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Assessing sulfate reduction and methane cycling in a high salinity pore water system in the northern Gulf of Mexico

J.W. Pohlman [a,*], C. Ruppel [a], D.R. Hutchinson [a], R. Downer [b], R.B. Coffin [c]

[a] U.S. Geological Survey, Woods Hole Science Center, 384 Woods Hole Road, Woods Hole, MA 02543, USA
[b] Milbar Hydrotest, Shreveport LA, USA
[c] Naval Research Laboratory, Washington DC, USA

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A B S T R A C T

Pore waters extracted from 18 piston cores obtained on and near a salt-cored bathymetric high in Keathley Canyon lease block 151 in the northern Gulf of Mexico contain elevated concentrations of chloride (up to 838 mM) and have pore water chemical concentration profiles that exhibit extensive departures (concavity) from steady-state (linear) diffusive equilibrium with depth. Minimum $\delta^{13}C$ dissolved inorganic carbon (DIC) values of −55.9‰ to −64.8‰ at the sulfate–methane transition (SMT) strongly suggest active anaerobic oxidation of methane (AOM) throughout the study region. However, the nonlinear pore water chemistry-depth profiles make it impossible to determine the vertical extent of active AOM or the potential role of alternate sulfate reduction pathways. Here we utilize the conservative (non-reactive) nature of dissolved chloride to differentiate the effects of biogeochemical activity (e.g., AOM and/or organoclastic sulfate reduction) relative to physical mixing in high salinity Keathley Canyon sediments. In most cases, the DIC and sulfate concentrations in pore waters are consistent with a conservative mixing model that uses chloride concentrations at the seafloor and the SMT as endmembers. Conservative mixing of pore water constituents implies that an undetermined physical process is primarily responsible for the nonlinearity of the pore water-depth profiles. In limited cases where the sulfate and DIC concentrations deviated from conservative mixing between the seafloor and SMT, the $\delta^{13}C$-DIC mixing diagrams suggest that the excess DIC is produced from a ^{13}C-depleted source that could only be accounted for by microbial methane, the dominant form of methane identified during this study. We conclude that AOM is the most prevalent sink for sulfate and that it occurs primarily at the SMT at this Keathley Canyon site.

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1. Introduction

Hydrocarbons and brines from deep reservoirs in the northern Gulf of Mexico migrate to the seafloor along faults and conduits that are often genetically related to salt-driven tectonics and release of overpressures (Bouma and Roberts, 1990). Seafloor manifestations of the discharge of gas and hydrocarbon-rich fluids include widespread cold seeps, brine pools, mud volcanoes and gas hydrate mounds, often associated with chemosynthetic communities (MacDonald et al., 1996; Roberts et al., 1990; Roberts and Carney, 1997; Sager et al., 2004). Although poorly constrained (e.g., Whelan et al., 2005), the transmission of hydrocarbons (primarily methane) from the sediments to the water column and possibly the atmosphere (MacDonald et al., 2002) is of great interest owing to the potency of methane as a greenhouse gas. Compared to other continental margin settings, hydrocarbon flux at the seafloor may be particularly enhanced in the Gulf of Mexico (MacDonald et al., 1993; MacDonald et al., 1996). Gas hydrate has been hypothesized to sequester large quantities of hydrocarbons in the northern Gulf of Mexico (Sassen et al., 2001), but elevated salinity and locally increased temperatures in some locations reduce the capacity for hydrocarbon capture in gas hydrate deposits (Paull et al., 2005; Ruppel et al., 2005).

Offsetting the potential impact of seafloor methane emissions is the anaerobic oxidation of methane (AOM) in the shallow sedimentary section (Hinrichs and Boetius, 2002; Niemann et al., 2006). AOM is mediated by a consortium of archaea and sulfate reducing bacteria within the sulfate–methane transition (SMT) (Hoehler et al., 1994; Boetius et al., 2000; Valentine and Reeburgh, 2000; Orphan et al., 2001; Niemann et al., 2006) according to:

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

The availability of sulfate for AOM, and hence its capacity to consume methane, is limited by sulfate transport from the overlying seawater and competition for that sulfate among microbes utilizing different sulfate reduction (SR) pathways (Niemann et al., 2006). In some settings, methane is the dominant substrate for SR

* Corresponding author. Tel.: +1 508 457 2213.
E-mail address: jpohlman@usgs.gov (J.W. Pohlman).

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(Niewohner et al., 1998; Boetius et al., 2000). Studies in other areas, including northern Gulf of Mexico hydrocarbon seeps (Joye et al., 2004; Kniemeyer et al., 2007), Hydrate Ridge offshore Oregon (Claypool et al., 2006), and the Guaymas basin in the Gulf of California (Kniemeyer et al., 2007), suggest that oxidation of organic compounds other than methane (i.e., organoclastic SR) is the primary sulfate sink. These conclusions are based on measured rates of AOM and SR, diagenetic modeling, and incubation studies. Understanding the fate of sulfate in methane-charged sediments is critical for predicting the effectiveness of the AOM biofilter in preventing methane from reaching the overlying ocean and possibly the atmosphere.

In this study, we determine the pathways (organoclastic SR v. AOM) and spatial occurrence of SR in near-seafloor sediments with high pore water salinity and distinctively nonlinear pore water concentration-depth profiles recovered from the Keathley Canyon area of the northern Gulf of Mexico. Adopting an approach that has been applied to differentiate the effects of physical mixing and biogeochemical alterations along estuarine salinity gradients (Cifuentes and Eldridge, 1998; Chanton and Lewis, 1999; Coffin and Cifuentes, 1999; Kaldy et al., 2005), we evaluate deviations from conservative mixing between the seafloor and the SMT for sulfate and DIC. The results lead to a robust biogeochemical assessment of the role of anaerobic cycling of organic matter in the near-surface sediments of Keathley Canyon.

2. Methods

2.1. Site description and core collection

The study site is located within the salt tectonics province of the northern Gulf of Mexico (inset, Fig. 1). The continental slope in the northern Gulf is bounded on the north by the shelf break and on the south by the Sigsbee Escarpment. During Plio-Pleistocene times, deeply buried Jurassic-age salt was mobilized as the result of sediment loading that accompanied the shifting position of the ancestral Mississippi River. The salt mobilized to form structural highs and adjacent salt withdrawal minibasins, thereby imparting an irregular bathymetry on the seafloor (Peel et al., 1995).

The cores were collected along the southeast edge of the Casey minibasin and the adjacent structural high in water depths of 1230–1455 m (Fig. 1, Table 1) during a cruise aboard the *R/V Gyre* in August 2003. The core sites were chosen from multichannel seismic profiles (Hutchinson and Hart, 2004) displaying a bottom simulating reflection (BSR). The BSR has been mapped along the southeast portion of the Casey Basin and beneath a 2-km wide, 80-m high seafloor mound – the Alpha mound – located on the adjacent structural high (Hutchinson et al., in press). The Alpha mound may be intensely faulted because of its location at the intersection of three structural highs along the edges of nearby minibasins. The core sites were laid out in three transects across the Alpha mound, along seismic reflection profiles KC01, KC11 and KC57 (Fig. 1). Two smaller mounds near the Alpha mound have been interpreted as potential localized seep sites, although it is uncertain if they are currently active (Hutchinson et al., in press).

The Joint Industry Project (JIP) Keathley Canyon drill site that is discussed elsewhere (e.g., Kastner et al., 2008) is ~3 km northwest of the Alpha mound on the eastern edge of the Casey minibasin (Fig. 1). Hutchinson et al. (in press, 2008) provide a detailed geological framework for the Keathley Canyon area and describe the features and geologic structures that occur near the JIP drill site.

2.2. Core processing

A total of 247, 10-cm-long, whole round sections from 18 piston cores up to 6 m long were cut at a spacing of ~25 cm. Sampling was more frequent near the SMT, which was identified visually by a color transition and proximity to the first gas expansion cracks.

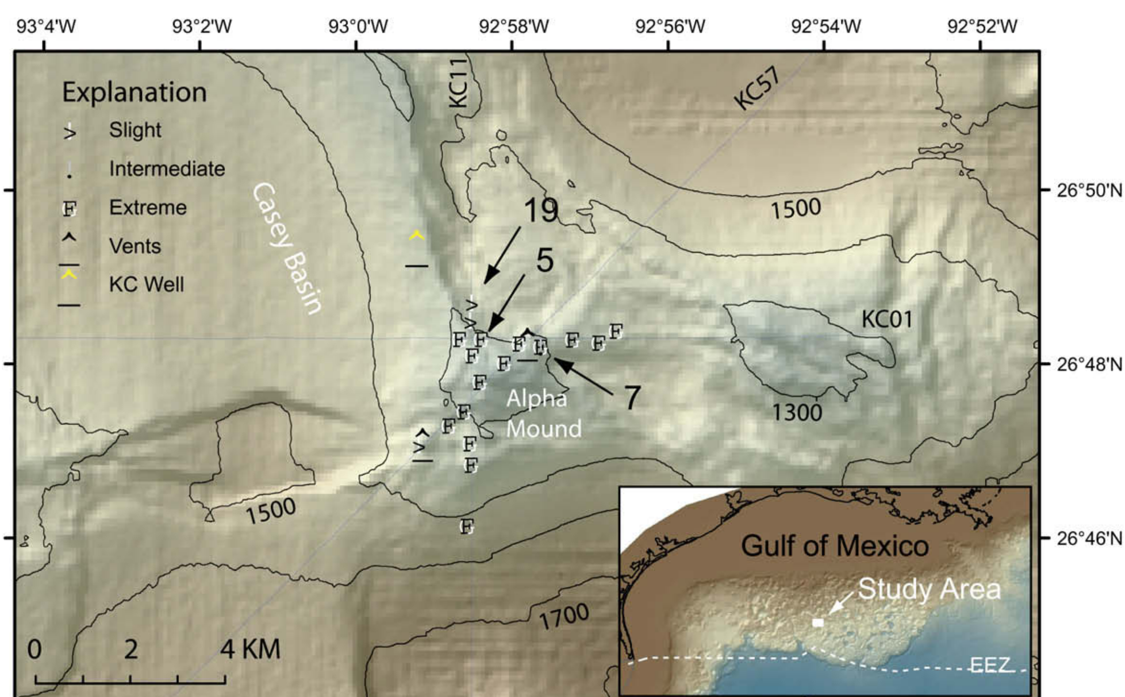

Fig. 1. Map showing the location of the core sites along the eastern edge of a salt withdrawal minibasin in Keathley Canyon Lease Block 151. The core locations were chosen to coincide with U.S. Geological Survey multichannel seismic profiles KC01, KC11, and KC57 (Hutchinson et al., in press). Core locations (Table 1) are identified using symbols that denote the degree of concavity of the pore water geochemistry profiles. Cores subjected to detailed biogeochemical analysis are indicated by arrows and the core number. The labels "5," "7," and "19" show the locations of cores KC03-05, KC03-07 and KC03-19, respectively. The 2005 DOE-JIP drill site KC151 is located to the northwest of this study area. Inset shows the location of the study area within the context of the minibasin province of the northern Gulf of Mexico.