

GAS LOSS FROM ENCELADUS' OCEAN DUE TO LONG-TERM PLUME ERUPTION. L. M. Fifer^{1*}, J. D. Toner¹, D. C. Catling¹, ¹Earth and Space Sciences, University of Washington, Seattle, WA 98195 (*lufifer@uw.edu).

Introduction: Enceladus erupts ice and gas from its subsurface ocean via plumes originating from fissures at the south pole [1]. The Cassini mission flew through these plumes and measured the composition of gases and solids [e.g., 2, 3]. The gas phase is primarily composed of water vapor, followed by carbon dioxide (CO₂), methane (CH₄), hydrogen (H₂) and ammonia (NH₃) [3].

Gases in the Plume and Ocean: Our knowledge of the plume composition is vital to understanding the ocean chemistry, ongoing chemical or biological processes in the ocean, and Enceladus' origin. While fractionation processes cause significant differences between the abundances in the plume versus the ocean [4-6], modeling studies and analyses of the plume suggest that the ocean is generally rich in volatiles, possibly inherited from comet-like building blocks [3, 7]. CO₂ could be primordial as in comets [7, 8], and its concentration in the ocean is critical to finding the pH [4-6] and free energy for methanogenic life [9, 10]. CH₄ in the ocean could also be primordial [7], produced by abiotic hydrothermal processes [9], or biology [8]. H₂ is likely produced via serpentinization reactions [9], and would be vital to hydrogenotrophic methanogens [9, 10]. Oceanic NH₃ is most likely primordial in origin, being a relatively abundant constituent in cometary ices [7], and the bulk of total ammonia may be in the form of NH₄⁺ if the pH is <-10 [6].

An Evolving Ocean: Plume measurements and modeling studies indicate the *modern* ocean composition, but Enceladus' composition today may be different from the original composition it acquired during formation. Understanding the evolution of volatile abundances is crucial to the interpretation of potentially biogenic gases like CH₄. For example, a modeling study by Affholder et al. 2021 [8] showed that CH₄ is more easily explained by biological fluxes than abiotic hydrothermal processes, with the caveat that CH₄ could also be primordial. However, this model assumed that Enceladus' ocean composition is in a steady state, and therefore that all loss of methane via the plumes is balanced by input fluxes (from biology or hydrothermal processes). The possibility that Enceladus is continuously losing primordial volatiles *without* replenishment has yet to be explored in the literature, motivating our current work. It is also worth noting that, while Enceladus has similar D/H ratios and high volatile abundances to comets [9], Enceladus seems to have lower concentrations of CO₂ and CH₄ than expected for

a comet-like composition [7]. Even the recent high estimates for Enceladus' oceanic CH₄ concentrations appear to be much (>2 orders of magnitude) lower than cometary abundances [6]. This begs the question – where did the methane go?

Here, we explore the potential evolution of Enceladus' volatile content, with a focus on the role of plume eruption in removing gases from the ocean. We also consider the effects of preferential removal of light isotopes (e.g., greater loss of H than D in water vapor) on the long-term evolution of isotopic abundances.

Methods: Beginning with modern estimates for ocean concentrations, we extrapolate current levels of plume activity backwards in time, “reversing” the process of volatile loss via eruption to recover possible past ocean compositions. We use total water vapor eruption rates of ~200-300 kg/s based on visual observations of the plume [11] and scale the eruption rates of non-water gases according to their relative ratios in the plume [9]. While the exact mechanism(s) driving gas exsolution from Enceladus' ocean are uncertain [6, 7], the exsolution rate of a given gas should be linearly proportional to its concentration in the ocean. Thus, a higher concentration in the past would mean a proportionately higher exsolution rate.

At each timestep, we also consider aqueous speciation in the ocean, including both carbonate species (CO₂ ↔ HCO₃⁻ ↔ CO₃²⁻) and ammoniacal species (NH₃ ↔ NH₄⁺). We assume that oceanic CO₂ is buffered by interactions with the rocky core, so that the present-day dissolved CO₂ is unchanged over time, but HCO₃⁻ and CO₃²⁻ are allowed to fluctuate. As we run Enceladus' eruption in reverse, adding into the ocean any gases that were lost, aqueous species that exceed solubility limits (based on minerals or clathrates) are capped, and additional gas beyond that point is funneled into these alternative phases.

To determine the relationship between the plume D/H and the ocean D/H, and how the ocean D/H changes over time, we consider isotopic fractionation of water vapor during evaporation from the ocean surface, and condensation onto the fissure ice walls. During evaporation, the gas phase should be enriched in the light (H) isotope, as the heavy (D) isotope is left behind in the ocean. Later, as some water vapor condenses onto the fissure walls due to decreasing temperatures towards the surface, the heavy (D) isotope will tend to condense preferentially, with the light (H) isotope remaining in the gas phase. Because of the rapid equilibration of

water vapor with the icy fissure walls [4], we use an equilibrium constant [12] to relate the D/H of plume water vapor to the D/H in the ice shell and assume that the D/H of the ice shell is equal to that in the ocean.

While the persistence of Enceladus' plume activity is unconstrained, geomorphological evidence exists for older tiger stripe fissures at different orientations to the present-day fissures [13] (which could suggest plume activity even before the current fissures existed), and we are interested in the *most* that plume eruption could have altered the ocean composition. Thus, we run our model for long (100 Myr–4.5 Gyr) timescales, allowing for the possibility that Enceladus is as old as the solar system, or much younger [14].

Results: We find that for CH₄, running plume eruption in reverse can recover cometary abundances on timescales between 0.1–100 Myr (Fig. 1). Longer eruption timescales (at least ~1.5 Gyr) are necessary to recover cometary abundances of total ammonia (NH₃ + NH₄⁺). The relatively slower loss of ammoniacal species is due to its speciation (NH₃ ↔ NH₄⁺, for which CH₄ lacks an equivalent). Running in reverse, as NH₃ is added back into the ocean, some is distributed to NH₄⁺, which does not directly affect the eruption rate of NH₃. By contrast, as lost CH₄ is added back into the ocean, there is no opportunity for speciation, so CH₄ and its eruption rate must increase exponentially backwards in time. This exponential increase for CH₄ continues until a solubility limit based on clathrate formation is reached, at which point the exsolution rate becomes constant.

In the case of CO₂ and associated carbonate species, we find that eruption alone fails to recover cometary abundances, even over solar system timescales. The much slower loss rate for CO₂ compared to CH₄ or NH₃ is due to our prescribing a constant oceanic concentration of CO₂; because dissolved CO₂ is fixed at modern levels, so too is its exsolution rate, with no opportunity for the increased exsolution rates that the other species gain in the past. The failure to recover cometary abundances for CO₂ could indicate that our assumption of a buffered CO₂ concentration is oversimplified, and/or that a significant portion of Enceladus' starting CO₂ content has been sequestered in carbonate minerals in the rocky core [5].

We find that Enceladus' bulk D/H may have become isotopically heavier over time because of the preferential loss of light isotopes. However, even over the age of the solar system, the bulk D/H that we find for Enceladus remains within cometary ranges of D/H.

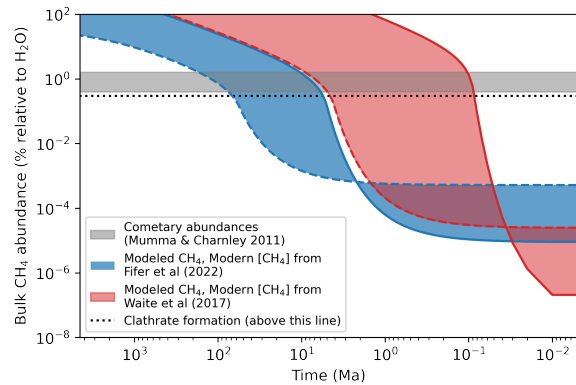


Figure 1: Modeling results for bulk CH₄ that start from modern estimates for oceanic CH₄, and integrate present plume eruption rates over long timescales. Model time runs from right to left.

Conclusions: Our finding that CH₄ is the most readily lost of the volatiles considered (CH₄, CO₂, NH₃) is consistent with it having the largest gap between estimated modern abundances and an expected starting cometary abundance. Generally, a steady state does not appear to be a requirement for Enceladus' gases, but the specific timescales of eruption required to reconcile starting cometary abundances and present abundances are inconsistent between the three species. A possible solution to this discrepancy could be partial conversion of CO₂ into CH₄ (either through biotic or abiotic means). This reaction would both allow oceanic CO₂ to be lost faster, and allow oceanic CH₄ to persist longer. Thus, our preliminary results may indicate that CH₄ is not purely primordial, and therefore some input of biological or hydrothermally generated CH₄ is needed to compensate for loss via the plumes.

Acknowledgments: Supported by NASA Habitable Worlds Grant #80NSSC19K0311 and NASA FINESST Grant #80NSSC21K194.

References: [1] Porco, C. C. et al. (2006) *Science*, 311, 1393–1401. [2] Postberg, F. et al. (2009). *Nature*, 459, 1098–1101. [3] Waite, J. H. et al. (2009). *Nature*, 460, 487–490. [4] Glein, C. R. et al. (2015). *Geochim. Cosmochim. Acta*, 162, 202–219. [5] Glein, C. R. and Waite, J. H. (2020). *GRL*, 47, 1689–1699. [6] Fifer, L. M. et al. (2022). *PSJ*, 3, 191. [7] McKinnon, W. B. et al. (2018). *Enceladus and the Icy Moons of Saturn*, 17–38. [8] Affholder, A. et al. (2021). *Nature Astro.*, 5, 805–814. [9] Waite, J. H. et al. (2017). *Science*, 356, 155–159. [10] Higgins, P. M. et al. (2021). *JGR: Planets*, 126, 11. [11] Hansen, C. J. et al. (2020). *Icarus*, 344, 113461. [12] Lamb, K. D. et al. (2017). *PNAS*, 114, 5612–5617. [13] Patterson, G. M. et al. (2018) *Enceladus and the Icy Moons of Saturn*, 95–125 [14] Cable, M. L. et al. (2021). *PSJ*, 2, 132.