The oxidation state of hydrothermal systems on early Enceladus

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Abstract

The discovery of CO2, CH4, and N2 in a plume at Enceladus provides useful clues about the chemistry and evolution of this moon of Saturn. Here, we use chemical equilibrium and kinetic calculations to estimate the oxidation state of hydrothermal systems on early Enceladus, with the assumption that the plume’s composition was inherited from early hydrothermal fluids. Chemical equilibrium calculations are performed using the CO2/CH4 ratio in the plume, and kinetic calculations are conducted using equations from fluid dynamics and chemical kinetics. Our results suggest that chemical equilibrium between CO2 and CH4 would have been reachable at temperatures above \( \sim 200 \) °C in hydrothermal systems. The oxidation state of the hydrothermal systems would have been close to the pyrrhotite–pyrite–magnetite (PPM) or fayalite–magnetite–quartz (FMQ) redox buffer (i.e., terrestrial-like) if the plume’s CO2 and CH4 equilibrated in hydrothermal systems long ago. As for minerals, we suggest that iron metal would have been oxidized to magnetite by the escape of H2 from the early satellite. Our calculations also indicate that, assuming CO2 and CH4 reached chemical equilibrium, magnetite would not have been oxidized to hematite in hydrothermal systems, perhaps due to insufficient H2 escape. It is shown that, if Enceladus accreted as much NH3 as comets contain, the presence of N2 and deficiency of NH3 in the plume can be understood in the context of chemical equilibrium in the C–N–O–H system. We conclude by proposing an evolutionary hypothesis in which the fairly oxidized nature of the plume can be explained by a brief episode of oxidation caused by short-lived radioactivity. These suggestions can be rigorously tested by acquiring gravity and isotopic data in the future.

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1. Introduction

Observations by the Cassini spacecraft on July 14, 2005 revealed that Saturn’s icy satellite Enceladus has a geologically active south polar region (Porco et al., 2006; Spencer et al., 2006). Cassini’s instruments also detected a plume emanating from the region (Hansen et al., 2006; Waite et al., 2006). The plume was chiefly composed of water vapor and other gases (mole fractions: 0.91 H2O, 0.04 N2, 0.032 CO2, 0.016 CH4; Waite et al., 2006; Matson et al., 2007). It came from linear depressions (Porco et al., 2006) that were warmer than surrounding terrains (Spencer et al., 2006). Vaporization of liquid water (Porco et al., 2006) or decomposition of clathrate hydrate (Kieffer et al., 2006) may have been responsible for the formation of the plume.

The minor plume gases may have originally formed inside Enceladus. Matson et al. (2007) proposed that chemical reactions produced the plume’s N2 at high temperatures (\( \sim 500–800 \) K). Presumably, Enceladus did not accrete N2 because the source of Titan’s atmospheric N2 was reduced N (NH3; Niemann et al., 2005), and Enceladus and Titan most likely accreted similar materials in Saturn’s accretion disk. Thus, N2 serves as evidence for thermal processes in the past. Because N2 is not primordial, it must have formed inside Enceladus, presumably from NH3 (Matson et al., 2007). A similar argument applies to CO2 because it would not have been a major species in the outer region of the solar nebula (the solar nebula is discussed because the dense subnebula concept is outdated; see Canup and Ward, 2002). Instead, CO and organic matter probably took up the carbon, as in comets (Bockelée-Morvan et al., 2004; Sandford et al., 2006). The carbon-bearing gases in the plume may have once been organic matter (Zolotov et al., 2005). Overall, cosmochemical considerations imply that high-temperature oxidation–reduction (redox) reactions made the minor plume gases somewhere inside Enceladus at some point in the past.

Thermal models of early Enceladus agree with inferences from the plume’s chemistry. Models that include short-lived radionuclides predict that temperatures up to \( \sim 1000 \) °C could have been reached in the moon’s interior during the first several million years after the satellite’s formation (Schubert et al., 2007; Castillo-Rogez...
et al., 2007). It is likely that Enceladus presently has a rocky core and a water ice-liquid shell because it is difficult to reconcile current geological activity with an undifferentiated interior (Schubert et al., 2007). The existence of a hot core beneath a cold ocean in the past implies that rocks may have been in contact with aqueous solutions in hydrothermal systems below the water–rock interface. Chemical reactions would have been unavoidable in these hot systems. Here, it is argued that the plume’s composition is a hydrothermal signature from the distant past. Chemical equilibrium and kinetic calculations are used to estimate the oxidation state of hydrothermal systems on early Enceladus, and explore its implications for the composition of the plume, and the plume’s connection to early chemical processes.

2. Methods

2.1. Thermodynamic formulation

Several chemical equilibria may have been reached in hydrothermal systems on early Enceladus. High temperatures in the core would have increased reaction rates, which could have allowed the elements to approach equilibrium states. For simplicity, we assume that chemical equilibrium characterized the composition of hydrothermal systems on early Enceladus, which often takes place in terrestrial hydrothermal systems owing to elevated temperatures and mineral catalysts (e.g., Gigenbach, 1989). Cassini observations are placed into an equilibrium framework by considering the plume’s CO2/CH4 ratio (=2), which is assumed to be a chemical fossil from the early evolution of Enceladus. We posit that the CO2/CH4 ratio in the plume is approximately the same as that in ancient hydrothermal fluids to do chemical equilibrium calculations. Imbedded in this assumption are the additional assumptions that CO2 and CH4 were sequestered into their current reservoir, then released from it with no substantial fractionation between them. We realize that it is difficult to evaluate the legitimacy of these statements given that the nature of the reservoir itself remains obscure (see Porco et al., 2006; Kieffer et al., 2006; Nimmo et al., 2007). Thus, we adopt the observed CO2/CH4 ratio at face value for practicality. For completeness, ratios displaced by two orders-of-magnitude from the nominal value are also considered.

The CO2/CH4 ratio can provide information about redox conditions because CO2 and CH4 contain oxidized and reduced carbon, respectively. We adopt the equilibrium model by writing equations that describe chemical equilibrium between CO2 and CH4 in a hydrothermal fluid

\[ \text{CH}_4(aq) + 2\text{H}_2\text{O}(l) = \text{CO}_2(aq) + 4\text{H}_2(g). \]  

(1)

where \( K_1 \) stands for the equilibrium constant for reaction (1), \( \alpha \) signifies activity in aqueous solution, \( f \) denotes fugacity, and \( X \) designates mole fraction in the plume. The approximation in Eq. (2) is made by assuming that the activity of \( \text{H}_2\text{O} \) in aqueous solution is unity, and the CO2/CH4 mole fraction ratio in the plume is equivalent to the CO2/CH4 activity (~concentration) ratio in early hydrothermal systems. The oxidation state that represents chemical equilibrium between CO2 and CH4 can be obtained by solving Eq. (2) for \( f_{\text{H}_2} \), which is a common redox variable.

We interpret the inferred oxidation state of hydrothermal systems on early Enceladus by comparing \( f_{\text{H}_2} \) values from Eq. (2) to those from mineral redox buffers (Table 1), which are convenient benchmarks for assessing redox conditions in geologic systems (see Frost, 1991). Equilibrium constants are calculated using the program SUPCRT92 (Johnson et al., 1992), along with parameters for the revised Helgeson–Kirkham–Flowers equation of state for aqueous species from Shock and Helgeson (1990) and Shock et al. (1989), and thermodynamic properties for water and minerals from Johnson and Norton (1991) and Helgeson et al. (1978), respectively. The calculations are carried out using a total pressure of 500 bar, which is the pressure at the center of a hydrated Enceladus (Barr and McKinnon, 2007). This value is used because water–rock reactions may have occurred throughout the core (Vance et al., 2007). Indeed, terrestrial hydrothermal circulation occurs down to at least the ~3 kbar level (e.g., Kelley et al., 2002). Pressure is a minor factor since the equilibrium constants are not sensitive to the modest changes in pressure expected inside Enceladus (e.g., at 250 °C, \( K_1 = 10^{-3.2} \) at 500 bar and \( K_1 = 10^{-3.4} \) at 100 bar).

2.2. Kinetic formulation

The validity of the use of the equilibrium model can be evaluated by estimating the temperatures where CO2 and CH4 could have reached chemical equilibrium in hydrothermal systems on early Enceladus. The rate of equilibration between CO2 and CH4 is notoriously slow in laboratory experiments (e.g., Seewald et al., 2006) and in hydrothermal systems on Earth (e.g., Shock, 1990). The use of the equilibrium model would be unwarranted if the rate of equilibration was too slow. Alternatively, the rate of equilibration would have been immaterial if the timescale of hydrothermal circulation was long enough. We thus estimate the temperatures where chemical equilibrium between CO2 and CH4 would have been feasible by performing kinetic calculations.

It is assumed that convective hydrothermal circulation was driven by buoyancy differences between cold oceanic water and hot hydrothermal fluids, and that flow resistance occurred mostly in the upwelling limb of convection cells. If these conditions were met, hydrothermal circulation can be described using the form of Darcy’s law given by Lowell and DuBose (2005)

\[ Q = \frac{\rho_w \alpha_w g k A (T - T_{ocean})}{\nu_w}, \]

(3)

where \( Q \) stands for the mass discharge of the flow, \( \rho_w \), \( \alpha_w \), and \( \nu_w \) signify the density, thermal expansion coefficient, and kine-
motic viscosity of water, respectively, \( g \) denotes the acceleration due to gravity, \( k \) designates the permeability of the substrate, \( A \) stands for the cross-sectional area of the flow, \( T \) signifies the temperature of hydrothermal fluid, and \( T_{\text{ocean}} \) denotes the temperature of oceanic water. Using the relationship \( u = \frac{Q}{(\rho_w A)} \), where \( u \) represents the speed of the flow, we can derive an expression for the transport time \( (\tau_{\text{tran}}) \), which is the amount of time it takes for a fluid parcel to sink from the water–rock interface to depth \( z \) then rise back up to the ocean floor:

\[
\tau_{\text{tran}} = \frac{2z}{u} = \frac{2z v_w}{\alpha_w g k (T - T_{\text{ocean}})}. \tag{4}
\]

Transport times for the single passage of parcels through hydrothermal systems (i.e., the single-pass model) are calculated using \( v_w \) and \( \alpha_w \) evaluated from the thermodynamic properties of water (Johnson and Norton, 1991), \( g = 0.25 \text{ m s}^{-2} \text{ m}^2 \) at the water-rock interface of a hydrated Enceladus, \( k = 10^{-12} \text{ m}^2 \) (Lowell and DuBose, 2005), \( T_{\text{ocean}} = 0^\circ\text{C} \), and by assuming a \( z \) and varying \( T \).

The chemical time constant \( (\tau_{\text{chem}}) \) for the reaction \( \text{CO}_2(\text{aq}) + 4\text{H}_2(\text{aq}) \rightarrow \text{CH}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \) in serpentinite-containing hydrothermal systems is estimated using the approximate so-called pseudo-first-order rate expression that was originally formulated by Giggenbach (1997)

\[
\frac{dm_{\text{CO}_2}}{dt} = -k' m_{\text{CO}_2}, \tag{5}
\]

where \( m \) stands for molality in aqueous solution (1 mol solute per kg H_2O), \( k' \) signifies the pseudo-first-order rate constant for the reaction, and \( t \) denotes time. The reduction of \( \text{CO}_2 \) rather than the oxidation of \( \text{CH}_4 \) is considered because the reduction of \( \text{CO}_2 \) is associated with lower temperatures, while the oxidation of \( \text{CH}_4 \) is associated with higher temperatures (e.g., at 500 bar, \( k_1 = 10^{-25.1} \) at 0°C and \( k_1 = 10^{2.2} \) at 500°C), and the attainment of chemical equilibrium is always more questionable at lower temperatures. Using data from laboratory experiments, Giggenbach (1997) estimated that \( \log_{10} k' (\text{year}^{-1}) = 6.53 - \frac{4440}{T(\circ\text{C}) + 273.15} \). The chemical time constant (also known as the lifetime) for the above reaction is defined as the amount of time an average molecule of \( \text{CO}_2 \) would survive until it is converted to \( \text{CH}_4 \), and is equal to \( 1/k' \).

2.3. Nitrogen speciation

We calculate the speciation of nitrogen in hydrothermal systems on early Enceladus by writing equations that can be used to find the chemical equilibrium between aqueous \( \text{N}_2 \) and \( \text{NH}_3 \)

\[
2\text{NH}_3(\text{aq}) = \text{N}_2(\text{aq}) + 3\text{H}_2(\text{g}). \tag{6}
\]

\[
K_6 = \frac{(\text{N}_2)(\text{NH}_3)^3}{(\text{N}_2)(\text{NH}_3)^2} \approx \frac{m_{\text{N}_2}(f_{\text{H}_2})^3}{m_{\text{NH}_3}(f_{\text{H}_2})^2}. \tag{7}
\]

\[
m_{\text{total}} = 2m_{\text{N}_2} + m_{\text{NH}_3}, \tag{8}
\]

where \( K_6 \) stands for the equilibrium constant for reaction (6). The approximation in Eq. (7) is made by assuming that the activity coefficients of \( \text{N}_2 \) and \( \text{NH}_3 \) in aqueous solution are unity. Reactions (1) and (6) are coupled by substituting \( f_{\text{H}_2} \) values from Eq. (2) into Eq. (7). We then derive the equilibrium concentrations and predominance fields of \( \text{N}_2 \) and \( \text{NH}_3 \) by solving Eqs. (7) and (8) subject to a specified total nitrogen concentration, which is needed because \( \text{N}_2 \) and \( \text{NH}_3 \) have different stoichiometric coefficients in reaction (6). Note that \( \text{NH}_3^+ \) is ignored here because the basic pH in ultramafic hydrothermal systems (e.g., Kelley et al., 2002) favors \( \text{NH}_3 \) instead.

The effect of temperature on the redox chemistry of carbon and nitrogen in hydrothermal systems on early Enceladus is illustrated using a suitable buffer (prototype system) to approximate redox behavior. The \( f_{\text{H}_2} \) values of the buffer are substituted into Eqs. (2) and (7) to calculate the proportions of \( \text{CO}_2, \text{CH}_4, \text{N}_2, \) and \( \text{NH}_3 \). In effect, reactions (1) and (6) are sent on a representative \( f_{\text{H}_2} - T \) trajectory. The buffer simply mimics the rock system; it may not actually exist.

3. Results and discussion

3.1. Oxidation state

Hydrogen fugacities \( (f_{\text{H}_2}) \) calculated with Eq. (2), which are consistent with the plume’s \( \text{CO}_2/\text{CH}_4 \) ratio, are shown in Fig. 1. Higher \( f_{\text{H}_2} \) values are necessary to satisfy the \( \text{CO}_2/\text{CH}_4 \) ratio in the plume at higher temperatures. The inferred \( f_{\text{H}_2} \) is generally between the MH and FMQ buffers (see Table 1), depending on the temperature. Inferred redox conditions become more reducing compared to the buffers as temperature increases. The inferred \( f_{\text{H}_2} \) is near MH at 0°C and close to FMQ at 500°C. The IM buffer is always too reduced, which is not surprising given that IM requires unphysical \( f_{\text{H}_2} \) values that are much greater than the total pressure. It can also be seen that, broadly speaking, the inferred oxidation state is not that sensitive to the \( \text{CO}_2/\text{CH}_4 \) ratio in the plume (Fig. 1), which suggests that general conclusions can be reached using the measured ratio. Of course, we should nevertheless approach the calculations with caution because it could be the case that the ratio in early hydrothermal systems was vastly different from the plume’s ratio. A many orders-of-magnitude difference is possible, and must be recognized as such given our ignorance, although such a situation would require an unexplored, strong fractionation mechanism. As stated before and reiterated here, our first-order analysis relies on the assumption that the plume’s chemistry reflects ancient hydrothermal chemistry within a few orders-of-magnitude.

According to the plume’s \( \text{CO}_2/\text{CH}_4 \) ratio, fluids and altered rocks on early Enceladus would have been far more oxidized than accreted materials, which most likely contained iron metal (e.g., Brearley and Jones, 1998). Because \( f_{\text{H}_2} \) in the hydrothermal systems would have been too low for iron metal to be thermodynamically stable, hydrothermal iron oxidation should have taken place.
It turns out that the approximate temperature limit for chemical equilibrium between CO₂ and CH₄ is model-dependent because the depth of circulation and number of passes are unknown. Fig. 2 shows that CO₂ and CH₄ could have equilibrated at lower temperatures in deeper flows. If single-pass fluid parcels reached a great depth (e.g., Vance et al., 2007), such as 100 km, chemical equilibrium between CO₂ and CH₄ may have been feasible at temperatures as low as ∼100–150 °C (Fig. 2). Likewise, it is reasonable to infer that CO₂ and CH₄ would have been able to equilibrate at lower temperatures if the entire ocean was hydrothermally processed many times since fluid parcels would have interacted with hot rocks for a longer net duration. Yet, we also suspect that an increased number of passes might have been incompatible with lower temperatures because longer transport times at lower temperatures (Fig. 2) would have slowed the hydrothermal processing of oceanic water. Such uncertainties concerning the physics of hydrothermal systems on early Enceladus make it wise to use the equilibrium model conservatively. Consequently, we set 200 °C (single-pass, terrestrial-like depth model) as the lower limit for the applicability of the model, although this value should be regarded as a soft limit owing to the approximate nature of the calculations (e.g., first-order kinetics, constant g, k, and T profiles).

Our interpretation of the redox evolution of Enceladus is that, for the most part, the satellite quickly (in terms of geologic time) stopped evolving, analogous to aqueously processed asteroids. Kinetic calculations indicate that the inferred fH₂ in Fig. 1 is unrealistic below ∼200 °C, which implies that the MH buffer is too oxidized, as the fH₂ values of MH above ∼200 °C are ∼1–2 orders-of-magnitude less than those required to reproduce the CO₂/CH₄ ratio in the plume (Fig. 1). Thus, we suggest that hematite did not form in hydrothermal systems on early Enceladus if CO₂ and CH₄ equilibrated in them with the assumptions invoked in this study at least reasonably satisfied. In our opinion, the values of fH₂ inferred from the plume’s CO₂/CH₄ ratio suggest that H₂ production and escape did not occur throughout the history of Enceladus because these processes would have caused intense oxidation (see Zolotov and Shock, 2003a), and presumably, the formation of hematite. If they had been active for a substantial period (as may have occurred on Europa; Zolotov and Shock, 2003b), one explanation for the inferred fH₂ may be transient heating. We argue that the extinction of short-lived radionuclides may have limited oxidation by restricting H₂ escape because a cooler core would not have been able to sustain appreciable H₂ production via water reduction reactions without sufficient thermal energy to enhance reactivity. In this scenario, the length of the redox evolution of Enceladus would have been relatively short, and may have thus been similar to that of aqueously processed asteroids (e.g., Krot et al., 2006).

To first-order, what can kinetic calculations tell us about the oxidation state of hydrothermal systems on early Enceladus? Fig. 1 shows that CO₂ and CH₄ could have reached chemical equilibrium in two kinetically accessible fH₂–T regimes: a PPM-like, moderate-temperature regime, and an FMQ-like, high-temperature regime. Note, if low temperatures (<200 °C) prevailed, we cannot say much about the oxidation state because the equilibrium model may not apply. Nevertheless, thermal models of early Enceladus appear to support the equilibrium model by showing that core temperatures above ∼200 °C could have been reached easily if Enceladus formed with sufficient quantities of short-lived radionuclides (i.e., early enough; Schubert et al., 2007; Castillo-Rogez et al., 2007). Thus, it seems conceivable that chemical equilibrium may have controlled reaction (1) in hydrothermal systems. If so, the oxidation state of hydrothermal systems on early Enceladus may have been similar to that of submarine hydrothermal systems on Earth. The oxidation state of hydrothermal systems at the seafloor is near PPM (Haymon and Kastner, 1981; Shock, 1990), while far below the seafloor, the oxidation state

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**Fig. 2.** Dynamic timescales in hydrothermal systems on early Enceladus. The thick curve denotes the chemical time constant (lifetime) for the reduction of CO₂ to CH₄ in the presence of the catalyst magnetite, a common mineral in serpentinite. The thin curves depict transport times for the single passage of fluid parcels through hydrothermal systems to different depths below the water–rock interface (ocean floor). In general, chemical equilibrium between CO₂ and CH₄ should be reachable at temperatures where the transport time is greater than the chemical time constant.

The reaction rate should have been fast; see Zolotov and Mironenko, 2007;

$$3\text{Fe}(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g).$$

(9)

If chemical and hydrostatic equilibrium were attained, the progress of reaction (9) would have been complete (i.e., iron metal would have been exhausted); otherwise, the inferred fH₂ would be substantially higher than what is deduced (Fig. 1). The escape of H₂ (Zolotov and Shock, 2003a) may have significantly hampered the progress of the reaction by shifting the reaction to the right. The plume’s CO₂/CH₄ ratio could be indirect evidence for considerable H₂ escape from an originally reduced body having a chondritic composition, which makes sense because relatively low total pressure would have allowed H₂ to more readily enter the gas phase, where it could then accumulate beneath Enceladus’ icy shell, seep through the shell, and finally escape into space. H₂ escape increases the CO₂/CH₄ ratio by decreasing fH₂ (see Eq. (2)). It is expected that an object that did not suffer much H₂ escape would be dominated by CH₄, like Titan. Reaction (9) appears to have been unavoidable wherever iron metal interacted with liquid water in a low-pressure environment during the early history of the Solar System, as evidenced by aqueously altered chondrites (e.g., Brearley and Jones, 1998; Krot et al., 1998), and as we suggest, Enceladus’ plume.

Further constraints on the oxidation state of hydrothermal systems on early Enceladus can be obtained from the results of kinetic calculations, which are shown in Fig. 2. In general, the relationship between the characteristic transport time and chemical time constant determines whether a reaction can reach chemical equilibrium. A rule of thumb that is often used for judging the likelihood of chemical equilibrium in dynamic systems is that equilibrium is instantaneous when the characteristic transport time is greater than the chemical time constant. We refer the interested reader to a recent review of aqueously altered chondrites (e.g., Krot et al., 2006).
cometary models of Shock and McKinnon (1993) and Owen et al. (2004). Comets are the best known analogues for hydrothermal systems. Recently, Zolotov (2007) has explored various geochemical consequences of this oxidation state.

3.2. Fate of nitrogen

The equilibrium concentrations and predominance fields of N₂ and NH₃ at redox conditions consistent with the plume’s CO₂/CH₄ ratio are shown in Figs. 3 and 4, respectively. The equilibrium concentration of N₂ is a weak function of temperature from ~0 to 500 °C, while that of NH₃ is a weak function of temperature from ~100 to 400 °C, and a strong function of temperature below ~100 °C, and above ~400 °C (Fig. 3). At temperatures higher than ~400 °C, the equilibrium concentration of NH₃ decreases dramatically with increasing temperature (Fig. 3), thus the oxidation of NH₃ to N₂ should be profound at high temperatures. In contrast, Fig. 3 shows that the equilibrium concentration of NH₃ reaches its highest values at moderate temperatures (~250 °C). Minor quantities of NH₃ should be present at moderate temperatures, depending on the total nitrogen concentration. In terms of total nitrogen concentration, we can see that the equilibrium concentrations of N₂ and NH₃ increase markedly as total nitrogen concentration increases (Fig. 3); however, Fig. 4 shows that higher total nitrogen concentrations also tend to preferentially favor the formation of N₂. Thus, nitrogen-rich hydrothermal fluids should be dominated by N₂.

The total nitrogen concentration is required to estimate the speculation of nitrogen in hydrothermal systems on early Enceladus (see Eq. (8)). Although the nitrogen content of Enceladus is unknown, a reasonable estimate can be made by considering the cometary models of Shock and McKinnon (1993) and Owen et al. (2004) for Triton and Titan, respectively. We assume that, because Enceladus and comets formed in the outer Solar System, where presolar NH₃ would have been present (Lunine and Gautier, 2004), the icy planetesimals that formed Enceladus had as much NH₃ as comets currently do (~0.5–1.5 mol% relative to H₂O; Bockelée-Morvan et al., 2004). Comets are the best known analogues for ice-rock bodies in the outer Solar System. Consistent with the cometary model, the total nitrogen concentration in early oceanic water and hydrothermal fluids would have been ~0.3–0.8 molal, if the water ice shell melted completely, or perhaps ~1 molal, if melting was extensive but incomplete (see Schubert et al., 2007). The range 0.1–1 molal should thus provide a representative estimate of the total nitrogen concentration.

Why was N₂ in the plume, whereas NH₃ has yet to be detected? Fig. 4 shows that hydrothermal fluids on early Enceladus would have resided deeply in the predominance field of N₂, assuming a cometary abundance of primordial NH₃. This situation would have resulted in a strong thermodynamic drive for the oxidation of NH₃ to N₂. Thus, we argue that the production of N₂ at the expense of NH₃ would simply have been a consequence of hydrothermal systems advancing toward chemical equilibrium. The dominance of N₂ over NH₃ in the plume is entirely consistent with chemical equilibrium in the C–N–O–H system, or in other words, equilibrium predictions agree with Cassini observations to first order. Overall, the deficiency of NH₃ in the plume would make perfect sense if most of the early ocean equilibrated within hydrothermal systems. Yet, the situation is also more complex than at first glance because, despite the dominance of N₂, small amounts of NH₃ may still have been present in hydrothermal fluids and hydrothermally processed oceanic water. The ocean would have been dilute with respect to NH₃ if hydrothermal systems processed it completely. If so, the concentration of NH₃ in the ocean may not have been greater than ~10⁻¹ molal (~0.2 wt%), and may have instead been orders-of-magnitude less than ~10⁻¹ molal if high temperatures (>400 °C) were reached in hydrothermal systems (Fig. 3). For now, these predictions cannot be assessed in detail because NH₃ was not detected in the plume. In light of Cassini observations to date, all we can say is that when the C–N–O–H system is modeled at chemical equilibrium, the broad NH₃–N₂ dichotomy of the plume arises naturally. The simplest explanation for this consistency is that C–N–O–H equilibrium was indeed reached.

The effect of temperature on the redox chemistry of carbon and nitrogen in hydrothermal systems on early Enceladus can be deduced by examining Fig. 5. This figure was made using PPM as a proxy for the general redox behavior of the hydrothermal systems, as it can reproduce the plume’s CO₂/CH₄ ratio at temperatures consistent with chemical equilibrium between CO₂ and CH₄ (see Section 3.1). As mentioned above, it must be stressed that PPM was used to illustrate the behavior of the C–N–O–H system with respect to temperature in the broadest sense. Again, we do not require that pyrrhotite, pyrite, or magnetite were ever present inside the satellite. The figure was also constructed using a 1 molal...
netite, like in aqueously altered chondrites. Oxidation–reduction calculations indicate that iron metal was oxidized to magnetite. The oxidation of accreted materials, for example, chemical equilibria suggest that Enceladus once had hydrothermal systems. The equilibrium speciation of C and N in the prototype system at 500 bar total pressure. The top panel shows the distribution of C between CO₂ and CH₄, and the bottom panel shows the distribution of N between N₂ and NH₃. The total N concentration is 1 molar in the bottom panel. The pyroxinite–pyrite–magnetite (PPM) redox buffer represents the oxidation state of the system.

total nitrogen concentration, consistent with the cometary model outlined in the previous section. The major trend in Fig. 5 is that higher temperatures favor the oxidation of carbon and nitrogen. At chemical equilibrium, CO₂ and N₂ would dominate at higher temperatures, while CH₄ and NH₃ would dominate at lower temperatures. Fig. 5 also shows that lower temperatures would be necessary to oxidize NH₃ to N₂ than CH₄ to CO₂. This result implies that NH₃ is more susceptible to oxidation than CH₄ is. Since the minor plume gases were mostly oxidized, a higher temperature (i.e., hydrothermal) origin seems sensible for them, although the exact temperature remains to be elucidated. Fig. 5 cannot be used to pinpoint the temperature because we cannot independently constrain the oxidation state.

4. Concluding remarks

In summary, Enceladus undoubtedly has a fascinating yet complex history that will almost certainly take many years to understand in any detail. As such, we believe that this work should be regarded as a first step toward unraveling the chemical story of this enigmatic moon. Only tentative inferences can be made at this point given the uncertainties surrounding Enceladus, and the idealized nature of the calculations that were done in this study. It is our hope, though, that our interpretations will lead to some novel, although perhaps controversial, hypotheses. We acknowledge that we do not have a complete understanding of the oxidation state of hydrothermal systems on early Enceladus, nor its relationship to Enceladus’ present-day plume. Currently, there are simply not enough analytical data from Enceladus to reach firm conclusions. Yet, we also believe that our results can still provide some useful insights into Enceladus’ history. Thus, a speculative scenario that is generally consistent with our results is outlined below, which should be viewed as a starting hypothesis for the general redox evolution of the moon.

In our view, the composition of the plume, chemical models of the solar nebula and early Titan, and thermal models of early Enceladus suggest that Enceladus once had hydrothermal systems. The decay of short-lived radionuclides may have provided most of the heat that powered the hydrothermal systems. One profound consequence of the existence of hydrothermal systems may have been the oxidation of accreted materials. For example, chemical equilibrium calculations indicate that iron metal was oxidized to magnetite, like in aqueously altered chondrites. Oxidation–reduction reactions may have led to the production and escape of H₂. As H₂ was lost, the moon should have become more oxidized. Major changes in the chemistry of nitrogen and carbon may have taken place due to high temperatures and H₂ escape. If NH₃ ices were accreted, large quantities of NH₃ may have been oxidized to N₂, consistent with the lack of NH₃ in the plume. At least some organic matter may have decomposed into CO₂ and CH₄, which according to kinetic calculations, could have equilibrated above ~200 °C in slow-moving hydrothermal fluids. We hypothesize that satellite oxidation diminished once short-lived radionuclides went extinct. Afterward, a large drop in heat production may have caused hydrothermal systems to disappear, eliminating the instigators of oxidation, and perhaps, precluding the formation of hematite. In terms of redox evolution, Enceladus might have lived fast and died young, reminiscent of aqueously processed asteroids. The redox chemistry of carbon and nitrogen in hydrothermal systems may have been subsequently quenched in cold aqueous solution or clathrate hydrate, preserving a signature from the distant past. If so, the plume’s CO₂, CH₄, and N₂ may arguably be relics of chemical equilibrium in early hydrothermal systems. The oxidation state of those hydrothermal systems, as suggested by the CO₂/CH₄ ratio in Enceladus’ plume, may have been near the PPM or FMQ buffer, and thus, may have also been in close proximity to that of submarine hydrothermal systems on Earth, if chemical equilibrium between CO₂ and CH₄ was reached in them. Yet, even if equilibrium was not attained but only approached, the fairly oxidized nature of the plume gases generally implies that higher temperatures may have prevailed when they formed. Early hydrothermal geochemistry may explain at least part of the plume’s composition.

In the future, the suitability of the equilibrium model should be evaluated by determining the structure and temperature of the interior of early Enceladus. The internal structure of early Enceladus can be estimated by calculating the moment of inertia factor of Enceladus using gravity-field measurements. It seems likely that a strongly differentiated interior would argue for higher temperatures in the past, and therefore, would perhaps support the equilibrium model; in contrast, a weakly differentiated or undifferentiated interior would most likely oppose the model. The internal temperature of early Enceladus can be constrained by determining the isotopic composition (i.e., the 13C/12C ratio) of CO₂ and CH₄ using in situ measurements. Isotopic ratios of CO₂ and CH₄ that are consistent with isotopic equilibrium at elevated temperatures would tend to favor the equilibrium model, while incoherent ratios would presumably argue against the model. The above hypothesis and especially its assumptions should also be tested by obtaining a better understanding of the nature of the plume source through observational and theoretical studies. Lastly, we suggest measuring the 15N/14N ratio of N₂ in a plume so that it can be compared to the accepted value for solar nebula N₂ to determine whether Enceladus’ N₂ is truly not primordial.

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