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# Shallow water methane-derived authigenic carbonate mounds at the Codling Fault Zone, western Irish Sea

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## Abstract

Methane-derived authigenic carbonate (MDAC) mound features at the Codling Fault Zone (CFZ), located in shallow waters (50 to 120 m) of the western Irish Sea were investigated and provide a comparison to deep sea MDAC settings. Carbonates conststed of aragonite as the major mineral phase, with $\delta^{13}C$ values as low as -50‰. These isotope signatures, together with the co-precipitation of framboidal pyrite confirm that anaerobic oxidation of methane (AOM) is an important process mediating methane release to the water column and the atmosphere in this region. The $^{13}C$ depletion of bulk carbonate and sampled gas (-70‰) suggests a biogenic source, but significant mixing of thermogenic gas and depletion of the original isotope signature cannot be ruled out. Active seepage was recorded from one mound and together with extensive areas of reduced sediment, confirms that seepage is ongoing. The mounds appear to be composed of stacked pavements that are largely covered by sand and extensively eroded. The CFZ mounds are colonized by abundant Sabellaria polychaetes and possible Nemertesia hydroids, which benefit indirectly from available hard substrate. In contrast to deep sea MDAC settings where seep-related macrofauna are common reported, seep-specialist fauna appear to be lacking at the CFZ. In addition, unlike MDAC in deep waters where organic carbon input from photosynthesis is limited, lipid biomarkers and isotope signatures related to marine planktonic production (e.g. sterols, alkanols) were most abundant. Evidence for microbes involved in AOM was limited from samples taken; possibly due to this dilution effect from organic matter derived from the photic zone, and will require further investigation.

Keywords: Methane-derived authigenic carbonate, gas seepage, Codling Fault, Irish Sea

Abbreviations: Anaerobic oxidation of methane (AOM), Codling Fault Zone (CFZ), Dimethyl disulfide (DMDS), Energy-dispersive spectroscopy (EDS), Fatty acid methyl ester (FAME), Methane-derived authigenic carbonate (MDAC), Mono-alkyl glycerol ethers (MAGE), Scanning electron microscopy (SEM), X-Ray diffraction (XRD).

## 1. Introduction

Methane is an important trace gas in the atmosphere and a potent greenhouse gas (Svensen et al., 2004; Forster et al., 2007). Seepage of methane from the ocean's seafloor is of global occurrence, yet one that is poorly quantified and understood (Fleischer et al., 2001; Knittel and Boetius, 2009). One result of seabed seepage is the formation of distinctive seafloor structures, such as pockmarks, mud diapirs, mud volcanoes and methane-derived authigenic carbonates (MDAC). MDAC, which may form pavements or mound structures, are produced as a direct result of methane supply from the subsurface to shallow sediment and the sediment-water interface (e.g. Bohrmann et al., 1998; Aloisi et al., 2000; Greinert et al., 2002; Bayon et al., 2009). There, methane is utilized by a consortium of methane-oxidizing archaea and sulfate-reducing bacteria in the anaerobic oxidation of methane (AOM) reaction (Hinrichs et al., 1999; Boetius et al., 2000; Reitner et al., 2005) according to Equation 1:

$$CH_{4(g)} + SO_4^{2-}{}_{(aq)} \rightarrow HCO_3^{-}{}_{(aq)} + HS^{-}{}_{(aq)} + H_2O_{(l)}$$

Eqn. 1

The reaction is maintained in expense of marine sulfate dissolved in pore waters (Boetius et al., 2000; Tsunogai et al., 2002; Niemann et al., 2005). If the supply of methane is sufficient, AOM leads to supersaturation of pore fluids with respect to $HCO_3^-$ and in result facilitates the formation of MDAC (Hovland et al., 1987; Stakes et al., 1999; Greinert et al., 2001; Mazzini et al., 2005; Naehr et al., 2007; Paull et al., 2007; Feng et al., 2008). $HS^-$ is typically precipitated as pyrite ($FeS_2$) on reaction with Fe in pore fluids (e.g. Peckmann et al., 2001; Pechmann and Thiel, 2004). Recent evidence indicates that the bacterial partners involved in AOM may be more diverse than previously thought (Beal et al., 2009) and that ANME may be able to perform AOM without bacterial partners (Milucka et al., 2012). AOM is responsible for the oxidation of possibly 90% of marine methane (Knittel and Boetius, 2009) and hence AOM and MDAC formation are important for regulation of ocean to atmosphere carbon fluxes (e.g. Aloisi et al., 2002). Methane consumption via AOM is estimated to be in the range of 5 to 20% of net modern atmospheric methane flux (20 to 100 $x10^{12}$ g $a^{-1}$) (Valentine and Reeburgh, 2000). Many sites of active methane seepage have been shown to support unique macro- and micro-faunal biodiversity (e.g. Dando et al., 1991; Jensen et al., 1992; Sibuet and Olu, 1998; Van Dover et al., 2003; Olu-Le Roy et al., 2004). In addition, gas seepage features are important in relation to marine industrial and petroleum safety (Hovland et al., 2002), and also in petroleum and gas prospecting (Judd and Hovland, 2007).

Most cold seeps with extensive MDAC have been reported from the deep sea (e.g. Ritger et al., 1987; von Rad et al., 1996; Chen et al., 2005; Feng et al., 2010; Haas et al., 2010; Crémière et al., 2012; Magalhães et al., 2012), but reports of extensive MDAC occurrence within the photic zone (0 to ~200 m water depth) are also common. Shallow cold seep settings with extensive MDAC occurrence include the Coal Oil Point Seep field, off Santa Barbara (Kinnaman et al., 2010), St. Lawrence Estuary, Canada (Lavoie et al., 2010), Monterey Bay (Stakes et al., 1999), the Kattegat (Jørgensen, 1989; Jensen et al., 1992), the Adriatic (Capozzi et al., 2012), the northwestern Black Sea (Peckmann et al., 2001), the North Sea (Judd and Hovland, 2007), and recently the Texel 11 and Holden's Reef sites in the Irish Sea (Judd et al., 2007). Shallow water seep assemblages contain lower percentage of seep specialists than deep water sites and are instead dominated by background fauna (Levin et al., 2000; Rathburn et al., 2000; Dando, 2010), probably due to the increased influence and input of photosynthetic carbon in shallow depths (Levin, 2005). In contrast to deep water sites, which can support abundant assemblages of seep-restricted chemosymbiotic macrofauna, most symbiont-bearing taxa found in shallow water sites are shared with non-seep reducing environments (Sahling et al., 2003).

The Irish Sea contains extensive areas of shallow gas accumulation, as well as numerous occurrences of seabed features associated with gas migration (Croker, 1995; Croker et al., 2005). Twenty-three mounds features have recently been identified along the Codling Fault Zone (CFZ) in the east perimeter of the Kish Bank Basin in the western Irish Sea (Fig. 1) (Croker et al., 2002; 2005; Judd et al., 2007). Based on extensive mapping and ground-truthing, Croker et al. (2002; 2005) concluded that the mounds at the CFZ were MDAC and that this site is the most active site of gas seepage in the Irish designated zone of the Irish Sea. A number of the CFZ mounds were investigated in 2010 during INFOMAR (Integrated Mapping for the Sustainable Development of Ireland's Marine Re) survey CV10_28. The purpose of this study was to further ground-truth the CFZ carbonate mound features, to provide further mineralogical, geochemical and isotopic evidence that these features are formed by AOM, to provide evidence of current active seepage, and finally to compare this site to other extensive MDAC occurrences in shallow and deep sea settings.

## 2. Environmental and geological setting

The western Irish Sea (west of 5°20’) encompasses two Mesozoic sedimentary basins, namely the Kish Bank Basin and the southwest section of the Central Irish Basin, and is primarily underlain with Permian and Carboniferous rocks. Quaternary deposits up to 150 m thick occur, but are laterally discontinuous, locally revealing exposed bedrock (Croker et al., 2005). The northwest Irish Sea (north of 53°30’) is characterised by relatively weak hydrodynamic conditions, resulting in the seabed being dominated by fine silty mud. This is in contrast to the southern region where the CFZ is located. This region is subject to comparatively high-energy currents and is characterised by gravelly sands and cobbles, and high-energy bedforms such as sand streaks, sand ribbons, gravel furrows and sand waves (Croker et al., 2005). The water depth here is 50 to 60 m at the west of the fault and 80 to 120 m to its east. The CFZ is a major northwest-southeast trending strike-slip fault and consists of a complex fault zone several kilometers wide (Jackson et al., 1995). Croker et al. (2005) divided the fault into three zones: the northern muddy zone containing the Lambay Deep and its associated mud diapir; the central sandy zone characterised by large sand waves; and the southern zone characterised by current-swept seabed and patches of coarse sediments. The CFZ mounds have been identified in the central zone and have a relief of 5 to 10 m. They are typically greater than 250 m in length and over 80 m in width. For a detailed discussion of the setting and geology of the study area see Dobson and Whittington (1979) and Jackson et al. (1995).

## 3. Materials and Methods

Bathymetry data was collected from the CFZ from 2001 to 2002 during Celtic Voyager survey (Croker and O'Loughlin, 2001) and available through the INFOMAR program. Data was collected using a Kongsberg Simrad EM1002 multibeam echosounder (for details, see Croker and O'Loughlin, 2001). During survey CV10_28 water column echofacies were monitored using a Kongsberg Simrad EA400 single beam echosounder operated at 38 kHz. A Kongsberg Simrad OE14-208 underwater towed video system, housed in a Seatronics frame was used to obtain video and image stills of the mound features and surrounding seabed. Sediment sampling was conducted using Shipek and Van Veen grabs. Hardground material was retrieved from three stations, G103, G107 and G109, as shown in Fig. 1. Hardgrounds at each station were combined as one sample per station. Details for the sampling stations are given in Table 1. Samples for geochemical analysis were stored at -20°C onboard and at -80°C in the laboratory. The redox potential ($E_h$) of sampled sediments was assessed using an ORP ProcessProbe Ag/Cl redox probe (Bradley James Corp., Bedford, UK).

Unoriented rock slabs from G109 were cut using a diamond rock cutter and polished with sandpaper. Some polished slabs were used to prepare uncovered petrographic thin sections of standard size (48 mm x 28mm). Optical petrographic microscopy was performed using Leica DC 300 digital camera mounted on Leica DMLP microscope under the magnifications of 2.5, 5, 10, 20 and 40x. Relative abundances of grains in relation to pore space were estimated using comparison charts (Bacelle and Bosellini, 1965). Finely ground, hand-drilled carbonate samples from G109 were analysed for stable $\delta^{13}C$ and $\delta^{18}O$ isotope ratios using Finnigan MAT 251 and MAT 253 mass spectrometers coupled to automated Kiel devices. $\delta^{13}C$ measurement of methane from sediment samples in headspace vials from a core catcher was performed on a Finnegan MAT DeltaPlus irMS after conversion to $CO_2$ (Organic Mass Spectromety Facility, Woods Hole Oceanographic Institute). Isotope results are measured in relation to standard Vienna Pee Dee Belemnite (VPDB), with long-term analytical precision around 0.05% for $\delta^{13}C$ and 0.1% for $\delta^{18}O$.

Standard X-ray diffraction (XRD) in order to identify primary minerals was performed on mortar-ground samples using Siemens D5005 powder X-ray diffractometer. Scanning electron microscopy (SEM) was performed using a Hitachi S3400-N scanning electron microscopy operated at an accelerating voltage of 15.0 kV and a working distance of 10 cm. Elemental composition was assessed using an INCA Energy energy dispersive spectrometer (Oxford Instruments, UK) fitted to a Hitachi SU-70 SEM. SEM-energy dispersive spectroscopy (EDS) was performed at an accelerating voltage of 15.0 kV and a working distance of 1.6 cm. Elemental data was processed with the INCA suite software.

Sampled hardgrounds were acid solubilised (2 M HCl) and extracted according to Niemann et al. (2005) by ultrasonication-assisted extraction with the following solvent regime: 2:1 (v/v) methanol/DCM (x2), 1:2 (v/v) methanol/DCM (x2) and DCM (x2). Total lipid extracts were saponified with 6% KOH in methanol (80$^{\circ}$C for 3 hr) and neutral lipids and fatty acids (at ~ pH 1) were recovered by liquid-liquid extraction (x3) with 9:1 (v/v) hexane/diethyl ether. Neutral lipids were derivatised with N,O- bis(trimethylsilyl) trifluoroacetamide/pyridine (9:1, v/v), while fatty acids were methylated with 14% $BF_3$ in methanol at 70$^{\circ}$C for 1 hr. Fatty acid methyl ester (FAME) monounsaturation position was confirmed by formation of dimethyl disulfide (DMDS) adducts as outlined by Nichols et al. (1986). Analysis was performed on an Agilent 6890N gas chromatograph interfaced with an Agilent 5975C mass selective detector according to O'Reilly et al. (2012; 2014). The column temperature program was as follows: 65°C injection and hold for 2 min, ramp at 6°C $min^{-1}$ to 300°C, followed by isothermal hold at 300°C for 20 min. Quantification was performed using 5-α-cholestane internal standard. Samples were analysed in duplicate by continuous flow isotope ratio mass spectrometry (IsoPrime) according to O'Reilly et al. (2012; 2014), and using identical GC conditions as above. $\delta^{13}C$ values were calibrated against a stable isotope reference standard comprising a mixture of 15 n-alkanes (Mixture B2, Indiana University). Average $\delta^{13}C$ values are reported after correction for addition of derivative groups where necessary. Fatty acid nomenclature is according to $xC_{y\omega z}$, where x refers to the number of carbon atoms present, y refers to the number of double bonds on the carbon chain and z refers to the position of the first double bond from the methyl end.

# 4. Results

## 4.1 Underwater towed video, sampling and single beam echosounder

Collected video and image stills of the seabed at and in the vicinity of the mound targets are presented in Fig. 2. The sediment type was primarily fine- to coarse-grained sand, and there was widespread occurrence of exposed and semi-exposed hardgrounds on the seabed in the vicinity of target sites (Fig. 2A and B). These features appeared to be largely buried by sand. Fig. 2C shows an underwater still image of an area of exposed stacked pavement. This shows large 10 to 20 cm thick slabs and likely represents the characteristic morphology of the CFZ mounds. Patches of black, apparently reduced seabed several centimetres across were also recorded (Fig. 2D and F) during video surveying. A high density of asterozoans (likely ophiuroids) was observed in the vicinity of the mounds (not shown). In addition, possible hydroids colonising hardgrounds were also recorded (Fig. 2D to F).

Grab sampling of stations G103, G107 and G109 retrieved hardground material (hereafter referred to as G103, G107 or G109) and some black sediment. Sampled black surface sediments (Fig. 2G and I) were confirmed to be reducing, exhibiting $E_h$ readings as low as -177 mV. Colonising hydroids were also retrieved, still physically attached to sampled hardgrounds (Fig. 2G and H). These possibly belong to the genus Nemertesia, which have been found at the Texel carbonate mound sites (~ 53°27'N, 5°12'W) in the mid-Irish Sea (Whomersley et al., 2010). Grab sampling stations G103, G107 and G109 contained cemented tube worms (Fig. 2G). These are likely to have been formed by sedentary sabellarid polychaetes, possibly Sabellaria spinulosa, which are abundant at other hard grounds in the Irish Sea (Whomersley et al., 2010).

Single beam echosounder transects across one of the mounds (Fig. 1B) yielded characteristic acoustic echofacies in the water column. These appear as a rising vertical plume from close to the apex of the mound (Fig. 3). This acoustic signal is either caused by fish shoals or gas bubbles. However, fish shoals would normally display a broader more horizontal profile (Judd and Hovland, 2007), and by virtue of the source and vertical profiles this is very likely a gas plume emanating from the mound. The plume was detected rising a number of metres into the water column and the profile indicates at least moderate seepage is taking place at the CFZ.

**4.2 Mineralogy, petrographic analysis and stable isotope analysis**

Sub-samples from G103, G107 and G109 were also analysed using SEM-EDS analysis (Fig. 4). EDS spectra were dominated by calcium, silica, carbon and oxygen, confirming that the hard grounds are composed of carbonate and carbonate-cemented quartz grains (Fig. 4A and B). Individual quartz grains cemented by this carbonate are shown in Fig. 4C. Sulfur was also identified from EDS spectra, in particular for G109 (Fig. 4B). SEM micrographs highlighted the occurrence of amorphous to well-developed framboidal pyrite as the source of this sulfur (Fig. 4D and E). Based on the crystal shapes observed in SEM, the carbonate appears to a primarily acicular aragonite. Further petrographic analysis (Fig. 5, thin section PMO 217.327) and XRD (Fig. 6) of G109 confirmed that quartz and aragonite are the major mineral constituents of the rock. The rock can be subdivided into two main components. A detrital component is composed mostly of quartz sand (Fig. 5A), with small admixtures of other grains, such as mudstone lithoclasts, glaucony grains (Fig. 5B) and bioclasts. Among the bioclasts, possible red algae (Fig. 5B), echinoderms (Fig. 5B), bivalve fragments (Fig. 5C), balanid barnacles (Fig. 5D), foraminifera and gastropods (Fig. 5E and F) have been identified. This component can be linked with quartz and magnesian calcite, as identified by XRD (Fig. 6). The total grain fabric constitutes around 60% of the rock volume. Pore space partially occluded by the authigenic component occupies the remaining 40% of rock volume. The authigenic component is composed almost solely of aragonite (Fig. 6). It is represented by the microcrystaline variety, lining the surface of some of the grains and occasionally forming clothed microfabrics, followed by more abundant acicular crystals cementing the pore space (Fig. 5).

Carbonate stable isotope data have been obtained from sites G107 and G109. The $\delta^{13}C$ value from a single sample from site G107 are shown in Table 1. Samples from site G109 are presented in Table 1 (range) and Table 2 (all data points). Site G107 shows depleted $\delta^{13}C$ carbon (-36.97‰). Site G109 shows depleted $\delta^{13}C$ values between -48.97‰ and -53.71‰ (Fig. 7). $\delta^{18}O$ varied between -0.80‰ and 2.58‰

(Fig. 7). $\delta^{13}C$ values for methane sampled from surface sand at the CFZ mounds (Lat. 53°20'50"N, Long. 5°39'10"W) measured -70‰.

### 4.3 Lipid biomarkers and compound specific stable carbon isotope analysis

Fatty acids distribution was similar between G103, G107 and G109, whereby a range of saturated, monounsaturated, polyunsaturated, methyl- and cyclopropyl fatty acids were observed (Fig. 8A). Fatty acids ranged from $C_{12}$ to $C_{26}$ homologs. $C_{16:0}$ was the major fatty acid in all samples. $C_{14:0}$ and $C_{18:0}$ were other major saturated fatty acids. Monounsaturated $C_{16:1\omega7}$ and $C_{18:1\omega7}$ were also major fatty acids, followed by the polyunsaturated fatty acids $C_{20:5\omega3}$, $C_{20:4\omega6}$, $C_{22:6\omega3}$ and $C_{22:5\omega6}$. Iso and anteiso methyl branched fatty acids were also abundant and were dominated by odd carbon $C_{15}$ and $C_{17}$ homologs. These included $iC_{15:0}$, $aiC_{15:0}$, $iC_{16:0}$, $10MeC_{16:0}$ and $iC_{17:0}$. The average (n = 2) measured $\delta^{13}C$ values for selected lipids from G103, G107 and G109 are given in Fig. 9. The $\delta^{13}C$ measurements for fatty acids ranged from -24‰ to as low as -39‰. A general trend of between -25‰ to -29‰ was observed with overall little variation between samples for each compound. However, the branched fatty acids $aiC_{15:0}$, $iC_{16:0}$, $10MeC_{16:0}$ and $C_{17:1}$ were more depleted (below -30‰) for G109, as well as with $iC_{16:0}$ for G107. Sterols were the major lipid class in the neutral lipid fractions. $C_{27}\Delta^5$ was the major sterol in all samples. $C_{26}\Delta^{5,22}$, $C_{27}\Delta^{5,22}$, $C_{28}\Delta^{5,22}$, $C_{29}\Delta^{5,22}$, $C_{29}\Delta^5$ and $C_{29}\Delta^{5,24(28)}$ were also identified. $\delta^{13}C$ values were about -28‰ for well-resolved major sterols (Fig. 9). Other major lipids included phytol, n-alkanols ($C_{14}$ to $C_{26}$), a range of mono-alkyl glycerol ethers (MAGE) with n-alkyl chain lengths from $C_{14}$ to $C_{20}$. Pentamethylicosane was identified in G109 in low abundance, as well as crocetane co-eluting with phytane. Archaeol was tentatively identified in low abundance in G103 and G109 based on the peaks at m/z 130, 278 and 426. The abundance of these lipids was too low to permit $\delta^{13}C$ measurement.

## 5. Discussion

Methanogenesis in marine sediments can be subdivided into three main stages. The first stage takes place during shallow burial, when in temperatures lower than 50°C organic matter is being converted into methane by series of biochemical processes (Mah et al., 1977). In later burial at 80°C to 120°C, thermal cracking of organic matter forms gaseous and liquid hydrocarbons, which are further cracked to methane in when temperatures reach ca. 150°C (Claypool and Kvenvolden, 1983). Each of the formation stages leaves a characteristic trace in isotopic and chemical composition of the resulting gas (Schoell, 1988; Whiticar, 1999), which can be used to trace back the origin of the methane (e.g. Martens et al., 1991; Ivanov et al., 2010). Usually, the biogenic methane is significantly depleted in the heavy carbon isotope, with $\delta^{13}C$ values below -50‰, with thermogenic methane ranging between -50‰ to -30‰ (Sackett, 1978; Peckmann and Thiel, 2004; Judd and Hovland, 2007).

Heavily depleted carbon isotope (as low as -53.7‰) data from hardgrounds sampled at stations G107 and G109 confirm that the CFZ mounds are MDAC, and support previous work from Croker et al. (2002; 2005). Along with sites at Texel 11, Holden's Reef (Judd, 2005; Judd et al., 2007), and the mid-Irish Sea (Milodowski et al., 2009), the CFZ mounds are the fourth confirmed occurrence of MDAC in the Irish Sea. Usually MDAC is less depleted than the parent gas due to mixing with carbon from other sources, so the exact correlation between carbonate and parent gas is not straightforward (e.g. Bohrmann et al., 1998; Peckmann et al., 2001; Schmidt et al., 2002; Peckmann and Thiel, 2004). The amount of mixing is unknown, but seeping methane was likely isotopically lighter than cements (-70‰) and hence possibly of biogenic origin.

The CFZ MDAC samples are enriched in $^{18}O$ compared to typical marine carbonates, which usually range from -10‰ to +2‰ (Nelson and Smith, 1996). However, these values are in agreement with isotope signatures from MDAC recently sampled in the mid Irish Sea (Milodowski et al., 2009). The regression line in Fig. 7 for the cluster of data points shows a strong correlation ($n = 7$, $R^2 = 0.90$) and intersects the x-axis at $\delta^{13}C$ of -28‰. Assuming seawater $\delta^{18}O$ values between 0‰ to 0.5‰ for the Irish Sea (LeGrande and Schmidt, 2006) and that marine OM $\delta^{13}C$ typically ranges from -20‰ to -30‰, the non-AOM $\delta^{13}C/\delta^{18}O$ component may be associated with a marine water column OM signal. According to Milodowski et al. (2009), the $\delta^{18}O$ values for MDAC in the Irish Sea could be a result of precipitation in seawater colder than at present day. However, $^{18}O$ enrichment in MDAC at gas seeps sites is also well documented (e.g. Aloisi et al., 2000; Bohrmann et al., 1998; Chen et al., 2005), and may be due to MDAC precipitation with $^{18}O$-enriched water associated with decomposing deep gas hydrate (Aloisi et al., 2000; Bohrmann et al., 1998) or $^{18}O$-enriched water transported from deep petroleum sources (Milkov et al., 2005). Thus, the potential causes of $^{18}O$-enrichment in the Irish Sea cannot be reconciled here and will require further investigation.

Accumulations of unidentified shallow gas north of the study area have been suggested previously to be of biogenic origin (Yuan et al., 1992). Gas generation within these sediments is possible, however the volume of gas generated from thin and fairly recent sediment (Belderson, 1964) is probably much lower than that observed (Clayton, 1992; Judd and Hovland, 2007). Because the area of study is dominated by sands (Belderson, 1964; Croker et al., 2005), the gas is most likely sourced from the deeper subsurface. Subcropping Palaeozoic and Mesozoic rocks of the Kish Bank Basin (Naylor et al., 1993) are obvious candidates, with Carboniferous coals subjected to biogenesis to methane being of particular interest here (e.g. Flores et al., 2008; Li et al., 2008; Ulrich and Bower, 2008; cf. Moore, 2012). Alternatively, significant mixing and microbial reworking of seeping thermogenic gas in the shallow subsurface would result in a further depleted isotope signal from the original thermogenic signature and may be occurring here. Indeed, Croker et al. (2005) favoured a thermogenic gas source based on the distribution of gas accumulations in the western Irish Sea at both sandy and muddy sediment types, and due to the occurrence of most gas accumulations and features along faults (migration pathways from the deep sub-surface). Thus, the exact source of the gas remains difficult to determine at present.

Active water column seepage from the CFZ mounds has been documented on one other occasion at a separate feature in the CFZ, approximately 2.5 km west (53°20’30” N, 5°39’10” S) of the site described here (Croker et al., 2002). Based on surveys to date, the CFZ appears to be a site of active gas seepage. $\delta^{13}C$ analysis has confirmed that the precipitated carbonate is MDAC and SEM-EDS has also highlighted the presence of co-precipitated pyrite. This is in agreement with previous observations (Croker et al., 2002). Sulfate reduction is also evidenced by the presence of patches of black reducing sediments at the sediment-water interface (Fig. 2D and F). AOM is therefore a significant process regulating the flux of methane from the CFZ mounds and the formation of carbonate mounds at this site. The size and thickness of the slabs shown in Fig. 2C indicate considerable seepage over geological time, and together with echosounder data, and the presence of sulfide-rich reduced sediment indicates active methane seepage from the CFZ mounds is ongoing. Marine settings experiencing long-term erosion will eventually expose MDAC formed by AOM and, since carbonate-cemented sediments are more resistant to erosion than uncemented sediments, exhumed MDAC will accumulate as lag deposits in erosional environments (Paull and Ussler, 2008). The CFZ is a dynamic erosional setting with strong hydrographic conditions (e.g. Gowen and Stewart, 2005), and it is likely that the mounds formed in the shallow subsurface and have become exposed over time. The topography of these features is also likely extensively eroded post-exposure.

Both the character of the detrital and authigenic component suggests carbonate authigenesis within the sediment. This seems to be a common phenomenon in most of the seeps in the marine environment (e.g. Naehr et al., 2007; Pierre and Fouquet, 2007; Himmler et al., 2011), since AOM is localized to the anoxic zone at some depth within the sediment (Hinrichs et al., 1999; Boetius et al., 2000). Aragonite forms in favour over calcite in settings with relatively high alkalinity and increased sulfate concentrations (Walter, 1986; Burton, 1993). In this way, in seep settings aragonite is preferentially formed closer to the sediment-water interface (Aloisi et al., 2002; Savard et al., 1996). Formation of authigenic carbonate proceeds downward from the initial sulfate-methane transition to form carbonate crust (Greinert et al., 2002; Bayon et al., 2009). As AOM proceeds, marine sulfate enclosed in the pore water is successively consumed, giving way for more extensive precipitation of calcite in the succeeding stages (e.g. Aloisi et al., 2002; Bayon et al., 2009). Dominance of aragonite over calcite in carbonates sampled (Fig. 6) implies their formation in a sulfate-rich environment, most likely shaped by seawater reflux through permeable sandy sediment (Fig. 5).

Nemertesia and Sabellaria are epifaunal animals, which require a solid substrate for colonisation (Whomersley et al., 2010). Sabellaria spinulosa favours a sandy erosional environment but requires a hard ground in order to get established. This species was found in very high densities covering MDAC in the mid-Irish Sea (Whomersley et al., 2010) and may be an important coloniser of carbonate grounds throughout the Irish Sea. No known seep-specialist macrofauna, such as siboglinid tubeworms or thyasirid bivalves (Dando et al., 1991) were observed during video surveying. Nor were bacterial mats, which are commonly reported in active methane seep environments (e.g. Niemann et al., 2005; Bouloubassi et al., 2009). Seep-specialists such as some siboglinid tubeworms are rarely reported in shallow shelf and coastal cold seeps and are largely restricted to deep-sea active cold seep settings (Judd and Hovland, 2007). Thus they would not be expected to occur in a setting such as the CFZ seeps. However, a more comprehensive survey of the macrofaunal diversity of the mounds is needed to rule out the occurrence and activity of seep-specialists at the CFZ. It is evident that these hard grounds are of importance as a solid substrate for normal marine epifauna, allowing for diverse ecosystems to develop (Whomersley et al., 2010), as has been observed in the North Sea (Dando et al., 1991; Jensen et al., 1992).

The CFZ seep carbonates contain major fatty acids previously reported among sulfate-reducing bacteria implicated in AOM (Aloisi et al., 2002; Elvert et al., 2003; Niemann and Elvert, 2008). These included $iC_{15:0}$, $aiC_{15:0}$, $C_{16:1\omega5c}$, $C_{17:1\omega6c}$ and $cycC_{17:0}$ (Fig. 8A). $aiC_{15:0}$, $iC_{16:0}$ and $C_{17:1}$ fatty acids, in particular for G109 (and $iC_{16:0}$ for G107) were more depleted than other fatty acids, which suggests that sulfate-reducing bacteria involved in AOM are present. However, in general measured $\delta^{13}C$ values for most fatty acids were not significantly depleted in $^{13}C$ (Fig. 9) and suggests that methane is not a primary substrate for the dominant bacterial populations in this setting, as has been found in some other active seep settings (e.g.

Pancost et al., 2000; Elvert et al., 2003; Niemann et al., 2005). This is in agreement with recent work demonstrating the occurrence of $C_{15}$ and $C_{17}$ branched fatty acids in marine particulates and regional surface sediment throughout the western Irish Sea (O'Reilly et al., 2014). MAGE have previously been reported as diagnostic lipids for sulfate-reducing bacteria implicated in AOM (Pancost et al., 2001; Rütters et al., 2001). However, $\delta^{13}C$ measurements and the widespread occurrence of MAGE in sediments and in the water column in the western Irish Sea (unpublished data) indicate that water column input is the major source of MAGE in this study. This conclusion is supported by a recent study demonstrating the occurrence of MAGE in the water column in the Southern Ocean and eastern South Atlantic Ocean (Hernandez-Sanchez et al., 2014).

Commonly reported archaeal lipids such as crocetane (co-eluting with phytane), pentamethyleicosane and archaeol were observed, but in low abundance (Fig. 8B). This indicates archaea are a minor contributor to overall organic matter within these hardgrounds. These lipids are frequently among the most abundant and $^{13}C$-depleted at active methane seeps (Pancost et al., 2000; Aloisi et al., 2002; Niemann et al., 2005; Bouloubassi et al., 2009). In this case biomarkers diagnostic for microalgal water column input, such as sterols, phytol and $C_{14}$ to $C_{22}$ n-alkanols (Volkman et al., 1998) were dominant in all samples. This suggests that water column input derived from marine plankton, as well as benthic microalgae, is the dominant organic matter signal in the cemented sands. Considering that the CFZ zone is located in shallow shelf waters in a setting of known high primary productivity (Gowen and Stewart, 2005), a dominant input of organic matter from the water column may be expected. The significant contribution of phytoplankton and zooplankton OM to surface sediments in the western Irish Sea has recently been demonstrated (O'Reilly et al., 2014). In addition, since sand comprised over half the volume of the investigated hard grounds, one may expect to have significant contribution of marine OM and a subsequent dilution of AOM evidence in settings such as this. $\delta^{13}C$ values therefore likely reflect this major input from photosynthetic and related heterotrophic processes and may be diluting signals from microbial biomass that could be incorporating methane (Aquilina et al., 2010). It is noteworthy, however, that certain bacterial fatty acids were more depleted relative to other lipids, and compared to regional sediments (O'Reilly et al., 2014), with measured values as low as -40‰ (Fig. 9), which suggests that an unknown proportion of these fatty acids may be associated with sulfate-reducing bacteria involved in AOM. Similar moderately depleted fatty acids diagnostic for sulfate-reducing bacteria were obtained by Kinnaman et al. (2010) from MDAC concretions at 10 m water depth in the Brian Seep off Santa Barbara. AOM consortium biomass and their associated lipids are spatially highly variable and typically are highest in defined locales below the sediment surface where AOM rates are highest (e.g. Elvert et al., 2003; Aquilina et al., 2010). Therefore further targeted surveys in proximity to a venting site and from subsurface MDAC may reveal the nature of the microorganisms involved in AOM at this setting. This study highlights the complex interplay at shallow active gas seeps, between microbes utilising carbon derived from marine photosynthesis, and carbon from seeping gas.

## 6. Conclusions

Bulk isotope analysis and mineralogical analysis has confirmed that the carbonate mound features at the CFZ in the Irish Sea are MDAC. The principal authigenic mineral is aragonite. Active seepage was recorded from one of the mounds, with gas plumes detected in the water column. Underwater video footage highlighted the presence of sand-covered stacked and exposed carbonate pavements. The occurrences of high densities of cemented sabellarid tubes and extensive macrofaunal colonisation of carbonates indicate the CFZ mounds, like at other MDAC sites in the Irish Sea, represent an important solid substrate and habitat for local macrofauna. The common occurrence of patches of reduced sediment and the association of authigenic aragonite with framboidal pyrite indicate that AOM is taking place in shallow subsurface. In contrast to other deep sea methane seeps with widespread MDAC, lipid biomarker analysis suggests that microbial organic matter derived from methane is of minor significance in comparison to algal detrital organic matter from the water column. The co-existence of $\delta^{13}C$-depleted authigenic aragonite and isotopically light methane indicates a biogenic origin of the seeping gas, possibly related to Carboniferous coal deposits. However microbial reworking of deep thermogenic methane cannot be ruled out at present.

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## Tables and Figures

Table 1. Summary data of collected cemented carbonates from the Codling Fault Zone.

Table. 2. Carbon and oxygen stable isotope composition of the carbonate sample PMO 217.327-109 from site G109 (relative to Vienna Pee Dee Belemnite).

Fig. 1. The Codling Fault Zone mound features (white arrows), sampling stations (white crosses), underwater video tracklines (dark grey lines), and captured image stills of exposed carbonates or black reduced sediment (white stars). A. Location of the area of study. B. A 3D Fledermaus image showing the topography of some of the mounds features.

Fig. 2. Underwater towed video (A to F) and grab sampling (G to I) of Codling Fault mound targets. A. Semi-exposed nodules and pavement (P1). B. Semi-exposed hardgrounds (P2). C. Pavement stacking (P3). D. Reduced surface sediment (P4). E. Large exposed hardgounds (P5). F. Exposed colonised and non-colonised hardgrounds (P6). G. G103. H. G107. I. G109, a hardground colonised by a Nemertesia hydroid. Unlabelled scale bars = 25cm. The locations for underwater still images and sampling stations are given in Fig. 1 and Table 1.

Fig. 3. Single beam echosounder profile showing topography of mound features and active gas seepage to the water column from close to its apex. The location of the mound is shown in Fig. 1.

Fig. 4. A, B. Representative SEM-EDS analyses of the composition of sampled hard grounds. C. SEM micrograph showing carbonate-cemented quartz grain. D. Aragonite crystals and framboidal pyrite. E. Detail of framboidal pyrite.

Fig. 5. Aragonite cemented allochemic sandstone with bioclasts (G109). All microphotographs from PMO 217.327. A. Low magnification view of petrographic thin section; transmitted light. Note the large contribution of quartz grains in the rock volume. Empty cavities visible in the lover part of the picture are a product of sample preparation. B Detail showing a possible glaucony granule (black arrow) and an echinoderm skeletal fragment (grey arrow). C. Detail showing a bivalve fragment, possibly an oyster (black arrow), and a red algal fragment (grey arrow). D. Detail showing a balanid barnacle fragment (black arrow). E. Detail showing a gastropod (black arrow) and a possible foraminiferan (grey arrow). F. Same area as in E in polarized light.

Fig. 6. X-ray powder diffractogram of sample PMO 217.327. The blue rhombi represent quartz, red squares represent aragonite and red triangles represent Mg-calcite.

Fig. 7. Crossplot of carbon and oxygen stable isotope data from sample PMO 217.327, with data from Milodowski et al., (2009).

Fig. 8. Total ion chromatograms of a representative phospholipid fatty acid sample (A) and an alcohol fraction (B) from extracted aragonite-cemented quartz (G109 and G. Major compounds are labeled. Fatty acid nomenclature is according to X:YωZ, where X refers to the number of carbon atoms present, Y refers to the number of double bonds on the carbon chain and Z refers to the position of the first double bond from the methyl end. Sterol nomenclature is according to $C_X\Delta^Y$ where Y refers to the position of double bond(s) on the sterol skeleton.

Fig. 9. Measured $\delta^{13}C$ values for selected biomarkers extracted from samples G103, G107 and G109. See Fig. 1. for station location. IS = internal standard (5α-cholestane).