HOW MUCH HYDROTHERMAL HYDROGEN MIGHT WE FIND IN ENCELADUS' PLUME?

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Introduction: Geochemical [1,2] and geophysical [3,4] data obtained by the Cassini spacecraft strongly suggest the existence of a liquid water ocean [5] in contact with a rocky core on Saturn's satellite Enceladus. This leads to the possibility of hydrothermal activity that could support life [6]. Indeed, it has been proposed that there are hydrothermal vents inside Enceladus to explain the formation of silica nanoparticles that are derived from Enceladus [2]. It has also been suggested that Enceladus has an alkaline ocean as a result of serpentinization reactions between water and rocks [7]. If there are serpentinizing hydrothermal systems on Enceladus that are currently active, then we should search for other clues in the plume to confirm their existence. In this respect, a smoking gun may be molecular hydrogen (H_2), which is abundant in hydrothermal systems on Earth (in particular Lost City) that may be analogous to those on Enceladus [8].

During previous Cassini flybys of Enceladus, the Ion and Neutral Mass Spectrometer (INMS) detected counts at mass channel 2 in closed source neutral mode that are attributed to H_2 [9]. The signal was enhanced at faster flyby velocities as a result of impact-induced chemistry in the antechamber of the instrument [10], but up to ~15% H_2 was still detected consistently during the slowest flybys [9]. At present, it is unclear if this H_2 is native to the plume or an artifact of high-speed sampling of the H_2O-rich plume [11]. In an attempt to resolve this question, a search for H_2 was performed using the open source neutral beam mode of INMS during the E21 flyby, for which the data are being analyzed [12]. To assist in the interpretation, we have made three theoretical estimates of how much hydrothermal H_2 could be present for different geochemical/geophysical scenarios.

Estimate based on redox mass balance: We have constructed a mass balance model of serpentinization and H_2 production on Enceladus. In this model, H_2 production from H_2O is stoichiometrically coupled to the oxidation of iron, which may be the most abundant and strongest reductant in rocks on Enceladus (sulfide S and organic C are likely to be present, but may not be as important to H_2 production). The geochemical model quantifies phase transformations in the Mg-Si-Fe-S-O-H system. We estimate the abundance of iron by assuming a solar composition of rock-forming elements in the core [13], and scaling it to the internal structure model of [14]. We then calculate the amount of H_2 that can be produced, which depends on the evolution of the oxidation state ($Fe^0/Fe^{+2}/Fe^{+3}$) of the core. Here, we consider a two-stage scenario of redox evolution: (1) silicates are hydrated and metallic iron is oxidized to ferrous serpentine as a result of low-temperature water-rock interaction during differentiation; (2) a more prolonged period of hydrothermal oxidation follows that is driven by heating of the core and subseafloor fluid flow [15]. In the latter stage, which may be occurring today [2], H_2 generation is coupled to the transformation of ferrous serpentine to magnetite.

We find that the theoretical yield of H_2 is large. The geochemical mass balance indicates that ~10^{20} moles of H_2 can be produced during the differentiation stage. If this process were to occur over 100 Myr, then the mean production rate would be ~10^{12} mol/yr. This is large when compared to the present rate of H_2O emission in the plume (~3.5×10^{11} mol/yr; ref. 16). For the later stage of redox evolution, we find that up to ~5×10^{19} moles of H_2 can be produced, depending on the unknown extent of reaction progress (0-100%). The mean production rate over 4500 Myr could be as large as ~10^{10} mol/yr in the limit of reaching 100% progress today. This rate can be converted to an upper limit for hydrothermal H_2 in the plume of ~3%.

This is an upper limit for three reasons. First, it seems unlikely for stage two to just be finishing. Instead, it could have ended in the past [17], in which case there would be very little H_2 in the plume; or stage two may be only partially complete. Second, the H_2 production rate may not be constant but may decrease through time, as an oxidation front migrates downward into the core. Reactant rocks would be deeper and less accessible to ocean water at later times, so the average rate may be an overestimate for the present. Third, not all of the H_2 may be lost via the plume – there could be diffuse emissions. These effects are difficult to quantify, but provisionally we suggest that a possible range for hydrothermal H_2 in the plume may be ~0.1-1%.

Estimate based on hydrothermal energy balance: In addition to H_2 and other chemical species, hydrothermal fluids would deliver heat from the core to the ocean on Enceladus [15,18]. The heat flux provides a geophysical constraint on hydrothermal H_2 in the plume. The rate of delivery of H_2 can be expressed as

$$F_{H_2} = Q_{hyd}[H_2]/(C_w T_{hyd}),$$

where Q_{hyd} stands for the hydrothermal heat flux, $[H_2]$ the concentration of H_2 in the fluid, C_w the specific heat capacity of water, and T_{hyd} the hydrothermal system temperature in °C (for a 0°C ocean; ref. 7). The concentration of H_2 may be controlled by the oxidation of iron-bearing minerals [17], and here we assume ferrous serpentine-magnetite equilibrium in a hydrated core [3,14]. We calculate the H_2 delivery rate as a function of the thermal parameters, and convert it to a plume mixing ratio based on the H_2O emission rate of [16].

We can gain insight by examining relationships between F_{H2}-T_{hyd}-Q_{hyd}. Here, we consider temperatures of 50-300°C [2], and heat fluxes of 0.3 GW (radiogenic heating only), 1 GW (moderate tidal heating), and 10 GW (intense tidal heating) based on [19,20]. For the case of radiogenic Q_{hyd}, we compute small mixing ratios <0.1%, unless temperatures are high (>250°C). However, a plausible temperature for this case may be ~50°C, which would yield a mixing ratio of ~10^{-7} owing to the steep temperature dependence of the H_2 concentration in the hydrothermal fluid [17]. If there is more heating in the core, then higher flow rates can deliver more H_2 to the ocean and plume, although the temperature may still need to be relatively high. As an example, if we assume an H_2 mixing ratio of ~1%, then the model would imply a temperature of 200-300°C for 1-10 GW of heat transfer by hydrothermal circulation.

It is difficult to use this model to predict the H_2 content of the plume because we do not know how much of the observed heat emission [20] comes from tidal heating in the core. If this process is not significant [21], then hydrothermal fluids may not be hot and rich in H_2 according to our model of redox buffering. This does not mean that they could not provide some H_2 for possible life [6,7], but INMS would not detect low levels of hydrothermal H_2 in the plume. On the other hand, the inferred existence of hydrothermal silica suggests elevated temperatures [2], which opens up the possibility of unexplained tidal heating in the core [22] that could enhance both silica and H_2 production.

Estimate based on a hydrothermal H_2/CH_4 ratio: A simple geochemically based estimate of the H_2 mixing ratio in the plume can be made by scaling the CH_4 mixing ratio by the H_2/CH_4 molar ratio of the assumed hydrothermal source: $y_{H2} = (H_2/CH_4)_{hyd} \times y_{CH4}$. The mixing ratio of CH_4 is ~0.2% from the most recent analysis of the INMS data [9,12,23]. We do not know the H_2/CH_4 ratio in hydrothermal fluids on Enceladus, but we can guess and explore the potential implications. As a starting point, here we adopt a representative value from Lost City ($H_2/CH_4 \approx 10$; ref. 24) based on the proposal that this serpentinizing hydrothermal system may be the closest terrestrial analogue of the water-rock system on Enceladus [2,7,8]. This would lead to a predicted mixing ratio of hydrothermal H_2 of a few percent.

While this Lost City-like model can help to guide our expectations, there are several complicating factors that could invalidate its direct application to Enceladus. First, it assumes that the detected CH_4 came from a hydrothermal vent. However, the source of CH_4 in the plume is unknown [25], and indeed there could be multiple sources of CH_4 and their mixtures on a planetary scale. Alternative sources include primordial CH_4, CH_4 produced by thermal/impact-induced decomposition of organic material (inside Enceladus or INMS), biogenic CH_4, or hydrothermal CH_4 that was stored in a clathrate reservoir [23]. If these sources are significant, the estimate of hydrothermal H_2 in the plume would be lowered considerably.

Another complication would arise if the Enceladan hydrothermal fluid has a smaller H_2/CH_4 ratio than at Lost City. This could occur if there is enhanced CH_4 synthesis resulting from a more carbon-rich feedstock, longer residences times [17], and/or more abundant nickel catalysts [26]. The above arguments suggest that the simple estimate may be an upper limit, although it is not a strict limit because we can also envision cases that would lead to higher estimates of hydrothermal H_2 in the plume. This could occur if not all of the hydrothermal CH_4 goes into the plume because of clathrate formation [23], or if the hydrothermal fluid has a large H_2/CH_4 ratio because of kinetically inhibited CH_4 formation if temperatures are not sufficiently high.

From this analysis, a possible range for the mixing ratio of hydrothermal H_2 in the plume is 0-3%.

Concluding remarks: The theoretical considerations in this work may converge on a scenario of vigorous hydrothermal activity inside Enceladus that results in ~1% H_2 in its plume. This is being tested by the INMS team using the E21 data. A key test for a future mission will be to measure separately the D/H ratios in H_2 and H_2O, and to look for a deuterium depletion that would be characteristic of H_2 emanating from a subsurface ocean [24].

Acknowledgements: This work is supported by the Cassini project through NAS703001TONMO711123, and the INMS and IDS investigations.

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