within large mounds that contained very little siliciclastic material. Well preserved specimens were identified as Arcthoplites (common), including A.(?) cf. belli (McLearn), as well as rarer Cleoniceras aff. canadense Jeletzky, Beudanticeras(?), Puzosia aff. sigmoidalis Donovan (Fig. 8J) and Freboldiceras aff. irenense (McLearn). Taken together, these indicate the Beudanticeras affine regional ammonite zone (Jeletzky, 1964), and the Douvilleiceras mammillatum international standard zone (Jeletzky, 1968), which is latest Early Albian in age, from 113 to 107 Ma (Ogg and Hinnove, 2012).

Worm tube fossils were abundant (>500 specimens) in the Ellef Ringnes seep deposits (Fig. 8L). Some of the tubes were enclosed by micrite, others by botryoidal calcite and yellow calcite cements. The tubes had a variety of infillings, including micrite with peloids (sometimes geopetal), botryoidal yellow calcite (Fig. 8M), and, less commonly, blocky calcite cement. The worm tubes were preserved in various orientations and tended to cluster in groups that were aligned parallel or sub-parallel to one another, oriented from sub-horizontal to vertical within a given deposit (Fig. 8L). The tubes reached up to 12 cm in length and ~0.5 cm in diameter. The tube walls were formed of concentrically laminated layers of calcite that ranged from 40 μm to 330 μm thick (Fig. 8M). These are the same fossils that previously had been described as large serpulid tubes and smaller possible serpulid tubes in Beauchamp et al. (1989; Fig. 2) and Beauchamp and Savard (1992; Fig. 5). However, they lack the chevron tube wall microstructure typical of this group of polychaetes, and instead appear identical to tubular fossils from other Cenozoic and Mesozoic seep deposits that have been identified as calcified probable vestimentiferan worm tubes (e.g. Haas et al., 2009; Hilário et al., 2011).

Many of the Ellef Ringnes seep deposits contained fossilized wood, ranging from microscopic particles to pieces over 30 cm in length (Fig. 8N). The wood pores were cemented with calcite that preserved much of the original wood structure, including growth rings and knots. Some pieces of wood had fractures filled with late blocky calcite, but the majority of the wood was filled with early marine calcite with δ^{13}C values consistent with that of the seep carbonates (Fig. 5). The size and abundance of wood debris correlated with the size of the seep deposit, with small deposits containing microscopic or small fragments or wood and large deposits hosting large, isolated and very well preserved pieces of wood. Wood is also present in the enclosing Christopher Formation mudstone.

4.7 Paleo-redox geochemistry

The Christopher Formation mudstone contained between 0.22 to 2.29 ppm of Mo (Table 3), with the exception of one high value of 9.9 ppm immediately above the zone of seep deposits. Most samples had Mo concentrations (average of 0.98) that are below the PAAS concentration of 1.0 ppm (Turekian and Wedepohl, 1961) (Fig. 6). The Ellef Ringnes Island seep carbonates had values between 0.05 and 10.95 ppm (Table 2; Fig. 6).

5.0 INTERPRETATIONS AND DISCUSSION

5.1 Ellef Ringnes Island carbonates as seep deposits

The morphological variation, petrography, stable isotope values and biomarker contents of the carbonate deposits found on Ellef Ringnes Island are typical of both modern and other fossil seep carbonates, confirming that they were formed by the seepage of methane into the Sverdrup Basin in the Lower Cretaceous. We show that rather than being isolated occurrences, the original two seep mounds described by Beauchamp et al. (1989) are part of a previously unrecognised widespread occurrence of seep deposits on the island.

The very negative $\delta^{13}C_{VPDB}$ values of the Group 1 carbonates $\delta^{13}C$= -52.6‰ to -32.3‰) are characteristic of carbonates that obtained carbon from AOM (Whiticar, 1999). The associated $\delta^{18}O_{VPDB}$ values between -3‰ to 1‰, suggest carbonate precipitation near ambient seawater temperature (O'Neil et al., 1969). As such the Group 1 carbonates are interpreted to represent early diagenetic phases precipitated in the subsurface close to the seafloor via methane oxidation.

In contrast to Group 1, the Group 2 cements are exclusively blocky calcite and are the latest phase of cements within the deposits. The range of $\delta^{13}C$ values are less negative than Group 1, but still significantly more depleted in ^{13}C-depleted than normal marine carbonates (Fig. 5), suggesting they formed from either an alternative carbon source, or different degree of mixing between methane and seawater alkalinity. The $\delta^{18}O_{VPDB}$ values of group 2 cements are much more ^{18}O-depleted than the early diagenetic material, suggesting precipitation under warmer temperatures (O'Neil et al., 1969). Using the relationship that ~0.2‰ in $\delta^{18}O$ equates to a shift of 1 °C from the ambient seawater temperature (Faure, 1987), the late burial cements of the Ellef Ringnes seep deposits would have precipitated in waters between 65 and 95 °C. This range is higher than the maximum burial temperatures of the Christopher Formation, ~55 °C, as derived from a burial history model for Hoodoo Dome (Dewing et al., 2016). This discrepancy may relate to localized high geothermal gradients associated with the salt diapirs. High heat flow in salt can create local thermal anomalies above and adjacent to salt structures. This was shown to be the case in the Hazen F-54 well to the southwest of Ellef Ringnes Island, where geothermal gradients affected by a salt diapir are significantly higher than background (Chen et al., 2010;

Lerche and O'Brien, 1987). There may have also been localized hydrothermal circulation near the diapirs (Grasby et al., 2012) that could have formed the Group 2 cements.

The newly discovered seep deposits are similar in scale to the two previously described seep mounds on Ellef Ringnes Island (Beauchamp et al., 1989; Beauchamp and Savard, 1992; Savard et al., 1996), but the identification of carbonate beds and crusts increases the range of morphologies of seep deposits in the Sverdrup Basin. Compared to other Phanerozoic seep deposits, the Ellef Ringes examples are fairly typical in size (e.g. Campbell, 2006; Campbell et al., 2002; Hammer et al., 2011; Kauffman et al., 1996; Kelly et al., 2000; Majima et al., 2005; Peckmann et al., 1999), although very large deposits of 100s metres diameter and 10s metres thickness, such as the Miocene Rocky Knob deposit from New Zealand (Campbell et al., 2008) or the Devonian Hollard Mound (Peckmann et al., 2005) are not present. In general, the greater the duration of seepage and/or increased methane flux will lead to larger deposits. Whether any genetic information can be gleaned from the morphologies of the Ellef Ringes deposits is equivocal, because of the eroded nature of the deposits at outcrop, particularly those with a mound shape. Nevertheless, the presence of beds and crusts is mirrored by the common occurrence of exhumed methane derived crusts and pavements at modern seeps (e.g. Campbell 2006; Himmler et al., 2015). The overall small sizes may also indicate a relatively short duration of growth.

The potential growth rate of individual seep deposits can be estimated by comparison with modern examples. A study using U-Th analyses found seep carbonate crusts, similar to our crust morphology, have growth rates that vary from 0.4 cm/kyr during early seep development, and 5.0 cm/kyr during late stages of seep development (Bayon, 2009), suggesting that carbonate crusts we observe that up to 50 cm thick could represent 10,000 to 125,000 years growth. Much higher growth rates of 47 cm/kyr have been reported for columnar structures in the Arabian Sea (Himmler et al., 2016). Using these growth rates the seep mound morphologies exposed on Ellef Ringnes Island, from 20 to 310 cm high, would require methane seepage duration of only ~ 425 to 5,200 years to form – but upwards of 775,000 years at the lowest growth rate for modern crusts. The shorter growth rates are more consistent with age dates of modern seep deposits, however (Bayon, 2009; Berndt et al., 2014; Crémière et al., 2013). Given that there are 139 seep deposits over an area of ~10,000 km^2, and that each deposit probably was active for thousands to 10s thousands of years, at least some may have been active at any time. Alternatively, the entire system may have shut off and on during the period of formation, as suggested by the presence of corrosion surfaces within individual seep deposits. Regardless, the density of seep deposits exposed on Ellef Ringnes Island rivals that of other areas with abundant ancient seep deposits (see section 1).

The areal extent of the seep deposits on Ellef Ringnes Island (10,000 km^2) is likely even great than documented here. The methane seep mound reported on Prince Patrick Island, ~ 500 km distant, is of the same age (Beauchamp et al., 1989). Other nearby islands with Cretaceous exposure (e.g. Amund Ringnes, Axel Heiberg, northern Ellesmere) have more steeply dipping strata that would make carbonate mounds more difficult to observe without a focused search. In general though the areal of extent of methane seepage is of the same order of magnitude as that observed in regions of extensive modern methane seeps, such as the Gulf of Mexico (e.g. Roberts and Aharon, 1994)

5.2 Biomarkers of the anaerobic methane oxidation consortium

The $\delta^{13}C_{org}$ values of organic matter within the Group 1 carbonates (-47.9 to -31.7 ‰) is consistent with the cements, and distinct from $\delta^{13}C_{org}$ of organic matter in the surrounding Christopher Formation mudstone (-25.9 to -17.1‰). This indicates a distinct habitat associated with the seep mounds, with C metabolised from methane oxidation. This is seen further by the significantly ^{13}C depleted isoprenoids ($\delta^{13}C$ of = -118 ‰ and -113 ‰ for PMI and phytane/crocetane respectively), and iso- and anteiso-C_{15} fatty acids ($\delta^{13}C$ of = -92 ‰ and -87 ‰ respectively), that clearly indicate the incorporation of methane-derived carbon into the preserved lipids by anaerobic methane oxidation and their syntrophic partners, sulphate-reducing bacteria. The isoprenoids found in the hydrocarbon fraction indicate high thermal overprint of the sample, as short-chain head-to-tail linked isoprenoids are present as pseudohomologues (c.f. Birgel et al., 2008a; Heindel et al., 2015; Saito et al., 2015), consistent with the overall burial history of the region (Dewing et al., 2016). Apart from the high temperature pseudohomolgue signatures, the tail-to-tail linked isoprenoids crocetane and PMI are preserved unchanged in the sample. Head-to-tail linked phytane is produced from the degradation of archaeol and/or hydroxyarchaeol, former diether-bond membrane lipids of archaea, characteristic for Anaerobic Methanotrophic archaea (ANME) (Niemann and Elvert, 2008). Further isoprenoids are biphytanes, degradation products of former glycerol dialkyl glycerol tetraethers (GDGTs)(Liu et al., 2016). Interestingly, biphytanes did not contain pseudohomologues, as found for the short head-to-tail linked isoprenoids, and as described from other studies (e.g. Birgel et al., 2008a; Heindel et al., 2015; Saito et al., 2015).

The substantial amounts of GDGTs with a predominance of the monocyclic homologue accompanied by strong ^{13}C depletion, are indicative of ANME-1 (Niemann and Elvert, 2008). In old samples, high biphytane contents still bearing rings with strong ^{13}C depletions were present in Cretaceous and Eocene seep sites (Natalicchio et al., 2015; Peckmann et al., 2009), and may also be used as ANME-1 indicators. However, ANME-2 also produces GDGTs, but with lower contents (e.g. Blumenberg et al., 2004). The occurrence of abundant crocetane, which makes up around 50% of the mixed phytane/crocetane peak in the sample, is a reliable indicator that ANME-2 were present during carbonate formation. Crocetane and their unsaturated homologues are found in most recent methane seep microbial communities dominated by ANME-2; in contrast they are found only in minor concentrations in ANME-1 systems (Niemann and Elvert, 2008). Only a few Mesozoic seep deposits have so far been found to contain such high biphytane contents (Peckmann et al., 2009; Sandy et al., 2012). The distribution found here suggests a mixed community of both ANME-1 and ANME-2 consortia, although proving these were coeval is problematic because biomarker data in ancient seep carbonates represents a time averaged view of microbial activity during carbonate formation, which may have recorded seepage activity and changes in the intensity over longer time periods (cf., Feng et al., 2014).

5.3 Macrofauna

Fossils collected from the new seep deposits indicate that the macrofossil diversity was considerably greater than previously reported in Beauchamp et al. (1989) and Beauchamp and Savard (1992) from the original two Ellef Ringnes sites. The macrofaunal assemblage is, however, similar to that of other Mesozoic seeps, particularly those with a Boreal distribution, with nektic and passively floating elements (ammonites and wood respectively), and benthic elements (brachiopods, gastropods, scaphopods, bivalves and probable vestimentiferan tubes) (e.g. Hammer et al., 2011; Hryniewicz et al., 2014; Hryniewicz et al., 2015). The abundance of infaunal bivalves with probable chemosymbionts (e.g. lucinids, thyasirids, solemyids and nucinellids) is also typical of Mesozoic seep communities, and these taxa are also common in Cenozoic seeps, although not confined to this habitat (Hryniewicz et al., 2014). Their presence is a good indication that there were high concentrations of sulfides within the sediment during the early stage of formation of the seep deposits (micrite cement), and therefore a strong redox zone at the time, linked to AOM reactions.

Probable vestimentiferan tubes are common in Mesozoic and Cenozoic methane seep deposits and are typically associated with botyroidal cements (Haas et al., 2009 and references therein), that represent slightly later stages of cement formation related to higher fluid flow (e.g. Campbell et al., 2008) than micrites with peloids, infaunal molluscs, etc. This association can be explained by comparison with the ecology of living vestimentiferans at methane seeps, where firstly some hard substrate (i.e. exhumed seep carbonate and/or mollusc shells) is required for initial settlement of juveniles, and secondly during subsequent growth the posterior part of the tube projects into the substrate and is used to ‘mine’ sulphides (Dattagupta et al., 2008). Posterior tube portions often co-occur to form bundles between nodules and crusts formed of early-stage micrite cement (Haas et al., 2009; 2010). These ecological conditions are increasingly present during more mature stages of seepage, when seep fluid flux is more concentrated into discrete channels, often closer to the sediment-water interface. This is when slightly later stage cements, such as fibrous aragonite crusts form (e.g. Haas et al., 2010). The geopetal sediment and various cement phase infillings in the Ellef Ringnes seep worm tubes show that they often remained open after the death of the animals and then acted as traps for subsequent sediment influx, and/or channels for seep fluid flow, and/or late stage diagenetic cements (e.g. blocky calcite). This is illustrated by tube worm fill with stable isotope values consistent with our Group 2 late-stage cements (Fig. 5).

5.4 Methane source

The seep deposits on Ellef Ringnes Island display very high isoprenoid hydrocarbon contents, released from intact ether-lipids, but no obvious overprint by oil, as indicated by high amounts of n-alkanes or a pronounced unresolved complex mixture (e.g. Feng et al., 2014; Naehr et al., 2009; Sandy et al., 2012), in the seep fluids. This implies a dominant methane source with little input of higher hydrocarbons, and as such an oil seep can be ruled out.

The $\delta^{13}C$ values of carbonate minerals depend on the contributions of carbon obtained from methane, non-methane higher hydrocarbons (oil), organic matter, biogenic methane, and normal marine inorganic carbon (DIC). Carbon derived from petroleum (oil) has $\delta^{13}C_{VPDB}$ values between -25‰ and -35‰, organic matter between -24‰ to -30‰, and DIC ~0‰ (Schoell, 1982). However, as lipid extracts from the Ellef Ringnes samples do not have an oil signature, this is an unlikely carbon source. The range of $\delta^{13}C$ values of the Group 1 cements ($\delta^{13}C$= -52.6‰ to -32.3‰; average -42.6‰) is similar to thermogenic gas recovered from petroleum wells in the Sverdrup Basin ($\delta^{13}C$ average of -42.0‰) (Grasby et al., 2012; Leythaeuser, 1986). However, seep carbonates generally have higher $\delta^{13}C$ values than the source methane due to contribution from DIC (Peckmann and Thiel, 2004). Using the average stable carbon isotope values of the thermogenic gas recovered from the Sverdrup Basin (-42.5‰) and the values from the seep carbonates (-42.6‰), the ratio of carbon in the seep deposits derived from a thermogenic methane source would have to have been nearly 100%, with no other carbon mixing, a process unknown to occur in modern seep environments. In the northern Gulf of

Mexico, seep fluids dominated by biogenic gas ($\delta^{13}C$= -88.9‰) produce seep carbonates with $\delta^{13}C_{VPDB}$ values between -45.1‰ to -43.8‰ (Roberts et al., 2010). Similarly, seeps located offshore southern Californian have biogenic methane ($\delta^{13}C$= -81.1 to -73.1 ‰) that forms carbonates with $\delta^{13}C$values of -58 to -46 ‰ (Hein et al., 2006). These modern carbonate $\delta^{13}C$ values are similar to the seep carbonates preserved on Ellef Ringnes Island, and based on this we argue that the stable isotope values of the Ellef Ringnes seeps reflect a shallow biogenic, rather than a deeper thermogenic, methane source. This is supported by our biomarker analyses. The carbon isotope fractionation between methane and the membrane lipids formed from that carbon source is usually around -50 ‰. Given the values observed in seep mound biomarkers (PMI, crocetane/phytane; biphytane), the $\delta^{13}C$ value of the methane gas would be estimated at -68 to -59 ‰, again consistent with a biogenic methane source (Formolo et al., 2004).

The high density of seep deposits on the immediate flanks of the salt diapirs on Ellef Ringnes Island may suggest there was some linkage between the development of seep deposits and salt diapirism in the Sverdrup Basin. Geological maps of Ellef Ringnes Island (Evenchick and Embry, 2012a; Evenchick and Embry, 2012b) show that both the Isachsen and Christopher formations exposed on the flanks of salt diapirs are highly fractured and faulted, especially when compared to the same formations away from the diapirs. However, while mobile, the salt diapirs which are now exposed at the surface of the island had not penetrated the seafloor during the Early Cretaceous (Dewing et al., 2016). The seep carbonate geopetal fabrics and seep deposit bedding are also both parallel to the Christopher Formation strata, indicating that the seeps most likely formed above the salt domes prior to tilting. We also note that seep deposits were found at the same stratigraphic level away from any diapirs. Given this we argue that the apparent density of methane seeps near diapirs is likely an exposure bias, where Christopher Formation strata are preferentially exposed in uplifted beds surrounding the diapirs, making seep deposits more readily observable in those locations.

5.5 Environment of formation

The profile of both $\delta^{13}C$ of organic carbon and Mo in the Christopher Formation shales does not show any trend leading up to the zone of carbonate deposits, and only one data point shows high Mo values immediately above the zone (Fig. 6). These low values suggest that methane seepage occurred in normal, well-oxygenated bottom water conditions (Tribovillard et al., 2006) in the Sverdrup Basin. This is consistent with the abundance and diversity of benthic fauna in the Ellef Ringnes seep deposits. Modern methane seeps forming in anoxic basins and oxygen minimum zones are devoid of large animals, and instead contain only microbial mats only (e.g. Himmler et al., 2015).

The sequestration of Mo into pure carbonate phases involves the incorporation of low reactive molybdate ions (MoO_4^{2-}) into the crystal lattice of carbonates in a similar fashion to carbonate associated sulphate (CAS). The low chemical reactivity of molybdate ions in seawater results in a long ocean residency time but also in the limited incorporation of molybdate into carbonate minerals (Lyons et al., 2009). However, under anoxic conditions Mo can be reduced and then sequestered by sulfides, such that Mo enrichments can be an indicator of locally anoxic environments (Tribovillard et al., 2006). The Mo values of the Ellef Ringnes seep deposits vary widely, from 0.05 to 10.95 ppm, in comparison with typical Mo concentration in shallow marine carbonates of 0.4 ppm (Turekian and Wedepohl, 1961). In general, Mo values of the seep carbonates are significantly higher than average shallow carbonate deposits, indicating local anaerobic conditions associated with methane oxidation and carbonate precipitation. Consistent with this, lipids found within the carbonate deposits are almost only associated with the anaerobic oxidation of methane. No indications of prevailing oxic or microaerophilic conditions were found, since no ^{13}C-depleted hopanoids or lanostanes have been identified (Birgel and Peckmann, 2008; Natalicchio et al., 2015; Sandy et al., 2012). These results suggest the presence of a strong redox zone within the sediment during carbonate precipitation, as also indicated by the presence of infaunal bivalve species with potential chemosymbionts and the probable vestimentiferan worm tubes (Table 4).

5.6 Climate conditions during the methane seep event

During Cretaceous time, the high paleolatitude setting of the Sverdrup Basin (72° N) was characterised by numerous "cold-snaps" that punctuated otherwise warm Early Cretaceous conditions (Grasby et al., in press; Herrle et al., 2015). Evidence for cold climate intervals during the late Aptian-early Albian, including wood and pollen data, has been demonstrated for the circum-Arctic region, as well as for lower latitudes (e.g. Galloway et al., 2015; Harland et al., 2007; Kemper, 1987; Maurer et al., 2013; McAnena et al., 2013; Mutterlose et al., 2009). Possible ice-rafted debris are also observed in Aptian strata of Spitsbergen (Dalland, 1977). A cool climate in the Sverdrup Basin during Albian time is further supported by the widespread occurrence of glendonites (an ikaite pseudomorph) in the Invincible Point Member (Grasby et al., in press; Kemper, 1987; Kemper and Schmitz, 1975). Ikaite formation is considered to require near freezing temperatures (~1.9 to 7.0 °C) coupled with a ten-fold increase in alkalinity relative to normal seawater to form (Bischoff et al., 1993; Marland, 1975).

Previous studies have shown the co-occurrence of glendonites within active modern methane seeps, related to organic matter decomposition driven by the initial stages of methane seepage (Greinert and Derkachev, 2004; Teichert and Luppold, 2013). However, in our study area, the glendonite bearing horizon in the Invincible Point Member occurs as discrete layers over a 100 m stratigraphic range, ~200 m below the stratigraphic level of the seep carbonates. This horizon is equivalent to the glendonite occurrence observed in the Invincible Point Member of the Christopher Formation exposed at Glacier Fiord, Axel Heiberg Island (Herrle et al., 2015). Based on their composite $\delta^{13}C$ stratigraphy they date the youngest glendonite bed at ca. 112.8 Ma (lowermost Albian), and they indicate that the loss of glendonites is coincident with a return to warm temperatures at the end of a ~6 m.y. late Aptian to early Albian cooling event. A transition from cold to warm climate at this time is also recorded in the subtropical Atlantic Ocean, possibly related to volcanism (~114-110 Ma) of the Kerguelen LIP (McAnena et al., 2013). Given these constraints, the possible age range for the methane release event that formed the widespread carbonate seep deposits on Ellef Ringnes Island (between 113 to 107 Ma; section 4.6), corresponds closely to this climate warming event.

5.7 Controls on methane release

Where possible to observe, carbonate seep deposits occur at one single stratigraphic horizon, below the regional marker unit dated at 105.4 Ma (section 4.1) and above the last occurrence of glendonites dated at 112.8 Ma. The overall stratigraphic range of seep deposits across the island, relative to the regional marker unit, is quite narrow (34 m) and could easily reflect variations in seafloor topography and sedimentation rates. As such, the widespread occurrence of seep deposits on Ellef Ringnes reflects a transient event. This raises the question as to what may have influenced the short term, but aerially extensive, release of biogenic methane into the seafloor of the Sverdrup Basin during Albian time. One possible mechanism is diaper mobilisation causing gas migration along fracture systems. However, diapirs record a movement history for over 100 Ma (Dewing et al., 2016), suggesting that if this was the case than evidence of methane seepage should be more common in the basin. The observation of carbonate mounds not associated with diapirs further indicates that they do not directly control formation of methane seep deposits.

As described in section 5.6, the occurrence of widespread seep mounds in the Sverdrup Basin is coincident with a period of Albian climate warming. This is similar to modern high latitude methane seeps, where studies have shown that biogenic gas leakage occurred in response to post ice-age climate warming, with continuous methane flux for 3 to 10 kyr in response to post-glacial gas hydrate release (Berndt et al., 2014; Chand et al., 2016; Crémière et al., 2016). We hypothesize that a similar event may have occurred in the Sverdrup Basin, whereby the early Albian cold snap indicated by widespread glendonite occurrence would likely have been associated with development of gas hydrates, trapping biogenic gas formed during biodegradation of marine organics in the overall oxic depositional environment. Subsequent climate warming may have caused hydrate dissociation and the regional, but transient, occurrence of methane seep deposits. Modeled rates for hydrate melting shows gas release would occur on ~100 ky time scale (Majorowicz et al., 2014), consistent with the potential age range of the deposits.

6.0 CONCLUSIONS

The discovery of 137 new Early Cretaceous carbonate deposits on Ellef Ringnes Island, Canadian Arctic Archipelago demonstrate the presence of an extensive field of methane seeps that occur over an area greater than 10,000 km^2, throughout the central to southern part of the island. This discovery greatly increases the overall area of methane seep sites recognised on the island, the diversity of seep deposit types, and the macrofossil diversity present. Seep deposits range in size from less than 1 m^3 to over 2.4 m high by 7.6 m long and are exposed within a narrow stratigraphic range within the uppermost portion of the Invincible Point Member of the Christopher Formation. While predominately exposed on the flanks of four exposed salt diapirs, they are not restricted to this setting. The association of seep carbonates with diapirs most likely reflects an exposure bias related to uplifted beds along the diapir flanks.

Each seep deposit is composed of various portions of six major carbonate phases as well as moderately diverse fossil assemblages, including chemosymbiotic species. The carbonates have very low $\delta^{13}C_{VPDB}$ values, as well as $\delta^{13}C$ values of biomarkers, indicative of carbonate formed in the subsurface from the anaerobic oxidation of primarily biogenic methane.

The large geographical occurrence of seep deposits suggests widespread venting of biogenic methane rich fluids. However, methane seepage was a transient event that occurred during the latest Early Albian. We hypothesize that this may relate to possible gas hydrate dissociation related to climate warming during that time.

ACKNOWLEDGEMENTS

Gennyne McCune contributed valuable information regarding the environments of the formation and assistance in the field. Field work was supported by the Polar Continental Shelf Project. Discussions with A. Embry on Cretaceous stratigraphy of the Sverdrup Basin are greatly appreciated. ESS Contribution xxxx.

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FIGURE CAPTIONS

Figure 1 Map showing location of the study area. The inset (Canadian Arctic Archipelago) shows the location of the Sverdrup Basin (outlined by dashed black line). Ellef Ringnes Island, the focus of this study, is located near the centre of the basin.

Figure 2 Map of Ellef Ringnes Island, composed of Lower Jurassic rocks in the northwest and upper most Cretaceous rocks in the southeast. The Island is pierced by seven salt diapirs, composed of the Pennsylvanian Otto Fiord Formation. Within the Christopher Formation, 139 early Cretaceous methane seep deposits have been discovered. The majority of the seep deposits are concentrated on the periphery of salt diapirs; with the exception of 8 seep deposits, not closely associated with diapirs. Geology is derived from (Evenchick and Embry, 2012a; Evenchick and Embry, 2012b).

Figure 3 Stratigraphic column of Cretaceous and Paleogene strata of the Sverdrup Basin. Stratigraphy is modified from (Embry and Beauchamp, 2008). Ancient methane seep deposits on Ellef Ringnes Island occur within the upper portion of the Invincible Point Member of the Christopher Formation, an Upper Aptian to Upper Albian marine shale. The horizon with occurrence of abundant glendonites is also shown.

Figure 4 Field photographs and thin sections of carbonate deposits. A) Distribution of carbonate deposits (marked by red arrows) as positive relief features on the arctic tundra, B) large carbonate deposit with relief up to 3 m, C) Carbonate bed with a significantly greater length than height, D) Close up of outcrop showing characteristic banded cement texture, E) Photomicrograph of micritic cements within seep deposits, F) Photomicrograph under plain light showing banded cements, G) cross-polarised light image of banded yellow and botryoidal calcite, H) Close up of outcrop showing void filling blocky calcite. BC=blocky calcite, YC = yellow calcite, PL = peloid, OM = opaque mineral.

Figure 5 $\delta^{18}O_{VPDB}$ and $\delta^{13}C_{VPDB}$ plot of individual seep carbonate phases. All of the phases, excluding blocky calcite are very ^{13}C depleted, suggesting derivation from methane. The same phases have $\delta^{18}O_{VPDB}$ values close to zero, suggesting precipitation near ambient seawater temperature. Blocky calcite has much higher $\delta^{13}C_{VPDB}$ values and lower $\delta^{18}O_{VPDB}$ values, likely forming at increased temperature (depth) during burial diagenesis.

Figure 6 Geochemical plots of shale hosting carbonate seep deposits. Litholog of the Christopher formation shows section from the base of the formation to the resistant marker bed at the top of the Invincible Point Member. A) Plot of carbon isotopes of organic matter contained within the Christopher Formation as well as the seep carbonates (thought in part to be preserved biofilms). B) Plot of Mo concentration in both the Christopher Formation and seep carbonates. The Christopher shale contains less Mo than normal Post Archean Average Shale (Taylor and McLennan, 1985) suggesting precipitation under oxic conditions, whereas seep carbonates sequester much more Mo than normal carbonates, implying anoxic formation.

Figure 7 Chromatograms showing the lipid biomarkers found in the hydrocarbons and fatty acids recovered from seep carbonates. Stable carbon isotopes of the lipid biomarkers are also included.

Figure 8 Representative seep macrofossils. A) Solemyid bivalve; articulated specimen, internal mould lateral view. B) Lucinid bivalve; articulated specimen, internal mould lateral view; arrow points to anterior adductor muscle scar. C) Thyasirid bivalve: articulated specimen, internal mould lateral view. D) Same specimen as C), posterior view; arrow points to weak posterior sulcus. E) Nucinella sp.; articulated specimen, internal mould anterior view. F) Same specimen as E), lateral view; arrow points to lateral tooth. G) Malletid bivalve; partially articulated specimen, internal mould lateral view. H) Nuculid bivalve; articulated specimen, internal mould lateral view. I) Pectinid bivalve; articulated specimen, internal mould lateral view. J) Ammonite Puzosia aff. sigmoidalis Donovan; internal mould. K) Vetigastropod; internal mould lateral view. L) Cluster of probable vestimentiferan tubes. M) Photomicrograph under plain light of an oblique cross section through a probable vestimentiferan tube. Arrow points to ‘delamination’ structures. Note infilling of botryoidal banded calcite cement. N) Large pieces of wood preserved in seep carbonate at outcrop. Scale bars for A-K = 1 cm.