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Diagenetic Mg-calcite overgrowths on foraminiferal tests in the vicinity of methane seeps

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ABSTRACT

Methane is a potent greenhouse gas and some episodes of past global warming appear to coincide with its massive release from seafloor sediments as suggested by carbon isotope records of foraminifera. Here, we present structural, geochemical, and stable carbon isotope data from single foraminiferal calcite tests and authigenic Mg-calcite overgrowths in a sediment core recovered from an area of active methane seepage in western Svalbard at ca. 340 m water depth. The foraminifera are from intervals in the core where conventional bulk foraminiferal $\delta^{13}C$ values are as low as -11.3 ‰. Mg/Ca analyses of the foraminiferal tests reveal that even tests for which there is no morphological evidence for secondary authigenic carbonate can contain Mg-rich interlayers with Mg/Ca up to 220 mmol/mol. Transmission electron microscopy (TEM) of the contact point between the biogenic calcite and authigenic Mg-calcite layers shows that the two phases are structurally indistinguishable and they have the same crystallographic orientation. Secondary ion mass spectrometry (SIMS) analyses reveal that the Mg-rich layers are strongly depleted in ^{13}C ($\delta^{13}C$ as low as -34.1 ‰). These very low $\delta^{13}C$ values indicate that the authigenic Mg-calcite precipitated from pore waters containing methane-derived dissolved inorganic carbon at the depth of the sulfate–methane transition zone (SMTZ). As the depth of the SMTZ can be located several meters below the sediment-seawater interface, interpretation of low foraminiferal $\delta^{13}C$ values in ancient sediments in terms of the history of methane seepage at the seafloor must be undertaken with care.

1. Introduction

Since the discovery of methane emissions at the seabed, investigators have explored the potential of using tests of modern and fossil calcitic foraminifera as archives of seepage history. Remarkable carbon isotope excursions (CIE), characterized by very low $\delta^{13}C$ values in both benthic and planktonic foraminiferal calcite, have been interpreted to reflect widespread release of isotopically-light carbon from dissociating marine methane hydrates during the Paleocene–Eocene Thermal Maximum (PETM) at ∼54.95 Ma (e.g., Dickens et al., 1995; Zachos et al., 2005). Massive methane releases have been also used to explain CIEs at other time intervals related to abrupt global warming (Hesselbo et al., 2000; Jiang et al., 2003). However, it remains unclear if the very low $\delta^{13}C$ values of foraminifera reflect $\delta^{13}C$ values of dissolved inorganic carbon (DIC) in the primary biomineralization environment or whether they are associated with secondary overgrowths of authigenic carbonate.

Very low $\delta^{13}C$ values in foraminiferal calcite are widely considered to reflect seepage and incorporation of methane-derived, ^{13}C-depleted DIC at the time when foraminifera calcify their tests

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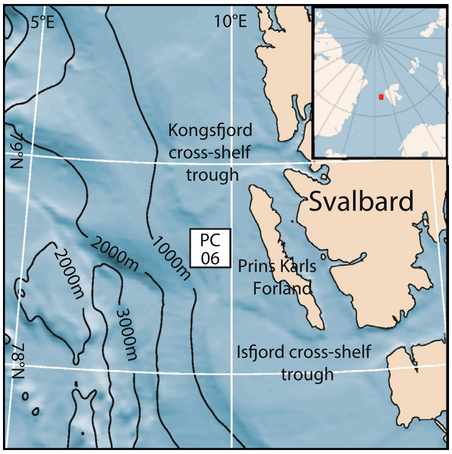

Fig. 1. Location of core PC06 offshore western Svalbard in the Arctic Ocean.

Table 1
Five foraminiferal tests (F1–F5) that have been studied in detail, their depth positions in core PC06 (cm bsf) and species specific bulk δ^{13}C values (determined on analyses of 3–10 specimens) at these core depths. Isotope data from Panieri et al. (2016).

Foraminifera	Species	Depth (cm bsf)	δ^{13}C
F1	*Nonionella labradorica* (specimen 2)	132	−10.6
F2	*Nonionella labradorica*	102	−4.7
F3	*Melonis barleenaum*	102	−5.1
F4	*Nonionella labradorica*	210	−11.3
F5	*Nonionella labradorica* (specimen 1)	132	−10.6

(Wefer et al., 1994; Dickens et al., 1995; Kennett et al., 2000; Hill et al., 2004). Alternatively, low foraminiferal δ^{13}C values may reflect precipitation of secondary overgrowths of methane-derived authigenic carbonates forming at the sulfate–methane transition zone (SMTZ) within subsurface sediments (Torres et al., 2010; Millo et al., 2005; Martin et al., 2010; Panieri et al., 2014, 2016; Consolaro et al., 2015). In this scenario, the original test surface merely acts as a template for authigenic carbonate precipitation. At the depth of the SMTZ, upward migrating methane and downward diffusing sulfate are consumed, by anaerobic oxidation of methane (AOM), according to the reaction (Boetius et al., 2000):

$$CH_4 + SO_4^{2-} \longrightarrow HCO_3^- + HS^- + H_2O$$

The bicarbonate (HCO_3^-) ions produced by AOM react with calcium and magnesium ions present in sediment pore waters to form Ca–Mg carbonates (Berner, 1970; Jørgensen et al., 2004; Ussler and Paull, 2008) which are typically strongly ^{13}C depleted.

Methane-derived authigenic carbonate occurring as sediment cements or as overgrowths on foraminifera tests are commonly rich in Mg with Mg/Ca often >20 mmol/mol. Mg is effectively complexed by sulfate in normal seawater which inhibits Mg incorporation into calcite, but if sulfate concentrations are very low, e.g. in pore waters affected by AOM, Mg is not complexed and can be more readily incorporated in calcite (Walter, 1986; Wright and Wacey, 2004). Hence Mg enrichment observed in foraminiferal tests can be indicative of the presence of diagenetic phases.

Here we present the results of analyses of individual foraminifera tests in a sediment core from an area of methane seepage west of Prins Karls Forland (ca. 340 m water depth), offshore western Svalbard (Fig. 1). Scanning Electron Microscopy (SEM), Electron Probe Micro Analysis (EPMA), Transmission Electron Microscopy (TEM), and Secondary Ion Mass Spectrometry (SIMS) studies reveal that there is significant variation in the geochemical and carbon isotope compositions *within* individual tests, and highlight the complexity of distinguishing primary *vs.* secondary signals. We demonstrate that diagenetic overprints on foraminifera can be very extensive, but not always evident using traditional methods such as optical microscopy and SEM.

2. Material selection

Foraminiferal tests were picked from three intervals (core depths 102, 132 and 210 cm below seafloor (bsf); Table 1) within a 224 cm long sediment core PC06 (78:36.66 N; 9:25.53 E; 374 m water depth) collected during RRS James Clark Ross cruise 253 in August 2011 (Fig. 1). The present-day depth of the SMTZ in this core is 184 cm bsf, and all sediments from between 100 and 220 cm bsf contain foraminifera with distinctly negative bulk δ^{13}C values (Panieri et al., 2016), outside of the range of normal marine values (ca. −1 to 1 ‰). From each of the three selected intervals calcitic tests of two benthic species, *Nonionella labradorica* (Dawson, 1860) and *Melonis barleeanus* (Williamson, 1858), were chosen for detailed study to assess whether the low δ^{13}C values (Table 1) are associated with primary biogenic calcite, or secondary overgrowths.

3. Strategy

Sediment samples were washed through a 63 μm sieve, and oven dried at 40 °C. Tests of benthic foraminifera, including both well preserved and altered (with obvious dissolution features and overgrowths) specimens, were picked from the larger size fraction, >100 μm, under a light microscope. The selected specimens (F1–F5) are listed in Table 1, together with results of analysis of the carbon isotope composition of bulk foraminifera (Panieri et al., 2016).

3.1. Scanning electron microscopy (SEM)

Polished cross-sections of a selection of tests were made by (i) placing the hand-picked tests on adhesive tape in a circular 25 mm diameter mold, (ii) mounting using Struers Epofix, and (iii) polishing to expose a cross-section through the interior of the tests. SEM examination of these polished sections was carried out at The Arctic University of Norway using an SEM Hitachi Tabletop Microscope TM-3000 equipped with Bruker Quantax 70 EDS Detector, and on a Zeiss Merlin Compact VP with the GEMINI I electron column.

3.2. Electron probe micro analysis (EPMA)

Quantitative Mg and Ca spot analyses and semi-quantitative elemental mapping were carried out using a JEOL JXA-8500F electron microprobe (field-emission electron gun) equipped with a high resolution wavelength X-ray dispersive spectrometer (WDS) at the Department of Materials Science and Engineering in Trondheim. Diopside $MgCaSi_2O_6$ (Mg = 11.23 wt%) and calcite $CaCO_3$ (Ca = 39.98 wt%) were used as standards. The mapping was performed using a 0.1 μm step size and beam scan with an image resolution of 512 × 512 pixels, 10 kV accelerating voltage and an electron beam current of 20 nA with a minimum probe size of 50 nm. Under such microprobe conditions the electron diffusion region of X-ray generation is in the range of 1 μm (X-ray spatial resolution during mapping). Optimum quantitative counting strategies from Mg and Ca were obtained with a total counting time of 60 s in both peak and background position, from an excitation cross-section of approx. 2 μm. The reproducibility of Mg and Ca determined from repeated analysis of standards was <1.5 %, and the detection limit was ∼100 ppm. Raw data were reduced to weight percentages using the ZAF algorithm. Performing WDS on carbonate material can result in beam damage to the specimen and lower