[PS]Effects of Brine Composition (NaCl, $MgSO_4$, $FeSO_4$) and Clay Minerals (Kaolinite, Nontronite, Montmorillonite) on the Stable Isotopic Composition of Methane and Hydrogen Sulfide in Gas Hydrates*

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Abstract

Stable isotopes of carbon, hydrogen, and sulfur in methane (CH_4) and hydrogen sulfide (H_2S) can be used as source-fingerprints of gas molecules trapped in hydrates. Isotopic fingerprints are useful for differentiation of methane from microbial and thermal processes, providing valuable context for economic recovery of natural-gas resources. It is challenging, however, to apply isotope systematics to hydrate-forming systems due to complex influences on nucleation and dissociation under varying conditions of salinity/pressure/temperature and interactions of gas molecules with clay minerals.

Here, a series of pressure-vessel experiments have been conducted with quantitative recovery of free-gas and hydrate-gas molecules of CH_4 and H_2S. These experiments allow nucleation of gas hydrates containing CH_4 and H_2S from solutions of deoxygenated Millipore water and from brines with varying concentrations (14 mM to 2M) of NaCl, $MgSO_4$, and $FeSO_4$. After addition of water or brine, the vessel is purged with low pressure N_2 for 30 minutes followed by pressurization with CH_4 (20 to 55 bars) or H_2S (0.35 to 2.32 bars) from tanks with known isotopic composition. Methane experiments show only small differences in carbon isotopic composition (max 0.63‰); between tank gas and both free gas and hydrate gas. In the same experiments, hydrogen isotopic compositions vary by up to 11‰. Sulfide experiments show sulfur isotopic differences up to 3‰ between gas phases. Future experiments will test the influence of microbial biosurfactants reported to occur at natural hydrate sites. The results of these experiments will refine interpretation of gas provenance and will improve risk assessment at sites where recurrent hydrate formation complicates hydrocarbon drilling and transportation in pipelines.

EFFECTS OF BRINE COMPOSITION (NaCl, $MgSO_4$, $FeSO_4$) AND CLAY MINERALS (KAOLINITE, NONTRONITE, AND MONTMORILLONITE) ON THE STABLE ISOTOPIC COMPOSITION OF METHANE AND HYDROGEN SULFIDE IN GAS HYDRATES

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1. Introduction

Gas-containing water ice structures, known as gas hydrates or clathrates, have been found in natural settings worldwide [1, 2]. A gas hydrate is typically formed when small guest molecules (diameter~0.9 nm), like methane (CH_4) and hydrogen sulfide (H_2S), interact with water at cold ambient temperatures (typically less than 300 K) and moderate pressures (0.6-8 MPa) [3]. These thermodynamic conditions are usually found in the Arctic permafrost [4, 5] and at the base of continental shelves and slopes [6, 7], underlying regions of moderate to high primary productivity. Interest in gas hydrates relies on their capacity to store large amounts of economically recoverable gas (ca. 20,987 trillion cubic meters) [8] and the particular interest in two of those gases stored inside these hydrates, methane and hydrogen sulfide, and their environmental effects. Stable isotopes of carbon, hydrogen, and sulfur in CH_4 and H_2S can be (and have been) used as source-fingerprints of the gas molecules trapped in hydrates [6, 9, 10]. For instance, isotopic fingerprints are useful for differentiation of microbial vs. thermally-produced methane, providing valuable context for economic recovery of natural-gas resources. It is challenging, however, to apply isotope systematics to hydrate-forming systems due to complex influences on nucleation and dissociation under varying conditions of salinity/pressure/temperature [11] and interactions of gas molecules with clay minerals biologically-produced surfactants [12, 13]. Here, pressure-vessel experiments explore the influences of brine solutions with varying concentrations (14 mM to 2M) and biosurfactants (Rhamnolipids and surfactin) on the isotopic composition of the different gas phases in CH_4 and H_2S hydrate systems. The results of these and forecoming experiments will refine interpretation of gas provenance and will improve risk assessment at sites where recurrent hydrate formation complicates hydrocarbon drilling and transportation in pipelines.

Figure1. Above, titanium reactor for hydrate nucleation experiments inside low-temperature freezer . Below, Methane hydrate inside reactor

2. Methods

Isotopic notation. Stable isotope ratios are typically reported in the delta notation in (1), as deviations with respect to a reference scale: Vienna Pee Dee Belemnite for carbon (V-PDB), Vienna Standard Mean Ocean Water for hydrogen (VSMOW), and Cañon Diablo Troilite for sulfur (CDT). Stable isotopes are reported using the following notation (carbon is used as an example): $\delta^{13}C = (^{13}R_{sample} / {}^{13}R_{standard} - 1)* 1000$, where, ^{13}R is the $^{13}C/^{12}C$ ratio (heavy over light isotope) in both the standard and the sample. The notation is expressed in parts per thousand or per mil (‰). The epsilon notation 'ε' is an accurate measure of the isotopic offset between two substances ($\delta^{13}C_A$- $\delta^{13}C_B$), when the offset is smaller than 10‰ and can be defined as: $^{13}\varepsilon_{A-B} = (^{13}\alpha_{A-B} - 1)*10^3$

Crystallization of gas hydrates. A titanium reactor from Parr Instruments© (reactor capacity= 450 mL) is used for both CH_4 and H_2S hydrate experiments (Figure1). It possesses two oblong windows, allowing visual monitoring of the hydrate formation process. Brines prepared with anoxic Millipore water are added to the vessel inside an Aldrich® AtmosBag purged with low pressure nitrogen gas for 1hr followed by pressurization with CH_4 (2 to 5.5 MPa) or H_2S (0.035 to 0.23 MPa) from tanks with known isotopic composition.

Sample collection. For carbon and hydrogen isotope analysis ($\delta^{13}C$ and δ^2H, respectively), CH_4 gas is collected in 50 mL serum-type glass bottles, through volume displacement. Hydrogen sulfide gas collection for sulfur isotope analysis ($\delta^{34}S$) from both free gas and hydrate phases are passed through a silver nitrate ($AgNO_3$) trap, precipitating silver sulfide (Ag_2S).

Stable isotope analysis. Both gas and hydrate phases with CH_4 and H_2S are then analyzed for carbon, hydrogen, and sulfur isotopes at the Stable Isotope Research Facility (SIRF), Biogeochemical Laboratories, Indiana University, Bloomington. For CH_4 gas samples are analyzed in a DeltaPlus XP mass spectrometer using a customized gas sampling and injection system [14], ideal for compound-specific analyses of gaseous mixtures. For H_2S, samples are analyzed as solid Ag_2S for $\delta^{34}S$ values in a Finnigan MAT 252 isotope ratio mass spectrometer.

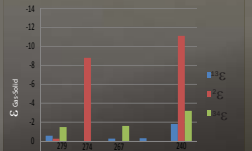

Figure 2. Here shown, carbon, hydrogen, and sulfur isotopic variations ($^{13}\varepsilon$, $^{2}\varepsilon$, and $^{34}\varepsilon$, respectively) between gas and hydrate phases of CH_4 and H_2S gas hydrate systems.Gas hydrates were nucleated from pure water solutions (no electrolytes added). Temperature (in Kelvin) is shown on the horizontal axis.

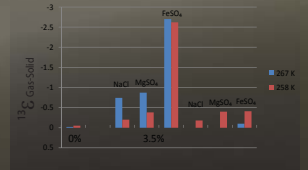

Figure 3. Variation in carbon isotopic composition between gas and hydrate phases ($^{13}\varepsilon$ G-S) for CH_4 hydrate systems nucleated from electrolyte solutions of sodium chloride, magnesium, and ferrous sulfate (NaCl, $MgSO_4$, and $FeSO_4$). Gas hydrates were nucleated at two different temperatures and salinities (3.5%-12%). Temperatures are shown in Kelvin.

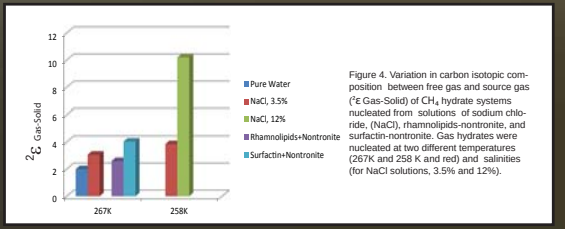

Figure 4. Variation in carbon isotopic composition between free gas and source gas ($^{2}\varepsilon$ Gas-Solid) of CH_4 hydrate systems nucleated from solutions of sodium chloride, (NaCl), rhamnolipids-nontronite, and surfactin-nontronite. Gas hydrates were nucleated at two different temperatures (267K and 258 K red) and salinities (for NaCl solutions, 3.5% and 12%).

Solution Composition	$\delta^{13}C_{gas}$ ($f_{recovered}$)	$\delta^{13}C_{solid}$ ($f_{recovered}$)	Isotope Mass Balance	Tank Measured	$\Delta^{13}C_{IMB-TM}$
3.5 % NaCl (267K)	-39.747 (0.73)	-39.060 (0.27)	-39.538	-39.513	-0.025
3.5 % NaC (258K)	-39.676 (0.88)	-39.483 (0.12)	-39.644	-39.509	-0.135
3.5 % $MgSO_4$ (258K)	-39.753 (0.85)	-39.377 (0.15)	-39.649	-39.509	-0.14
3.5 % Fe (II) SO_4 (258K)	-39.850 (0.87)	-39.734 (0.13)	-39.818	-39.509	-0.309
12% NaCl (258K)	-39.393 (0.78)	-39.216 (0.22)	-39.352	-39.291	-0.061
12 % $MgSO_4$ (267K)	-39.293 (0.84)	-38.834 (0.16)	-39.219	-39.294	0.076
12 % Fe (II) SO_4 (267K)	-39.256 (0.90)	-38.991 (0.1)	-39.221	-39.294	0.074
12 % $MgSO_4$ (258K)	-39.351 (0.85)	-39.310 (0.15)	-39.345	-39.291	-0.054
12 % Fe (II) SO_4 (258K)	-39.348 (0.88)	-39.188 (0.12)	-39.319	-39.291	-0.028
Rhamnolipids+Nontronite(267K)	-39.266 (0.90)	-38.268 (0.10)	-39.166	-39.132	-0.0342

Table 1. Here shown, carbon isotopic values of the different phases within hydrate systems nucleated from electrolyte solutions of sodium chloride, magnesium, and ferrous sulfate (NaCl, $MgSO_4$ and $FeSO_4$, respectively) and rhamnolipids-nontronite. Second and third column show (in parenthesis) the corresponding fraction of gas recovered from each phase, as a percentage of the total amount of gas injected. Last column shows the isotopic difference between the mass balance and the measured carbon isotopic value of the original gas (source).

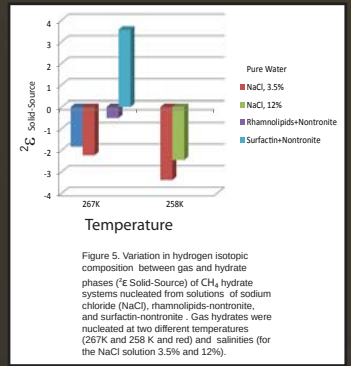

Figure 5. Variation in hydrogen isotopic composition between gas and hydrate phases ($^{2}\varepsilon$ Solid-Source) of CH_4 hydrate systems nucleated from solutions of sodium chloride (NaCl), rhamnolipids-nontronite, and surfactin-nontronite . Gas hydrates were nucleated at two different temperatures (267K and 258 K and red) and salinities (for the NaCl solution 3.5% and 12%).

Solution Composition	δ^2H_{gas} ($f_{recovered}$)	δ^2H_{solid} ($f_{recovered}$)	Isotope Mass Balance	Tank Measured	Δ^2H_{IMB-TM}
3.5 % NaCl (267K)	-160.10(0.73)	-162.76(0.27)	-160.82	-160.93	0.11
3.5 % NaC (258K)	-160.46(0.88)	-163.17 (0.12)	-160.79	-160.93	0.14
3.5 % $MgSO_4$ (258K)	-163.24(0.85)	-160.07 (0.15)	-162.77	-160.93	-1.84
3.5 % Fe (II) SO_4 (258K)	-160.95(0.87)	-160.77 (0.13)	-160.93	-160.93	0.00
12% NaCl (258K)	-150.80(0.78)	-160.99 (0.22)	-153.04	-158.53	5.49
12 % Fe (II) SO_4 (267K)	-158.62(0.90)	-157.75 (0.1)	-158.53	-158.53	0.00
12 % $MgSO_4$ (258K)	-157.92(0.85)	-161.72 (0.15)	-158.49	-158.53	0.04
12 % Fe (II) SO_4 (258K)	-156.73(0.88)	-154.88 (0.12)	-156.51	-158.53	2.02
Rhamnolipids+Nontronite	-151.65(0.9)	-154.24(0.10)	-151.91	-153.73	1.82
Surfactin+Nontronite	-146.15(0.90)	-150.18(0.10)	-146.55	-153.73	7.18

Table 2. Here shown, hydrogen isotopic values of the different phases within hydrate systems nucleated from electrolyte solutions of sodium chloride, magnesium, ferrous sulfate (NaCl, $MgSO_4$, and $FeSO_4$, respectively), rhamnolipids-nontronite, and surfactin-nontronite. Second and third column show (in parenthesis) the corresponding fraction of gas recovered from each phase, as a percentage of the total amount of gas injected. Last column shows the isotopic difference between the mass balance and the measured carbon isotopic value of the original gas (source).

3. Results and Discussion

We tried to replicate the results obtained by [15], where significant hydrogen isotopic fractionation between gas and hydrate phases was reported as a function of decreasing temperature (up to 10‰ ^{2}H-depletion in the hydrate phase) in CH_4 hydrates nucleated from pure water. Our CH_4 hydrates display a similar isotopic difference (11‰), between the gas and the hydrate phase (although at different nucleation temperatures) (Figure 2). In addition, H_2S experiments reported here for the first time, show ^{34}S-enriched hydrate-bound gas (up to 3‰) compared to the gas phases (Figure 2).

Interestingly, brine and clay-biosurfactant experiments have different carbon and hydrogen isotopic trends than those shown by the pure water experiments. Sulfate brines prepared under mildly suboxic conditions showed carbon isotopic fractionations of up to 3‰. Additionally, rhamnolipids-nontronite experiments show a ~1‰ ^{13}C enrichment in hydrate-bound gases compared to free gas (Table1). Carbon isotopic fractionation seems to be controlled by both decreasing temperature (274 to 258K) and the presence of oxygen (in the case of sulfate brines), and by the catalytic effect of the biosurfactant-clay complex.; Conversely, carbon isotopic fractionation between gas phases decreases with increasing salinity (Table 1, Figure 3). This behavior seems to correlate with the salting-out effect of increasing salinity over dissolved gases in an aqueous system (i.e., gas solubility decreases with increasing salinity) [16].

Hydrogen isotopes display variable behavior, in terms of ^{2}H enrichment in hydrate-bound gases compared to free gas (Table 2, Figures 4 and 5). Again, the salting-out effect and the catalytic effect of the biosurfactant-clay complex seem to be exerting some isotopic control in the type of molecules trapped within the hydrate. Further experiments involving variations in biosurfactant-clay concentrations and salt mixtures are necessary if the use the stable isotopes of CH_4 as source signatures is to be reassured. Ongoing experiments are designed to test if the presence of clays in briny fluids exerts some effect on the isotopic fractionation between gas and hydrate-bound phases in H_2S hydrates.

4. References:

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