

**THE COMPOSITION AND HABITABILITY OF ENCELADUS' OCEAN.** L. M. Fifer<sup>1</sup>, J. D. Toner<sup>1</sup> and D. C. Catling<sup>1</sup>, <sup>1</sup>Earth and Space Sciences / Astrobiology Program, University of Washington, Seattle, WA 98195 (lufifer@uw.edu)

**Introduction:** Plumes erupting at the surface of Enceladus propel samples of the moon's subsurface ocean into space, providing a window into the ocean's composition and habitability. Over the course of several flybys beginning in 2005, the Cassini spacecraft flew through the plumes and measured their composition with its Ion and Neutral Mass Spectrometer (INMS) and Cosmic Dust Analyzer (CDA). These measurements show that the plume is primarily composed of water vapor (H<sub>2</sub>O), with other gases such as hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>) also present [1,2]. The solid components of the plume consist of water-ice particles, with minor amounts of sodium salts and organics [3,4].

The composition of the plume measured by Cassini strongly suggests a subsurface ocean source for the plume. But do these measurements represent the bulk composition of the ocean? The answer lies in the processes that affect plume composition during eruption, fractionating the plume from its ocean source.

Here, we explore fractionation processes affecting plume gases through modeling and experimental measurements. We focus on condensation of water vapor and differential rates of gas exsolution. Our preliminary results indicate that the ocean is abundant in dissolved gases, and therefore has a high potential for habitability.

**The Importance of Plume Gases:** The concentrations of H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub> in Enceladus' ocean determine the pH, habitability and potential biological activity of the ocean, and present possible evidence for ocean-core hydrothermal interactions.

CO<sub>2</sub> affects the pH of the ocean because dissolved CO<sub>2</sub> reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Previous estimates of Enceladus' ocean pH have spanned a wide (~6-12) range due to differing methods of determining dissolved CO<sub>2</sub> concentrations. Marion et al. [5] found a pH of 5.7-6.8 by assuming that the ratio between H<sub>2</sub>O/CO<sub>2</sub> in the plume was equal to that in the ocean. Glein et al. [6] find a significantly more alkaline pH (10.8-13.5), by assuming that the H<sub>2</sub>O/CO<sub>2</sub> ratio was lower in the plume compared to its ocean source due to condensation of water vapor (discussed later in this abstract).

Dissolved NH<sub>3</sub> forms ammonium (NH<sub>4</sub><sup>+</sup>), which is a key ion in terrestrial metabolism and affects the types of salts expected in the ocean. The distribution between NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> in the ocean depends on the ocean pH and therefore on CO<sub>2</sub> concentration. This is because the reaction governing the partitioning of these two species

is pH-dependent (NH<sub>3</sub> + H<sup>+</sup> ↔ NH<sub>4</sub><sup>+</sup>). High H<sup>+</sup> concentrations (low pH) would drive the reaction to the right.

H<sub>2</sub> and CH<sub>4</sub> both imply the presence of hydrothermal activity at the boundary between Enceladus' ocean and the rocky, porous core, with their concentrations depending on the amount of activity [2]. Taken together, the presence of H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> suggest a possible biological origin to the CH<sub>4</sub> found in the plume, because hydrogenotrophic methanogens consume H<sub>2</sub> and CO<sub>2</sub> to produce CH<sub>4</sub>. Waite et al. [2] have shown that higher concentrations of H<sub>2</sub> and CO<sub>2</sub> (and associated lower pH) produce more favorable conditions for methanogenic life in Enceladus' ocean, due to a greater availability of free energy associated with the H<sub>2</sub>-CO<sub>2</sub> redox couple.

The gas composition of the plume implies the presence of all of the above species in the ocean as well, but does not tell the full story of their oceanic concentrations. Fractionation processes that occur during eruption must be accounted for in order to trace back ocean concentrations from plume concentrations.

**Condensation of Water Vapor:** To derive the concentrations of dissolved trace gases in the ocean from plume measurements, we must first account for the condensation of water vapor during eruption. As the plume travels upwards through the icy fissure, it encounters a drop in temperature [6]. The temperature at the ocean surface (where the ocean is in contact with the walls of the fissure) will be maintained at its freezing point, ~273 K for a dilute saline solution. The temperature at the plume outlet is much colder, estimated to be 200 ± 20 K from infrared observations of the tiger-stripe fissures [7]. Because of this drastic temperature difference, water vapor in the plume will condense out of the gas phase, primarily onto the walls of the fissure [6]. Water vapor has a higher freezing point than the other gas species, so trace gases will not undergo significant losses due to condensation - water vapor is the only plume gas affected. Water vapor loss due to condensation therefore enhances the concentrations of trace gases in the plume.

The total vapor loss can be constrained in two ways: assuming rapid equilibration between the plume vapor and the icy walls of the fissure [6], or considering a dynamically condensing gas phase with theoretically-derived condensation rates [8]. We adopt the equilibrium model of condensation, developed by Glein et al. [6], wherein the vapor loss may be calculated from a difference between the saturation vapor pressure above liquid at the ocean temperature (~273 K) and the saturation vapor pressure above ice at the outlet temperature (200 ±

20 K). The temperature dependence of saturation vapor pressures are well-constrained across these temperature ranges [9]. The assumption of condensation to the point of equilibrium provides a helpful lower limit to trace gas concentrations in the ocean: if the plume water vapor does not fully equilibrate, then less condensation occurs, so the ocean gas concentrations are closer to what is measured in the plume (i.e. higher).

**Gas Exsolution:** The second process fractionating trace gas concentrations between the ocean and the erupted plume is gas exsolution at the ocean surface. Nakajima and Ingersoll [8] propose a mechanism for plume eruption driven by low pressures throughout the icy fissure, including just above the surface of the ocean. Low pressure above the ocean would cause rapid evaporation and possibly boiling, providing a continuous flux of water to the plume. Low pressures above the ocean will similarly drive the exsolution of dissolved gases. However, the rates of evaporation and exsolution between gases measured in the plume spans a wide range, most notably between water and the trace gases, but among the trace gases as well.  $\text{NH}_3$  exsolves at a rate five orders of magnitude faster than the other trace gases, while  $\text{H}_2\text{O}$  evaporates several orders of magnitude faster than even  $\text{NH}_3$ . Because concentrations in the plume are proportional to their rate of input, rapidly exsolving species are overrepresented in the plume. Derivations of ocean gas concentrations that ignore this would severely underestimate the concentrations of slowly exsolving gases, and trace gases in general.

To determine rates of exsolution for different gas species, we use a thin-film model of mass-transfer. This model assumes a stagnant (non-convecting) thin film at the phase boundary (in this case, at the ocean surface). Rates of mass-transfer across this film are determined by rates of diffusion of gases through water, and solubilities of gases in water [10]. Determining the actual concentrations of gases in the ocean requires an estimate for the pressure difference between the low-pressure gas phase above the ocean and the partial pressure in the ocean itself. We use the pressure difference of water determined by Nakajima and Ingersoll [8] that reproduces observed mass eruption rates, and assume that rates of exsolution across all gases are proportional to their concentrations in the plume (after correcting for condensation).

**Gas Exsolution Experiments:** To confirm the validity of the exsolution rates predicted in our thin-film model, we have investigated the exsolution rates for  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  dissolved in water at temperatures relevant to the surface of Enceladus' ocean (~273 K).

To measure exsolution rates, we use the following experimental procedure, with a single trace gas species in each trial. The trace gas is introduced into a reaction

Source	pH Range	Composition
Zolotov 2007 [11]	10.9	$\text{NaCl}/\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
Postberg et al. 2009 [3]	8.5 – 9.0	$\text{NaCl}/\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
Hsu et al. 2015 [12]	8.5 – 10.5	N/A
Waite et al. 2017 [2]	9 – 11*	20x less $\text{H}_2$ and $\text{CH}_4$
Marion et al. 2012 [5]	5.7 – 6.8	$\text{CO}_2$ , $\text{CH}_4$ gas hydrates
Glein et al. 2015 [6]	10.8 – 13.5	$<10^{-6}$ bar gas pressures
This Study	8.3 – 10	Gas-rich, ~mbars-bars $\text{NaCl}/\text{NaHCO}_3$ or $(\text{NH}_4)\text{HCO}_3$

**Table 1:** Review of ocean pH, salt and gas compositions as determined in various studies. Waite et al. estimated pH from a rough average of the previous studies.

vessel that contains water, and is allowed to dissolve until equilibrium. A pressure transducer measures the pressure in the headspace, and the reading at equilibrium tells us how much gas is dissolved in the solution. By briefly pulling a vacuum on the system, gas in the headspace is removed, driving exsolution. By monitoring the increasing pressure in the vessel, we can determine the rate at which the trace gas exsolves. Because of the rapidity with which water evaporates, measurement of water's evaporation rate is not possible with the pressure transducer, and is instead performed using a cold trap to condense and freeze water vapor. The condensed water is later thawed and weighed to determine the total mass of water evaporated in a given time.

**Results/conclusions:** Preliminary modeling work, which accounts for both water vapor condensation and gas exsolution, predicts high concentrations of dissolved gases in Enceladus' ocean, and a corresponding pH of ~8.3-10. This pH, which is slightly more acidic than some recent estimates (see Table 1), implies high concentrations of ammonium, likely in the form of ammonium-bicarbonate salts ( $(\text{NH}_4)\text{HCO}_3$ ). High concentrations of gases like  $\text{H}_2$  and  $\text{CO}_2$  further imply a greater potential for life in the ocean, due to increased availability of reactants for methanogenesis, but their abundance could be a sign of other limited nutrients.

**References:** [1] Waite, J. H. et al. (2009). *Nature*, 460, 487–490. [2] Waite, J. H. et al. (2017). *Science*, 356, 155–159. [3] Postberg, F. et al. (2009). *Nature*, 459, 1098–1101. [4] Postberg, F. et al. (2018). *Nature*, 558, 564–568. [5] Marion, G. M. et al. (2012). *Icarus*, 220, 932–946. [6] Glein, C. R. et al. (2015). *Geochim. Cosmochim. Acta*, 162, 202–219. [7] Goguen, J. D. et al. (2013). *Icarus*, 226, 1128–1137. [8] Nakajima, M., & Ingersoll, A. P. (2016). *Icarus*, 272, 309–318. [9] Murphy, D. M., & Koop, T. (2005). *Q. J. R. Meteorol. Soc.*, 131, 1539–1565. [10] Cussler, E. L. (2009). Cambridge U. Press. [11] Zolotov, M. Y. (2007). *Geophys. Res. Lett.*, 34, 1–5. [12] Hsu, H. W. et al. (2015). *Nature*, 519, 207–210.