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Fluid source and methane-related diagenetic processes recorded in cold seep carbonates from the Alvheim channel, central North Sea

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ABSTRACT

Integrated petrography, mineralogy, geochronology and geochemistry of cold seep carbonate crusts and free gas from the Alvheim channel elucidate diagenetic carbonate precipitation and related seepage histories in the central North Sea. Free gas isotope characteristics coupled with carbonate $\delta^{13}C$ values as low as −66‰ VPDB, indicate a predominantly microbial methane source with minor thermogenic contribution. We estimate that ~70% of the carbon sequestered into carbonate precipitates was derived from local oxidation of methane. The early stage of crust growth is represented by microcrystalline aragonite and Mg-calcite (10 to 40% mol $MgCO_3$) cementing seafloor sediments consisting of clays, quartz, feldspar, and minor detrital low Mg-calcite and dolomite. Typical association of aragonite cement with coarse-grained detritus may reflect elevated fluid flow and flushing of fine particles prior to cementation close to the seafloor. Middle rare earth element enrichment in early generation microcrystalline cements containing framboidal pyrite indicates diagenetic precipitation within the zone of anaerobic methane oxidation contiguous to iron reduction. The later generation diagenetic phase corresponds to less abundant radial fibrous and botryoidal aragonite which lines cavities developed within the crusts. In contrast to early generation cements, late generation cavity infills have rare earth elements and Y patterns with small negative Ce anomalies similar to seawater, consistent with carbonate precipitation in a more open, seawater dominated system. Aragonite U–Th ages indicate carbonate precipitation between 6.09 and 3.46 kyr BP in the northern part of the channel, whereas in the southern part precipitation occurred between 1.94 and 0.81 kyr BP reflecting regional changes in fluid conduit position.

1. Introduction

Cold seeps are characterized by methane-rich fluid migration through sediment and discharge at the seafloor. This pervasive phenomenon has been widely reported at oceanic margins (Campbell, 2006; Kulm et al., 1986; Sibuet and Olu, 1998; Suess, 2014) with areas of active seepage often linked to offshore hydrocarbon reservoirs (Milkov et al., 2003). Seep morphology varies considerably, reflecting different mechanisms of fluid generation, tectonic and stratigraphic controls on fluid migration pathways, and seafloor hydrodynamic and sedimentation conditions (Klaucke et al., 2008; Naudts et al., 2006). Reduced fluids sustain the activity of chemosynthetic communities in such environments. The dominant biogeochemical process is sulfate-driven anaerobic oxidation of methane (AOM) which consumes a significant proportion of the methane rising to the seabed, and thus represents the main methane sink in marine sediments (Hinrichs and Boetius, 2002; Reeburgh, 2007; Wallmann et al., 2006)

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

The AOM is controlled by consortia of methane-oxidizing archaea and sulfate reducing bacteria (Boetius et al., 2000; Milucka et al., 2012). As a consequence of AOM, elevated carbonate alkalinity in the shallow subsurface results in the precipitation of methane-derived authigenic carbonates (MDAC), which constitute unique archives of the biogeochemical processes associated with the migration of

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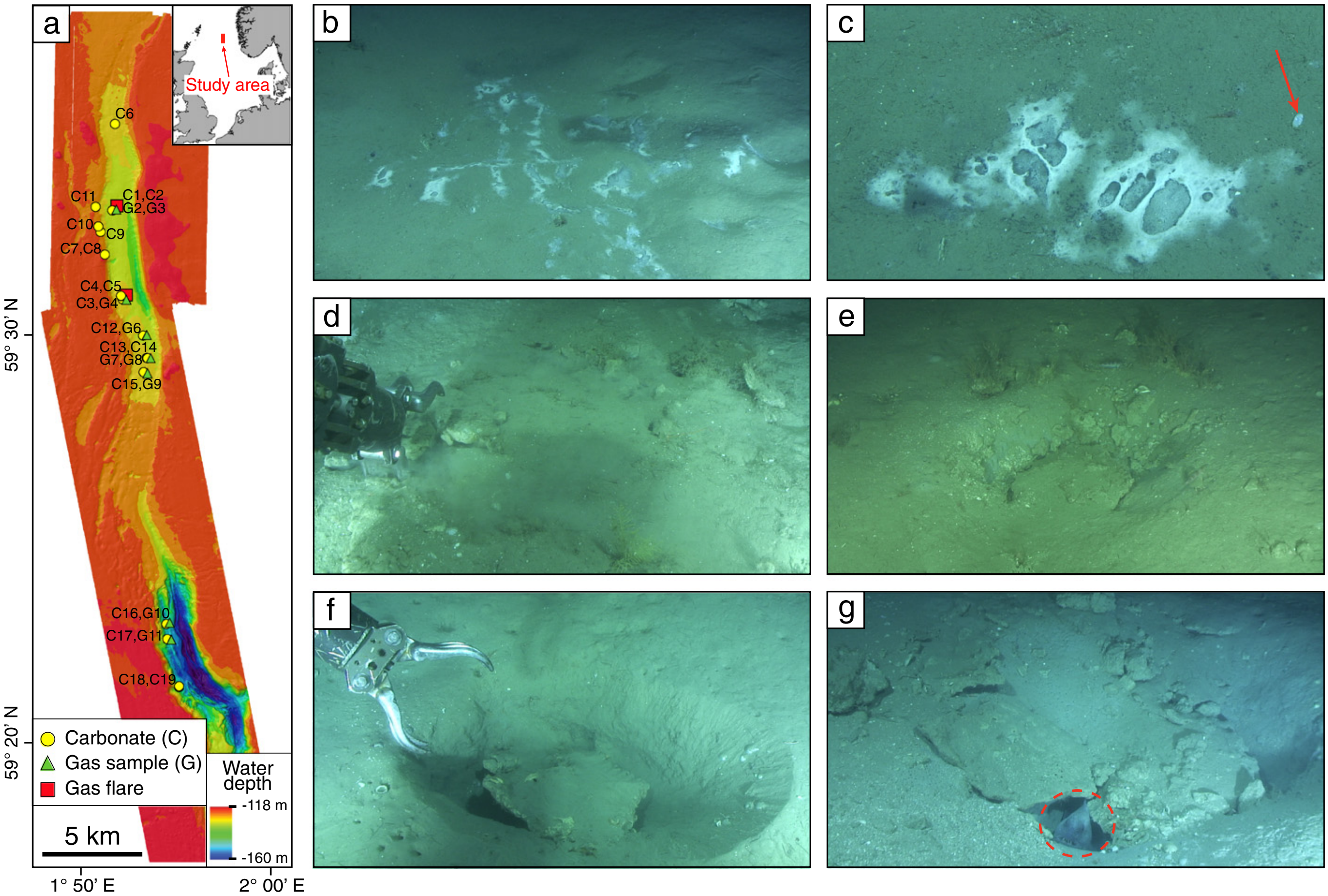

Fig. 1. Bathymetric map from the Alvheim canyon with sample positions, main gas flares and seafloor photos obtained during ROV dives. (b, c) White microbial mats resemble sulfur-oxidizing bacteria typically observed at cold seeps. (c) The arrow shows a gas bubble escaping from the seafloor. (d, e, f, g) Carbonate crusts collected at seafloor. Some crusts (f, g) were found in fish burrows.

methane-rich fluids (Aloisi et al., 2000, 2002; Bayon et al., 2013; Crémière et al., 2013; Hu et al., 2014; Luff et al., 2004; Magalhaes et al., 2012; Naehr et al., 2007; Peckmann et al., 2001; Pierre et al., 2014; Ritger et al., 1987; Roberts et al., 2010). A variety of proxies has been used over the last three decades to unravel the history of past fluid activity recorded in MDAC (Hovland et al., 1987; Ritger et al., 1987; Suess, 2014). Stable carbon and oxygen isotopes provide information on fluid source and environmental conditions during carbonate formation (Aloisi et al., 2000; Bohrmann et al., 1998; Crémière et al., 2012; Naehr et al., 2007; Peckmann and Thiel, 2004; Pierre et al., 2014; Ritger et al., 1987). Notably, MDAC are characterized by negative δ^{13}C values, which reflect the influence of methane-derived dissolved inorganic carbon (DIC), a by-product of AOM across the sulfate-methane transition zone (SMTZ) in marine sediments. The degree of ^{13}C depletion may also provide a means to indirectly trace fluid sources, and may be used to differentiate between microbial (−110 to −50‰ VPDB) and thermogenic methane (−50 to −20‰ VPDB) (Schoell, 1980; Whiticar, 1999).

Rare earth element (REE) characteristics of MDAC can provide further information about fluid sources and changes in redox conditions within diagenetic environments (Feng et al., 2009; Himmler et al., 2010; Rongemaille et al., 2011). The U–Th dating of MDAC has been employed to indirectly reconstruct the absolute timing and tempo of methane seepage in response to gas hydrate destabilisation and sea-level variations (Feng et al., 2010; Teichert et al., 2003; Watanabe et al., 2008), redox conditions in the water column (Bayon et al., 2013; Crémière et al., 2013; Himmler et al., 2015) or to constrain MDAC growth rates (Bayon et al., 2009; Liebetrau et al., 2014).

The stable C and O isotopes and petrography/mineralogy of MDAC from different sites in the North Sea have been previously studied (Hovland et al., 1987; Mazzini et al., 2016) but to date, the geochronology of MDAC formation in the North Sea remains unknown. This study is based on a multiproxy approach in order to reconstruct the fluid flow history of previously unstudied seepage sites in a paleo-meltwater channel from the central North Sea. The gas composition is used to assess the source of methane whereas carbonate petrography, mineralogy, geochemistry and geochronology are used to elucidate the nature, origin and sequence of fluid flow dynamics and related biogeochemical processes. High spatial resolution carbon isotope analyses carried out by secondary ion mass spectrometry (SIMS) allow us to investigate small scale carbon isotope heterogeneity of MDACs. Finally, we use the combination of seeping gas composition and past MDAC-based geochemical records for a model of carbonate formation.

2. Background information

The central North Sea hosts oil and gas reservoirs with Late Jurassic to Early Cretaceous marine shales identified as main source rocks (Cornford, 1998; Gautier, 2005). Seismic signatures from shallow gas accumulations, chimneys and pipes are well documented (Fichler et al., 2005; Heggland, 1997; Karstens and Berndt, 2015). Fluid flow indicators are also ubiquitous (Brekke et al., 1997; Hovland, 1981; Hovland et al., 1987; Judd and Hovland, 1992; Karstens and Berndt, 2015; Wegener et al., 2008), and include water column gas flares, elevated hydrocarbon concentrations in the shallow subsurface and seafloor pockmarks, formed by sustained fluid flow through fine grained