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THE IMPACT OF AMMONIA ON VOLATILE EQUILIBRIUM IN EUROPA'S PRIMITIVE OCEAN

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Abstract.
The potential presence of subsurface oceans on the Galilean moons raises the question of whether they could harbor habitable environments. Studying the current volatile inventory of these moons provides insights into their formation processes and how these processes affect volatile retention. To differentiate between possible scenarios, it is essential to consider post-accretion processes that could alter the volatile inventory. Specifically, an early "open-ocean" phase, occurring before the formation of the icy crust, likely influenced the composition of the volatile inventory. The abundance of ammonia in Europa's building blocks is particularly important, as it constrains both the habitability of the ocean and the volatile distribution in its primordial atmosphere. Our work models the ocean-atmosphere equilibrium during this period, based on different formation scenarios for Europa. We calculate vapor-liquid equilibrium between water and volatiles and examine chemical equilibria within the ocean to explore Europa's primitive hydrosphere. The model assesses how the initial distribution of volatiles results from the thermodynamic equilibrium between Europa's primordial ocean and atmosphere. We show that the ratio of dissolved CO_2 to NH_3 correlates with the partial pressure distribution in Europa's early atmosphere. By varying the ammonia content incorporated into the ocean post-accretion, we derive a range of primordial volatile distributions that can be compared with the current inventory. Additionally, we find ammonia thresholds beyond which CO_2 content is significantly reduced due to the formation of NH_2COO^-.

Keywords: Planetary science, Galilean Satellites, Europa, Primordial Hydrosphere

1 Introduction

Beneath its icy outer shell, Jupiter's moon Europa harbors a vast global subsurface ocean (Khurana et al. 1998; Pappalardo et al. 1999; Kivelson et al. 2000). This ocean likely interacts with both the rocky mantle and the icy surface, potentially driving hydrothermal processes (Zolotov et al. 2009) and transferring endogenous material to the surface (McCord et al. 2002; Dalton et al. 2005; Bierhaus et al. 2009). Europa's formation scenario, particularly the nature of the material that contributed to its ∼8 wt% water content, remains uncertain (Schubert et al. 2004; Gomez Casajus et al. 2021). Water may have been delivered via cometary ice (Canup & Ward 2002; Ronnet et al. 2017) or through the dehydration of chondrites (Melwani Daswani et al. 2021; Trinh et al. 2023; Mousis et al. 2023), each implying different volatile compositions for Europa's early hydrosphere.

To better understand Europa's formation history, it is essential to explore its early "open-ocean" phase, where a dense atmosphere coexisted and equilibrated chemically with the global ocean (Lunine & Stevenson 1987; Lunine & Nolan 1992). Over time, this evolved into the "closed-ocean" phase seen today, with the ocean covered by an ice crust. The present-day composition of Europa's subsurface ocean is therefore closely linked to its "open-ocean" stage, making it critical for tracing the evolution of the moon's hydrosphere. By modeling volatile distribution during this early phase, we can gain insights into Europa's current ocean and ice crust. The volatile content after accretion depends on the nature of the accreted material and formation

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conditions. Understanding the "open-ocean" phase also helps us evaluate how different formation scenarios affect volatile content, providing constraints that can be refined with data from upcoming missions like ESA's JUICE and NASA's Europa Clipper. Although nitrogen-bearing species have not yet been detected, their potential influence on habitability makes them important to investigate (Vance et al. 2023). Ammonia, a key nitrogen-bearing species found in cometary ices (Bockelée-Morvan & Biver 2017), is particularly relevant. The presence of NH_3 in Europa's hydrosphere could significantly impact the pressure distribution in the primordial atmosphere. Experiments by Van Krevelen et al. (1949); Göppert & Maurer (1988); Bieling et al. (1989) demonstrated a correlation between the dissolved CO_2–NH_3 ratio and partial pressures in the H_2O–CO_2–NH_3 system's liquid-vapor equilibrium.

Since the amount and chemical form of nitrogen delivered to Europa depends on the nature of the accreted materials, the formation scenario is crucial for understanding the CO_2 and NH_3 pressure distribution in the primordial atmosphere. To study this, we developed a model based on the approach of Marounina et al. (2018), calculating volatile partitioning between the primordial ocean and atmosphere. The model incorporates liquid-vapor equilibrium and chemical equilibrium in the liquid phase, allowing us to assess how the initial volatile distribution, particularly CO_2 and NH_3, influenced the equilibrium between Europa's primordial atmosphere and ocean.

This study explores how the initial volatile input, particularly the CO_2/NH_3 ratio, affects the partitioning of volatiles in Europa's primordial hydrosphere. To investigate this, we consider the possibility that Europa's water originated from cometary ice, using a range of comet compositions outlined by Bockelée-Morvan & Biver (2017) to constrain the potential distribution of volatiles.

2 Method

The model used in this study, focuses on the distribution of volatiles in the primordial hydrosphere of Europa. It computes the equilibrium taking place between two phases : the primordial atmosphere and the ocean at a shallow depth. We focus on the interface between the atmosphere and the ocean, meaning that atmospheric escape as well as geochemical exchanges with water and the rocky mantle are considered in this model. Temperature is assumed to be constant at the ocean-atmosphere interface, within a range of temperatures possible at the surface after accretion (Schubert et al. 1981; Bierson & Nimmo 2020). The partitioning of volatiles between the two phases is computed via the equations of phase equilibrium, combining Raoult's and Henry's laws. Moreover, the non-ideal behavior and interactions of volatiles in the atmosphere and the ocean are accounted for by computing fugacity coefficients using Peng-Robinson equation of state (Peng & Robinson 1976) and the Van der Waals one-fluid mixing rule. Then, the liquid-vapor equilibrium is coupled to the chemical equilibrium taking place within the ocean. In this model, only the speciation of the most reactive species, CO_2 and NH_3, is taken into account :

$$\begin{aligned} H_2O &\rightleftharpoons H^+ + OH^-, \\ CO_2 + H_2O &\rightleftharpoons HCO_3^- + H^+, \\ NH_3 + H_2O &\rightleftharpoons NH_4^+ + OH^-, \\ HCO_3^- &\rightleftharpoons CO_3^{2-} + H^+, \\ HCO_3^- + NH_3 &\rightleftharpoons NH_2COO^- + H_2O. \end{aligned}$$

The H_2O-CO_2-NH_3 chemical equilibrium is modeled via the the equations of dissociations, in which the molecular and ionic interactions between the species is accounted via the computation of the activity coefficients using the extended UNIQUAC model Thomsen & Rasmussen (1999). Finally, the model has been adjusted and bench-marked against UNIQUAC model results and experimental data from the literature (Van Krevelen et al. 1949; Göppert & Maurer 1988; Bieling et al. 1989; Darde et al. 2010).

3 Results

We have applied the model to an initial volatile distributions derived from data from Comet 67P/Churyumov-Gerasimenko (Rubin et al. 2019). In order to stress the impact of the total dissolved CO_2/NH_3 ratio on the distribution of volatiles in the primordial atmosphere, we vary NH_3 initially incorporated, while the fraction of other species remain unchanged. The calculation is done at a temperature of 300K, which is a credible surface temperature reached shortly after accretion (Bierson & Nimmo 2020). As water is in this case the main constituent of the atmosphere right after accretion, the initial total pressure is approximated to be $P_{\rm tot}{=}P^{\rm sat}_{\rm H_2O}$.

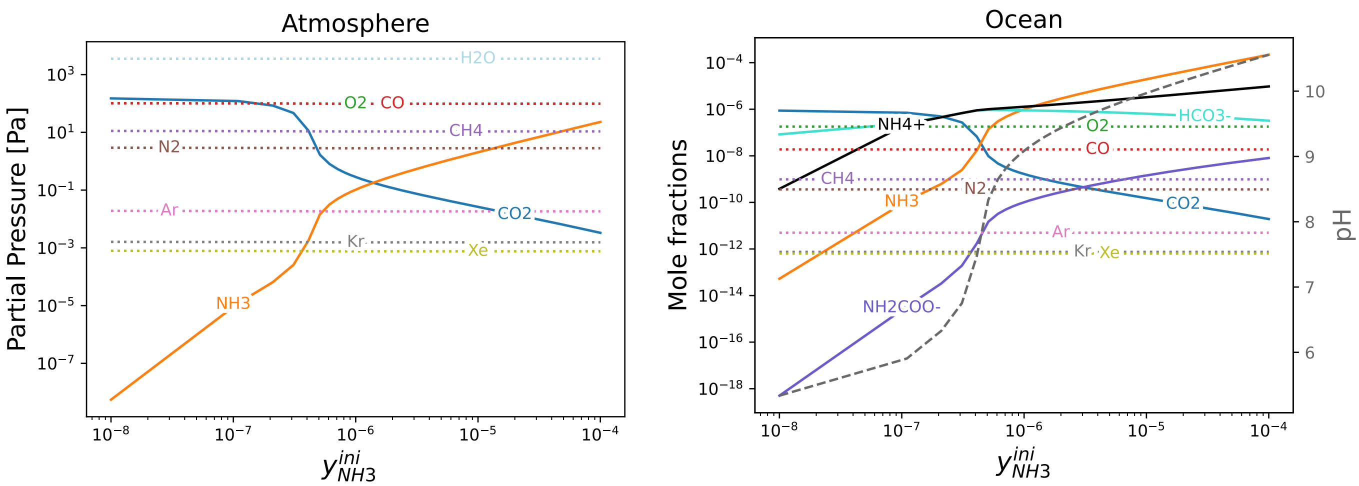

Fig. 1. Evolution at T = 300 K of the distribution of species in the atmosphere and ocean as a function of $y^{ini}_{NH_3}$, the initial mole fraction of NH_3 incorporated into the atmosphere. The initial mole fractions of all other species remain constant. Only the three most abundant ions–HCO_3^-, NH_4^+, and NH_2COO^-–are displayed in this figure.The dashed grey line corresponds to the pH of the ocean calculated as a function of $y^{ini}_{NH_3}$.

Figure 1 shows the effect of varying the initial NH_3 fraction on the distribution of molecules at T = 300K. The dotted lines represent the partitioning of other volatiles in both the primordial atmosphere and ocean. This highlights the chemical equilibrium between CO_2 and NH_3 in the ocean and their partial pressures. As detailed in Sec. 2, when CO_2 and NH_3 coexist in water, acid-base reactions lead to the formation of ammonium carbamate (NH_2COO^-) (Van Krevelen et al. 1949; Göppert & Maurer 1988; Bieling et al. 1989; Darde et al. 2010). The ratio of dissolved CO_2 to NH_3 determines whether CO_2 remains trapped in the liquid phase, reducing its abundance in the gas phase. A high CO_2/NH_3 ratio acidifies the ocean, while more NH_3 favors a basic pH and the formation of carbonates (HCO_3^-, CO_3^{2-}).

As the initial NH_3 fraction increases, the formation of N-bearing ions, particularly NH_2COO^-, also rises. Our results show a threshold in the CO_2/NH_3 ratio, where most CO_2 is stored in the ocean, reducing its atmospheric partial pressure. Specifically, when the initial NH_3 fraction exceeds $10^{-4} \times y_{CO_2}$, NH_3 dominates over CO_2 in the atmosphere. This inverse relationship shows that increasing CO_2 reduces NH_3 in the primordial atmosphere.

4 Conclusions

Our work provides an initial assessment of how the volatile partitioning in Europa's primordial atmosphere influences the distribution of volatiles in its early hydrosphere. We computed this partitioning using liquid-vapor equilibrium at the atmosphere-ocean interface and chemical equilibrium within the ocean. Special attention is given to how the initial NH_3 fraction in Europa's building blocks affects the primordial CO_2 distribution. We find that a CO_2-rich atmosphere can only be sustained above a certain CO_2/NH_3 threshold.

This model, however, focuses solely on the ocean-atmosphere interface and does not account for additional interactions that may have influenced volatile partitioning. For example, water-rock reactions at high pH could further suppress CO_2 levels in the ocean (Glein & Waite 2020). The model also assumes an isothermal atmosphere without escape, though atmospheric escape would deplete volatiles and alter hydrosphere equilibrium. Additionally, clathrate hydrates could form under favorable conditions, serving as another volatile reservoir and affecting the hydrosphere's composition over time (Prieto-Ballesteros et al. 2005; Zolotov et al. 2009; Mousis et al. 2013; Bouquet et al. 2019).

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