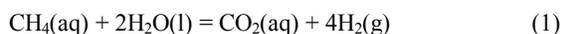


**HYDROTHERMAL GEOCHEMISTRY AS THE SOURCE OF PLUME GASES ON ENCELADUS: A THERMODYNAMIC EVALUATION.** C. R. Glein<sup>1</sup>, M. Yu. Zolotov<sup>1</sup>, and E. L. Shock<sup>1,2</sup>. <sup>1</sup>School of Earth and Space Exploration, <sup>2</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287. E-mails: cglein@asu.edu, zolotov@asu.edu, eshock@asu.edu.

**Introduction:** The *Cassini* spacecraft detected a gas plume emanating from Saturn's icy satellite Enceladus [1-3]. Its composition (91% H<sub>2</sub>O, 3.2% CO<sub>2</sub>, 4% N<sub>2</sub>, and 1.6% CH<sub>4</sub>) was inferred based on measurements by the Ion and Neutral Mass Spectrometer [2]. Jets from warm (110-160 K) fissures ("sulci") supply the plume [3], and boiling water in a subsurface reservoir may power the jets [1]. Liquid water is possible because radiogenic and tidal heating might be sufficient to prevent freezing [4]. Terrains near sulci are composed of water and CO<sub>2</sub> ices mixed with light organic compounds [5]. Here, we consider aqueous geochemistry in an attempt to interpret the plume's composition.

**Conceptual model:** Enceladus accreted from ices and rocky materials. After differentiation [6], Enceladus began cooling as it radiated heat to space. Presumably, a water ocean was present above a silicate core, and hydrothermal systems developed at the water-rock interface due to high temperatures generated by short-lived radionuclides [7,8]. Reactions between iron-bearing minerals and water governed redox conditions by controlling the fugacity of hydrogen ( $f_{H_2}$ ), influencing abundances of oxidized and reduced species. High-temperature reactions favored oxidation, while low gravity allowed H<sub>2</sub> escape [9], irreversibly oxidizing rocks in hydrothermal environments. It seems likely that Saturn's moons acquired carbon and possibly nitrogen from organic compounds [10,11], thus hydrothermal systems were sites where carbonaceous matter was broken down [12]. Outside hydrothermal systems, cold oceanic water mixed with hot fluids, quenching redox reactions. The plume's composition could represent ocean chemistry, which may reflect hydrothermal geochemistry. That is, subsurface waters may be envisioned as quenched hydrothermal fluids from the past.

**Thermodynamic model:** We constrained the oxidation state inside Enceladus by performing equilibrium calculations using the SUPCRT92 code [13]. Temperature-redox conditions that match the plume's CO<sub>2</sub>/CH<sub>4</sub> ratio were evaluated for environments near the water-rock boundary (P = 100 bar). Equations for CH<sub>4</sub>-CO<sub>2</sub> equilibrium are:



$$K_I = (a_{CO_2}/a_{CH_4})f_{H_2}^4 \quad (2)$$

where  $K_I$  is the equilibrium constant for Rxn. 1 and  $a$  stands for activity in aqueous solution.

We assumed that mineral assemblages set  $f_{H_2}$ , which occurs in terrestrial hydrothermal systems. For example, fayalite-magnetite-quartz (FMQ) and pyrrhotite-pyrite-magnetite (PPM) assemblages describe redox conditions in

seawater-basalt systems on Earth [14]. Hematite-magnetite (HM) and wüstite-magnetite (WM) assemblages were also considered because they represent oxidized and reduced (within reason) endmembers, respectively. For each mineral assemblage, equilibrium constants for a reaction involving H<sub>2</sub>O and H<sub>2</sub> were calculated and used to derive  $f_{H_2}$  values, which were substituted into Eqn. 2 to determine whether the assemblage could produce CO<sub>2</sub>/CH<sub>4</sub> ratios consistent with observations.

In addition, we simulated chemical reactions in putative hydrothermal systems on early Enceladus. Note that similar work has been done for Triton [15]. An equilibrium model for hydrothermal geochemistry was developed, which applies for temperatures above ~300°C because CH<sub>4</sub> and NH<sub>3</sub> do not rapidly equilibrate with CO<sub>2</sub> and N<sub>2</sub> below ~300°C [16]. We emphasize that 300°C is not a strict limit; equilibrium predictions for temperatures somewhat below ~300°C might be reasonable, especially if geologic timescales are involved. We assumed that ~300°C was an upper limit because sub-critical pressures (<220 bar) near the water-rock boundary prohibited supercritical water.

We used the GEOCHEQ code [17] to compute aqueous speciation in the C-N-O-H system. Thermodynamic parameters for a handful of inorganic (7) and organic species (40) were taken from the SUPCRT92 database [13]. Based on separate results, we assumed that PPM buffered redox conditions (i.e., fixed  $f_{H_2}$ ). The bulk chemistry of the aqueous phase was represented by protosolar material [18]. One percent carbon and nitrogen in protosolar material was allowed to equilibrate with the aqueous solution because only a small fraction of organic matter probably equilibrated with hydrothermal fluids. Presumably, some organic compounds were present in cool environments and/or mixed with silicate minerals in the core. Other organics might have reacted with water but did not reach equilibrium.

**Results and discussion:** Equilibrium calculations show that PPM and HM assemblages can reproduce the plume's CO<sub>2</sub>/CH<sub>4</sub> ratio (Fig. 1). However, HM is unrealistic because CO<sub>2</sub> and CH<sub>4</sub> do not equilibrate at low temperatures. HM strongly favors CO<sub>2</sub> at temperatures that permit equilibrium. WM and FMQ produce too much CH<sub>4</sub> because they yield  $f_{H_2}$  that corresponds to  $a_{CO_2}/a_{CH_4} < 2$ . FMQ could satisfy observations if temperatures higher than ~300°C were reached, which is unlikely because pressures near the water-rock interface were relatively low. PPM is favored because (1) it agrees with observations at high temperatures; (2) it buffers  $f_{H_2}$  in submarine hydrothermal systems on Earth (i.e., it occurs naturally); and (3) its existence could explain why no sulfur-bearing species were detected in the plume.

Any geochemical model must account for the following observations:  $\text{CO}_2/\text{CH}_4 > 2$ ;  $\text{N}_2/\text{CH}_4 \approx 2.5$ ;  $\text{NH}_3/\text{CH}_4 < 0.3$ ; and organic compounds associated with sulci [2,5]. The plume's  $\text{CO}_2/\text{CH}_4$  ratio most likely represents a lower limit because less  $\text{CO}_2$  than  $\text{CH}_4$  probably went into the gas phase owing to its greater solubility in liquid water, and some  $\text{CO}_2$  probably condensed onto water ice grains as gases rose through subterranean cracks and expanded into a vacuum. The most revealing datum is probably the plume's  $\text{N}_2/\text{CH}_4$  ratio because it most likely reflects the plume's source given that  $\text{N}_2$  and  $\text{CH}_4$  have similar solubilities and volatilities.

Speciation modeling shows that PPM-buffered hydrothermal fluids near  $300^\circ\text{C}$  can produce  $\text{N}_2/\text{CH}_4$  ratios consistent with observations (Fig. 2). At these conditions, our model yields high  $\text{CO}_2/\text{CH}_4$  ratios ( $\sim 15$ ) and low  $\text{NH}_3/\text{CH}_4$  ratios ( $\sim 0.25$ ), which agree with inferred constraints. The  $\text{NH}_3/\text{CH}_4$  ratio is important because it allows others to test our model. Efforts should be made to detect trace quantities of  $\text{NH}_3$  in a plume during the next *Cassini* flyby. In addition, *Cassini* may uncover isotope fractionations that reflect isotopic equilibrium near  $300^\circ\text{C}$ . Our results suggest that  $\delta(\text{CO}_2) - \delta(\text{CH}_4) \approx 25\text{‰}$  might be measured in a plume.

Equilibrium does not favor abundant organic compounds (Fig. 2), thus irreversible reactions must have been responsible for the production of organic compounds on Enceladus. We suspect that hydrothermal fluids partially broke down accreted organics, producing largely unreactive species that did not equilibrate with  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{NH}_3$ . Indeed, experiments demonstrate that, under hydrothermal conditions, chondritic carbonaceous matter decomposes into benzene derivatives [19], which do not equilibrate with  $\text{CO}_2$  and  $\text{CH}_4$  because of kinetic barriers [20]. We suggest that comparable geochemical processes took place on Enceladus. That is, primordial polyaromatic compounds might have been pyrolyzed in hydrothermal systems, then geysers could have carried residual monoaromatic compounds to sulci, where ultraviolet photolysis and ion bombardment might have produced species that did not derive from aqueous solution, such as acetylene [2,21]. This mechanism can explain why organics correlate with sulci.

**Conclusions:** Thermodynamic modeling indicates that hydrothermal systems that existed at temperatures close to  $300^\circ\text{C}$  and oxidation states corresponding to PPM redox buffering could have produced fluids with compositions that are consistent with the plume's chemistry. Inferred redox conditions imply that significant oxidation of primary minerals occurred, which may have been driven by  $\text{H}_2$  escape.

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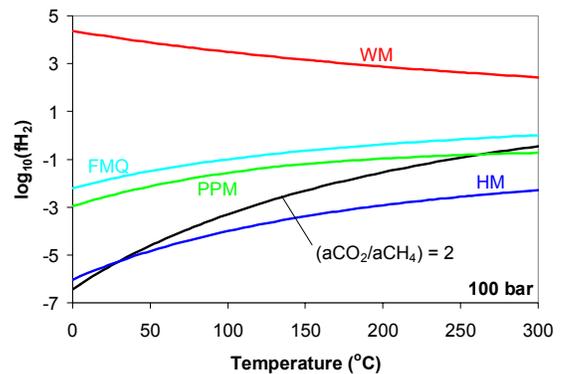


Fig. 1. Redox conditions near the water-rock boundary for different mineral redox buffers. The black line denotes activities of  $\text{CO}_2$  and  $\text{CH}_4$  that match the plume's composition. Temperatures where it crosses buffer curves correspond to equilibrium between  $\text{CO}_2$ ,  $\text{CH}_4$ , and buffers. WM: wüstite-magnetite; FMQ: fayalite-magnetite-quartz; PPM: pyrrhotite-pyrite-magnetite; HM: hematite-magnetite.

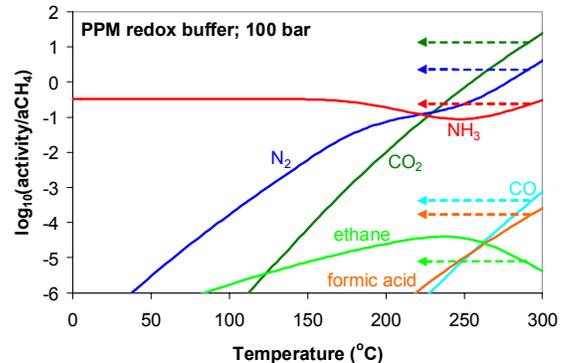


Fig. 2. C-N-O-H speciation in hydrothermal fluids. Solid curves and dashed lines signify equilibrium and quenched activities, respectively. Note that activities are relative to  $\text{CH}_4$ .