Deep-Sea Research II ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Patterns and variability in geochemical signatures and microbial activity within and between diverse cold seep habitats along the lower continental slope, Northern Gulf of Mexico

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ARTICLE INFO

Keywords:
Cold seeps
Gulf of Mexico
Biogeochemistry
Microbial activity
Brine flows
Nutrient fluxes

ABSTRACT

We collected 69 sediment cores from distinct ecological and geological settings along the deep slope in the Northern Gulf of Mexico to evaluate whether specific geochemical- or habitat-related factors correlated with rates of microbial processes and geochemical signatures. By collecting replicate cores from distinct habitats across multiple sites, we illustrate and quantify the heterogeneity of cold seep geochemistry and microbial activity. These data also document the factors driving unique aspects of the geochemistry of deep slope gas, oil and brine seeps. Surprisingly little variation was observed between replicate ($n=2$–5) cores within sites for most analytes (except methane), implying that the common practice of collecting one core for geochemical analysis can capture the signature of a habitat in most cases. Depth-integrated concentrations of methane, dissolved inorganic carbon (DIC), and calcium were the predominant geochemical factors that correlated with a site's ecological or geological settings. Pore fluid methane concentration was related to the phosphate and DIC concentration, as well as to rates of sulfate reduction. While distinctions between seep habitats were identified from geochemical signatures, habitat specific geochemistry varied little across sites. The relative concentration of dissolved inorganic nitrogen versus phosphorus suggests that phosphorus availability limits biomass production at cold seeps. Correlations between calcium, chloride, and phosphate concentrations were indicative of brine-associated phosphate transport, suggesting that in addition to the co-migration of methane, dissolved organic carbon, and ammonium with brine, phosphate delivery is also associated with brine advection.

1. Introduction

Cold seeps are highly heterogeneous environments in terms of both the megafaunal communities they support, e.g. clams, mussels, urchins, and tubeworms, and microbial inhabitants, and the diversity of geological settings where they occur, e.g. mud or asphalt volcanoes, brine flows, carbonate hard grounds, gas hydrate outcrops, gas/oil vents and chimneys (Levin, 2005; Joye et al., 2010). Cold seeps are found along both active and passive continental margins, and occur widely in the Gulf of Mexico (hereafter, Gulf) along the upper and lower continental slope (Levin, 2005; Aharon and Fu, 2000; Arvidson et al., 2004; Joye et al., 2004, 2010). Joye et al. (2010) postulated that microbial activity at cold seeps of the deep slope of the Gulf of Mexico was less than that of the upper slope, and documented differences in activity between the two depth regimes. To further explore this hypothesis, microbial activity and geochemistry in a variety of settings were compared, and characteristic features of these settings were identified (e.g. brines associated with elevated dissolved organic carbon (DOC) and ammonium; Joye et al., 2010). These data showed that: (1) the intensity of seepage, and possibly the depth along the slope, influenced microbial abundance and activity, (2) the composition of seeping fluid directly influenced local geochemistry and biological communities and their activity, and (3) though macro-biology is dependent on seepage and surficial expression, it also overprints geochemical and microbiological features. To date, deciphering the differences and driving factors of these highly interdependent biogeochemical features has been difficult due to variable sampling strategies and different parameters measured in a given research expedition. With replicate sampling across multiple habitats this work sought to identify and explain geochemical and microbial rate variability within and between sites.

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http://dx.doi.org/10.1016/j.dsr2.2016.02.011
0967-0645/

In cold seep sediments, biogeochemical gradients can be sharp, both vertically and laterally. These gradients result from the geological setting and/or the megafauna and microbial communities inhabiting the area. Gradients are apparent on relatively small scales (mm to cm) as well as larger scales (10's of m) (Lloyd et al., 2010; Niemann et al., 2006; Omoregie et al., 2009; Roy et al., 2007). Pronounced lateral gradients in the geochemistry of cold seeps are exemplified within and across sulfur-oxidizing bacterial mats (Lloyd et al., 2010). Sulfate reduction rates (SRRs), sulfate concentrations, and microbial community structure differed in the center of a *Beggiatoa sp.* mat compared to the edge of the mat, which was only 10 cm from bare sediments (Lloyd et al., 2010). The seemingly homogenous structure of the mat upon visual observation makes such differences somewhat counterintuitive, but subtle spatio-temporal variations in seepage generate heterogeneous geochemical and microbiological signatures on strikingly small scales. Niemann et al. (2006) investigated larger scale changes across the Haakon Mosby mud volcano, which included a variety of habitats with mats and tubeworms inhabiting surface sediments. Differences in geochemistry and microbiology were noted in the proximity of the mud volcano as a function of the sediment surface megafaunal biology (Niemann et al., 2006).

The goal of this work was to sample replicate cores from a given habitat as defined by its geologic or megafauna biological signature and to compare different habitats both within and between sites along the deep slope. We hypothesized variation between sites (e.g. brine vs. oil seep) would be greater than variation observed between habitats (e.g. brine flow or megafauna regimes). Rates of microbial sulfate reduction and anaerobic methane oxidation and concentrations of geochemical (gases and dissolved and solid phase) constituents were determined systematically from replicate cores at consistent depth intervals. The sampling strategy allowed the comparison of particular habitats within a given seepage cell, which we define as a broad area (10's to 100's of m^2) impacted by seepage of a similar fluid (gas, oil, brine or some combination thereof). The overarching hypothesis was that distinct habitats would generate unique signatures of microbial activity and geochemistry.

2. Methods

2.1. Study sites and sample types

During July 2007, samples were collected from 9 sites along the lower continental slope (Table 1) of the Gulf of Mexico using the ROV JASON II, which was operated from the R/V *Ron Brown* (National Oceanographic and Atmospheric Administration). Here we provide data from five sites described in Joye et al. (2010) (Atwater Valley block 340, hereafter AT340; Green Canyon block 852, hereafter GC852; Walker Ridge block 269/270, hereafter WR 269/270; Alaminos Canyon block 645, hereafter AC645; and Alaminos Canyon block 818, hereafter AC818) and four additional sites: Garden Banks block 697, hereafter GB697; Garden Banks block 647, hereafter GB647; Alaminos Canyon block 601, AC601; and the Red Crater. Sediment samples were described by their ecological or environmental signature, as follows: control (background sediment adjacent to seep features, but with no visible signs of active seepage), Siboglinids polychaete worms, bacterial mats (sediments with *Beggiatoa sp.* inhabiting the surface), heart urchins (cores taken from an area with urchin activity based on visible urchins and observable urchin trails), urchin/brine (urchins inhabiting sediments with elevated salinity), brine flow (discrete brine flows), brine pools (collections of brine from a lake or pond-like feature), oil (visibly oil-stained sediments), and mud volcano (sediments characterized by mud flows).

Cores are referenced by their site abbreviation and type (e.g. Atwater Valley block 340 control sediment is denoted AT340-control); a description of all core types and sites is presented in Table 1 with the value representing the number of cores collected at a given site. In total 69 cores are described here, with 2–5 cores collected for each habitat type within a given site. The area of coverage during the repetitive coring in each environment was $>2\ m^2$.

2.2. Dissolved gases, porewater, and microbial activity sample collection

Cores were retrieved from either the ROV JASON II or the elevator system that was used to transport equipment and cores from the seafloor to the ship during JASON operations. Upon return to the surface, cores were moved immediately to a 4 °C cold room and processed within 24 h of collection. General procedures utilized for porewater collection were described previously (Joye et al., 2010). Each replicate core from a given habitat was sampled for dissolved gases, porewater, solid phase, and microbial activity samples at depths of 1.5, 4.5, 8, and 12.5 cm; an additional overlying water sample was also collected generating 5 samples per core. Upon extrusion of a new interval, a 3 or 5 mL sample was collected for quantification of dissolved methane and hydrogen, respectively. Methane samples were collected with a 3 mL cut-end syringe, then ejected into a 12 mL headspace vial containing 3 mL He-purged 2 M NaOH, crimp sealed with a gray butyl rubber stopper, and vortexed until well mixed. The hydrogen samples were collected with a 3 mL cut-end syringe, then ejected into a 20 mL headspace vial, crimp sealed with a blue butyl rubber stopper, and flushed immediately with He.

Next, a 2 cm^3 sample was placed into a pre-weighed 7 mL vial with a teflon-coated cap to determine the porosity. Then, a 3 cm^3 sediment sample ($n=3$ per core per assay) for rate assays was collected for sulfate reduction (SR) and the anaerobic oxidation of methane (AOM) into a 5 mL cut-end syringe, which were then sealed with a butyl rubber stopper. Finally, the remaining sediment was collected for porewater extraction using a mechanical press (Joye et al., 2010). The sediment was placed in an Ar-flushed PVC cup and sealed with a PVC piston and cap. Then, porewater was collected into a 30 mL syringe and at least 20 mL of porewater

Table 1
Site depths, locations, and number and type of cores collected.

Site	Depth (m)	Lat. mean	Long. mean	Control	Siboglinids	Bacterial mat	Urchin	Brine edge	Brine feature	Brine	Oil	Mud volcano	Gassy
AT340	2216	27.64	−88.36	4		4	4			4			
GC852	1410	27.1	−91.16	2					4				4
GB697	1010	27.31	−92.11							2			
WR269	1950	26.68	−91.66	3	2								
GB647	950	27.19	−92.26								2		
AC645	2200	26.35	−94.49		4								
AC818	2740	26.18	−94.62	4	4		4						
AC601	2350	27.31	−94.8	5			3	3		3			
Red Crater	2300	26.36	−94.51		2							2	

Please cite this article as: Bowles, M., et al., Patterns and variability in geochemical signatures and microbial activity within and between diverse cold seep habitats along the lower.... Deep-Sea Res. II (2016), http://dx.doi.org/10.1016/j.dsr2.2016.02.011