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Rates of anaerobic oxidation of methane and authigenic carbonate mineralization in methane-rich deep-sea sediments inferred from models and geochemical profiles

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Abstract

Pore water chemical data obtained from a 10.5-m long giant gravity core collected in methane-rich sediments from 647 m water depth in the northern Gulf of Mexico (N 28°04.00′ W 89°43.15′) defines sub-bottom gradients in unprecedented detail. This core penetrated the sulfate-methane interface (SMI) at ~300 cm below the seafloor (cmbsf). At the SMI dissolved inorganic carbon (DIC) concentrations reach a maximum (13.5 mM) and pore water δ^{13}C DIC (−63.2‰ PDB) and δ^{13}C methane (−89.5‰ PDB) values are most negative. Below the SMI pore water sulfate is nearly depleted, methane concentrations rise sharply with simultaneous occurrence of a bubble-textured sediment, and fine-grained methane-derived authigenic carbonate nodules and cements are common. The sharp peaks in DIC concentration and isotope values centered at the SMI indicate that DIC is being produced by anaerobic oxidation of methane (AOM) within a narrow zone centered at the SMI. The detailed sulfate and DIC concentration profiles, and DIC δ^{13}C values have enabled geochemical models to be constructed that explore the rate of DIC formation by AOM and its effect on pore water DIC δ^{13}C values. Model results closely match measured DIC concentration and δ^{13}C isotope profiles and indicate that microbiological conversion of methane carbon to DIC is rapid in geologic terms and that AOM is occurring at the present position of the SMI. Isotope values for authigenic carbonate found immediately below the present-day SMI (δ^{13}C = −60.2 ± 0.7‰ PDB at 440 cmbsf) are consistent with derivation of the carbonate carbon from methane via AOM at the former location of a SMI. These observations and model results suggest that AOM is occurring at rates that would generate the observed profiles and begin the precipitation of methane-derived carbonate occur on time-scales of centuries. Model results also show that the time needed to produce the resulting authigenic cements is an order of magnitude greater than that for AOM to produce the observed DIC profiles. The metabolic rates for DIC production by AOM inferred from modeling the geochemical profiles compare favorably with available rate data obtained from laboratory microbial incubations and radiolabeled tracer experiments.

Keywords: anaerobic oxidation; methane; dissolved inorganic carbon; carbon isotopes; sulfate–methane interface; biogeochemistry

1. Introduction and background

The sulfate–methane interface (SMI) is becoming recognized as a fundamental biogeochemical redox

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boundary in methane-rich and methane-gas-hydrate-bearing marine sediments worldwide (e.g., Iversen and Jorgensen, 1985; Borowski et al., 1996, 1997, 1999; Niewohner et al., 1998) where anaerobic oxidation of methane (AOM; see Reeburgh, 2007, for a thorough review) is mediated by a consortium of microorganisms (e.g., Hoehler et al., 1994; Boetius et al., 2000; Orphan et al., 2001). The SMI is a thin interval at the base of the sulfate-reduction zone that separates sulfate-bearing sediments above from sulfate-depleted, methane-rich sediments below. During AOM upward migrating methane and downward diffusing sulfate are consumed at the SMI and dissolved inorganic carbon (DIC), predominantly bicarbonate (HCO_3^-), and bisulfide (HS^-) are produced (Reeburgh, 1976). The net reaction for the anaerobic oxidation of methane is:

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

This reaction converts carbon originally in methane into HCO_3^-, enriching the pore water DIC pool with ^{13}C-depleted carbon and increasing the carbonate alkalinity of the water at the SMI. This alkalinity increase will stimulate the formation of authigenic carbonates at and below the SMI (Rodriquez et al., 2000).

Field (e.g., Alperin et al., 1988; Martens et al., 1999) and laboratory (e.g., Barker and Fritz, 1981; Coleman et al., 1981) studies have shown that the isotopic fractionation effects of AOM are highly variable and could be quite large ($\alpha = 1.005–1.030$). Strongly ^{13}C-depleted pore water DIC and authigenic carbonate minerals are diagnostic indicators of the present (e.g., Borowski et al., 1997; Claypool et al., 2004) or past (e.g., Raiswell, 1988) occurrence of AOM at a SMI, indicating that the isotopic effects are generally large and recorded by the $\delta^{13}C$ values of the methane-derived authigentic carbonate (Ritger et al., 1987; Paull et al., 1992).

What is not well understood are the rates of DIC production by AOM and the associated precipitation of methane-derived authigenic carbonates in methane-rich deep-sea sediment (>2 meters below sea floor — mbsf). Estimates of AOM rates in methane-rich sediments in the published literature (Table 1) obtained by direct measurement of ^{14}C methane oxidation in intact cores and slurries, by laboratory incubations, and geochemical modeling span more than four orders of magnitude. In general higher rates of AOM are found in methane-rich sediments near the sediment-water interface. AOM rates decrease with increasing SMI depth in the sediment, which would be expected because population size (and presumably microbial activity) generally decreases with depth (Schippers et al., 2005) and the availability of appropriate electron acceptors (e.g., sulfate).

Knowing rates of DIC production by AOM in methane-rich deep-sea sediments can provide constraints on the rates at which authigenic carbonates form. This information is critical for interpreting the geological record of authigenic carbonate mineralization. One published biogeochemical model of shallow carbonate crust formation on the seafloor at methane vent sites on Hydrate Ridge (e.g., Luff and Wallmann, 2003) indicates that methane-derived carbonate crusts can form in a few hundred years near the seafloor, but how this extrapolates to greater depths is virtually unconstrained.

In general, our knowledge of DIC production rates and authigenic mineralization rates are hampered by the scale of sampling that is related to core length (the longer the core, the greater the spacing) and the inability to identify and sample across the SMI immediately after core recovery. Most studies have generated spatially-limited datasets that have prevented studies at the scale of resolution needed to understand DIC production in deep-sea sediments, where the SMI is meters into the bottom.

2. Context of this study

We collected a giant gravity core in the northern Gulf of Mexico (Fig. 1) as part of a larger study of sulfate gradients in methane-rich and methane-gas-hydrate-bearing sediments (Paull et al., 2005). The side plates of this giant gravity core were removed immediately upon recovery (Fig. 1 in the Appendix). The freshly exposed side of the core showed a distinct bubble texture beginning at approximately 300 cmbsf suggesting that the core degassed during recovery. We recognized that the SMI may occur at this textural transition (Fig. 2) and that this core presented an excellent opportunity to sample across the SMI. High-resolution targeted sampling of the fresh core across this textural transition was made within hours of recovery of the core on deck. We report the pore water and carbonate chemistry of this core and their relationship with AOM at the SMI and the observed textural changes along the length of the fresh core. A coupled DIC (bicarbonate) concentration and $\delta^{13}C_{DIC}$ isotope model is developed that places constraints on the rate of AOM and authigenic carbonate precipitation in these sediments.

3. Methods

A 10.5-m long giant core (MD02-2571) was taken near a gas chimney in the Mississippi Canyon area of the northern Gulf of Mexico (N 28° 04.00′ W 89° 43.15′) in