INFLUENCE OF SALTS AND CLAY MINERALS ON STABLE ISOTOPIC SIGNATURES OF METHANE AND HYDROGEN SULFIDE IN GAS HYDRATES. H. Carvajal-Ortiz[1] and L. M. Pratt[1], [1]Biogeochemical Laboratories, Department of Geological Sciences, Indiana University, 1001 E. 10th Street, Bloomington, IN 47405 (carvajah@umail.iu.edu; prattl@indiana.edu).

Introduction: Recent observations of the Martian atmosphere, using Earth-based telescopes, have detected persistent trace-level methane (CH_4) in the atmosphere as well as discrete plumes of CH_4 in the northern hemisphere, implying substantial subsurface fluxes of unknown origin [1]. Similarly, spectroscopic analyses have detected sulfur-bearing compounds, including hydrogen sulfide (H_2S) over the Jovian satellite Europa [2]. The inferred presence of CH_4 and H_2S in the crust of Mars and Europa is consistent with the presence of gas hydrates [2, 3, 4]. The stable isotopes of carbon, hydrogen, and sulfur in CH_4 and H_2S can be used as source-fingerprints of the gas molecules trapped in these types of hydrates [5, 6, 7, 8]. 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 [9, 10, 11, 12], conditions likely to be encountered in the shallow subsurface of Mars [10, 13] . Here we report pressure-vessel experiments that allow nucleation of gas hydrates containing CH_4 and H_2S from solutions of pure water and from brines with varying concentrations (14 mM to 2M) of NaCl, $MgSO_4$, and FeSO4. Also, gas hydrates are nucleated from solutions of pure water or brine mixed with 50 ppm smectite clays (nontronite and montmorillonite). Experimental results are assessed in terms of either re-enforcing or ruling out the use of stable isotopes from ices in planetary bodies as source fingerprints.

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 (V-SMOW), and Cañon Diablo Troilite for sulfur (CDT). Stable isotopes are reported using the following notation (carbon is used as an example):

$$\delta^{13}C = (^{13}R_{sample} / {}^{13}R_{standard} - 1)* 1000 \quad (1)$$

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:

$$^{13}\varepsilon_{A-B} = (^{13}\alpha_{A-B}-1)*10^3 \quad (2)$$

Where, $^{13}\alpha_{A-B} = {}^{13}R_A/^{13}R_B$.

Crystallization of gas hydrates. A titanium reactor from Parr Instruments© (reactor capacity= 450 mL) that can withstand a pressure regime of up to 6.8 Mpa is used for both CH_4 and H_2S hydrate experiments. 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 from both the gas and the hydrate phases is collected in 50 mL serum-type glass bottles, through gas bubbling in water. To prevent the release of gas from the hydrate phase during gas phase collection, the reactor is placed in a container filled with dry ice (173 K). 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): hydrogen sulfide is transported with nitrogen gas into glass traps filled with 0.1 N $AgNO_3$, reacting with hydrogen sulfide and precipitating 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 $\delta^{34}S$ analysis. Sulfur isotopes are analyzed in a Finnigan MAT 252 isotope ratio mass spectrometer.

Results: A series of hydrate nucleation experiments have been conducted with quantitative recovery of free-gas and hydrate-gas molecules of CH_4 and H_2S. Initially, we tried to replicate the results obtained by Hachikubo et al. [15], where significant hydrogen isotopic fractionation between gas and hydrate phases

was reported as a function of decreasing temperature (up to 8‰) 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 than the earlier report (Fig.1). In additionn, H_2S experiments show sulfur isotopic differences up to 3‰ between gas phases. Interestingly, CH_4 hydrates nucleated from different brine solutions (NaCl, $FeSO_4$, $MgSO_4$) show carbon isotopic fractionation from 0.37 to 2.69‰ between hydrate and gas phases at different nucleating temperatures (Fig. 2). In addition, hydrates nucleated from different brines, at the same temperature and salinity, display different fractionation patterns, with $FeSO_4$ showing the highest fractionation. (2.69‰). Hydrogen sulfide hydrates nucleated from both pure water and NaCl brine (3.5% at 267K) show sulfur isotopic fractionation as a function of decreasing temperature (a maximum of ~ 3‰ for pure water hydrates and 2.4‰ for the NaCl experiment).
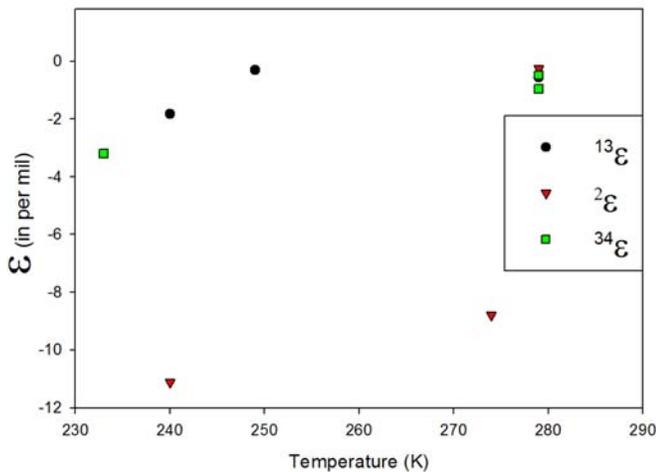

Figure 1. Here shown, carbon, hydrogen, and sulfur isotopic variations ($^{13}\varepsilon$, $^{2}\varepsilon$, and $^{34}\varepsilon$, respectively) between gas and hydrate phases of CH_4 and H_2S gas hydrate systems.Gas hydrates were nucleated from pure water solutions (no electrolytes added).

Discussion. Carbon and sulfur isotopic fractionation between gas and hydrate phases in methane hydrates nucleated from synthetic brines mimicking the oceanic average (i.e., 3.5%) are reported here for the first time. Carbon isotopic fractionation seems to be controlled by both decreasing temperature (274 to 240K) and increasing salinity (so far, 0 to 3.5%). If proven to be a trend (as it is being tested with ongo-

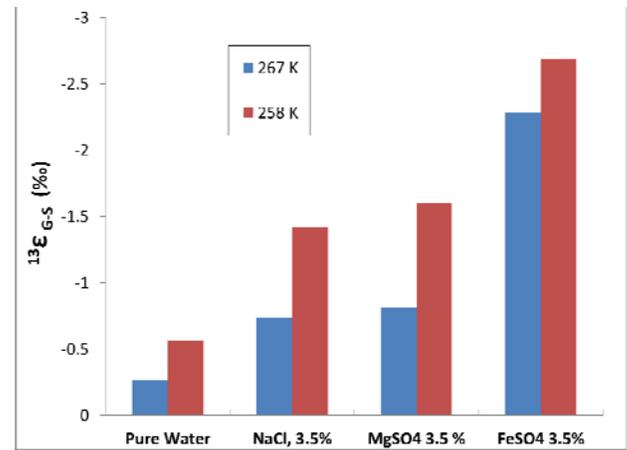*Figure 2. Carbon, isotopic variations between gas and hydrate phases ($^{13}\varepsilon_{G-S}$) of CH_4 hydrate systems nucleated from electrolyte solutions of sodium chloride, magnesium, and ferrous sulfate (NaCl, $MgSO_4$, and $FeSO_4$, respectively). Gas hydrates were nucleated at two differen temperatures and at average oceanic salinity (3.5%). Temperatures are shown in Kelvin.*

ing experiments), the isotopic behavior of hydrate systems developed from either the assumed Martian briny fluids present today, or formed in a salty ocean under the thick ice cap in Europa will be problematic, especially when trying to use the stable isotopes of CH_4 and H_2S to track their source. Ongoing experiments will test if the presence of clays in briny fluids exerts some influence on the isotopic fractionation between gas and hydrate phases.

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