Application of shallow sediment geochemical and geophysical data to infer methane flux from methane hydrate bearing strata in Alaminos Canyon, Gulf of Mexico

Midshipman 1/C Tracy Fridye, USN, Class of 2011

Advisor: CDR J. P. Smith

Abstract

Methane hydrate is methane enclosed in a solid lattice ice structure that forms under high pressures and low temperatures in permafrost and in marine sediments such as the Gulf of Mexico where there are significant methane sources. Estimates of methane hydrate global distributions vary, but the potential energy content in the global methane hydrate reservoir may equal or surpass that of all other fossil fuel reservoirs combined. Geophysical surveys and geochemical analysis can be combined to infer methane hydrate occurrence in marine sediments. Shallow sediment cores (<10 m) were collected in June 2007 from Alaminos Canyon, Gulf of Mexico, based on prior geophysical surveys. Geochemical analysis was performed on sediment porewaters (CH_4, SO_4^{2-}, Ca^{2+}, Mg^{2+}, dissolved inorganic carbon (DIC), Cl^-) and used to quantify SO_4^{2-} and DIC flux to infer the CH_4 flux from gas hydrate stability zone (GHSZ). SO_4^{2-} flux generally increased close to the area of probable gas venting shown in the geophysical data. Most core locations conformed to a 1:1 ratio of SO_4^{2-} to DIC, implying that anaerobic oxidation of methane (AOM) dominates SO_4^{2-} consumption. Thus, CH_4 flux from underlying hydrate deposits can be inferred from SO_4^{2-} flux. Coupling geophysical surveys with geochemical analysis of sediment porewaters offers a powerful method to infer methane hydrate occurrence in sediments of Alaminos Canyon.

Study Area and Methods

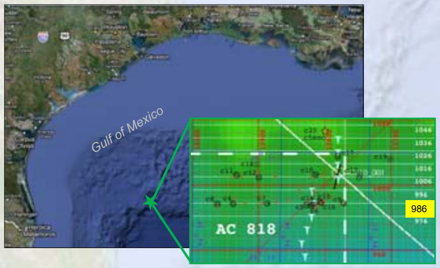

Figure 1. Alaminos Canyon, Gulf of Mexico showing Block 818, Line 986 with core locations (Coffin et. al, 2007).

- Geophysical surveys provided by WesternGeco
- Shalllow sediment coring, porewater collection and analysis for (SO_4^{2-}, DIC, CH_4, Ca^{2+}, Mg^{2+}, Cl^-) perfomed by the US Naval Research Lab (6114).
- Porewater ion (SO_4^{2-}, DIC, CH_4, Ca^{2+}, Mg^{2+}, Cl^-) analyzed using a Dionex DX-120 ion chromatograph.
- Headspace CH_4 concentrations analyzed with a GC-FID Shimadzu GC-14A gas chromatograph.
- DIC was measured using a UIC CO_2 coulometer .

Results and Discussion

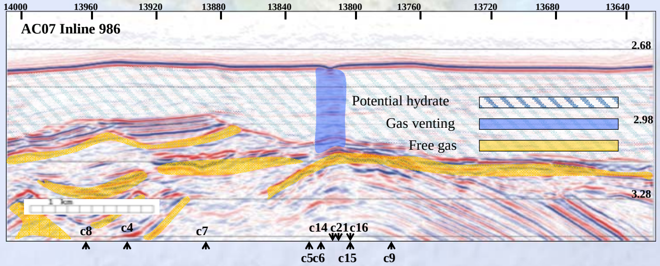

Figure 2. Line 986 seismic profile showing piston core locations in relation to potential hydrate deposits predicted from areas of bottom simulating reflectors (BSRs) and potential gas venting (Coffin et al., 2007)

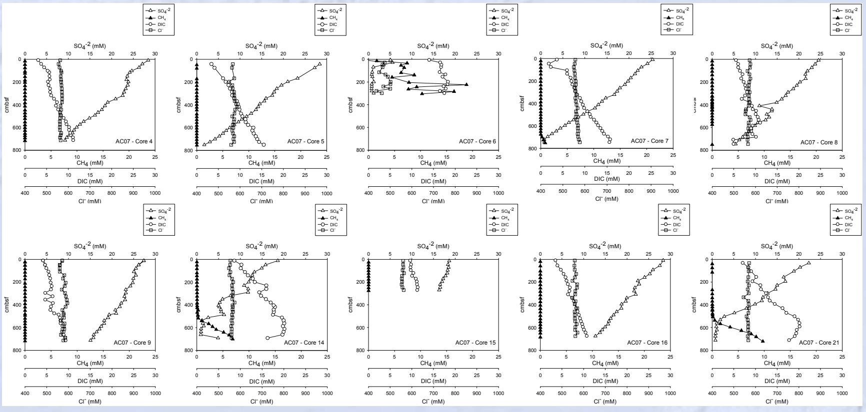

Figure 3. Sediment headspace CH_4 and porewater SO_4^{2-}, DIC, and Cl^- concentration profiles for each core location.

SO_4^{2-} diffuses downward into porewaters and, under anoxic conditions, depletes with depth due to organoclastic sulfate reduction (SR), $2(CH_2O) + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$, and/or the anaerobic oxidation of methane (AOM), $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$. SO_4^{2-} gradients were determined visually from the linear portion of each profile (**Fig. 3**). SO_4^{2-} flux was calculated using Fick's first law (Flux (J) = $-\Phi D_s(dC/dz)$) with the gradients, assuming an averaged porosity, and a constant SO_4^{2-} diffusion coefficient. DIC is the sum of CO_2, HCO_3^-, and CO_3^{2-}, which all contribute to alkalinity. Total DIC flux was calculated by subtracting the Ca^{2+} and Mg^{2+} flux from the DIC flux to account for chemical precipitation with HCO_3^- (**Table 1**).

Table 1. Sulfate flux calculations from the linear portion of the sulfate gradient in order of reference to core 8

Core	8	4	7	5	6	14	21	15	16	9
Sulfate Flux (mM cm^{-2} yr^{-1})	1.98	1.50	2.30	3.22	Nonlinear	Nonlinear	3.95	0.58	1.47	1.27
DIC Flux (mM cm^{-2} yr^{-1})	3.46	2.43	-0.20	2.74	Nonlinear	Nonlinear	2.15	-0.68	2.20	2.36

Comparing DIC to the SO_4^{2-} flux indicates whether SR or AOM dominates SO_4^{2-} depletion in shallow porewaters. If AOM dominates, DIC flux should compare to SO_4^{2-} flux with a 1:1 ratio above the sulfate methane interface (SMI). If SR dominates, the ratio will be closer to 2:1. Evaluations are based on the assumption of no advection and steady-state. On inline 986, AOM dominates five of the cores, so vertical CH_4 flux is proportional to SO_4^{2-} flux.

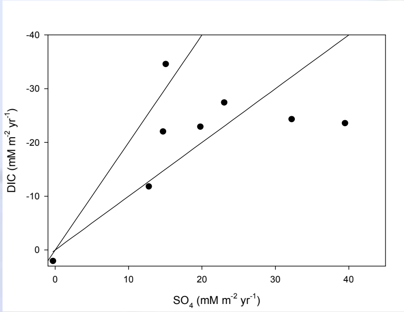

Figure 4. Comparison of DIC flux versus SO_4^{2-} flux

Core	CH_4 gradient (mM m^{-1})
5	3.28
7	2.23
8	1.99
9	1.23
16	1.46

Table 2. Estimated CH_4 gradients

Using the diffusion coefficient for CH_4, averaged porosity, and calculated SO_4^{2-} flux, the CH_4 gradient was calculated using Fick's first law (**Table 2**). Values obtained are large enough to reach diffusive equilibrium at the GHSZ and conditions are suitable for methane hydrate formation.

Conclusions

- Cores 5, 7, 8, 9 and 16 showed a 1:1 ratio of DIC to SO_4^{2-} flux, indicating AOM is dominant. Cores 4, 6, 14, 15, and 21 did not allow for interpretation of CH_4 flux, likely a result of advective processes near a potential active CH_4 seep (**Fig. 2**). The near 2:1 ratio of DIC to SO_4^{2-} flux in core 4 suggests SR is dominant. BSRs still suggest the presence of hydrate at depth.
- SO_4^{2-} flux increased close to the area of probable gas venting shown in the geophysical data.
- Results from the concurrent geochemical and geophysical methods employed in this study suggest that this approach can serve to validate Alaminos Canyon as a potential area for resource exploitation.

References

Coffin, R., and others, 2007, Geochemical Evaluation of Deep Sediment Hydrate Deposits on Alaminos Canyon, Block 818, Texas-Louisiana Shelf: Naval Research Laboratory, Marine Biogeochemistry Section, 74 p.

Spring 2011