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THE ROLE OF CLATHRATE TRAPPING IN THE COMPOSITION OF EUROPA'S OCEAN

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Abstract. We use a thermodynamic statistical model to evaluate how the composition of Europa's internal ocean may have been affected by clathrate hydrate formation. Assuming an input of the observed O_2 and CO_2 from the surface and considering the possibility of contributions by reduced (with CH_4 and H_2S) or oxidized (CO_2-bearing) hydrothermal fluids, we calculate the fractional occupancies in clathrate and deduce the effect on the ocean's composition. The structure of the clathrate formed, and therefore its density and composition, is influenced by the amount of O_2 compared to the other compounds present. In turn, the ratios of noble gases is influenced by the clathrate structure formed.

Keywords: astrobiology, Europa, clathrate hydrates

1 Introduction

The internal ocean of Jupiter's icy moon Europa is likely the host of a complex chemistry enabled by inputs from the radiation-processed icy surface (Hand et al. 2006; Paranicas et al. 2009; Greenberg 2010) and the interaction with the rocky interior (Kargel et al. 2000; McKinnon & Zolensky 2003; Vance et al. 2007). High pressure, low temperature and availability of water are favorable to the formation of clathrate hydrate (hereafter clathrate) that can preferentially trap some volatiles and affect the evolution of the ocean's composition. We apply here a thermodynamic statistical model to Europa's internal ocean. Considering an input of volatiles into the ocean, the model predicts the occupancy fraction of each chemical species in the clathrate phase and from there the evolution of these species' abundance in the ocean.

2 Model and assumptions

The thermodynamic statistical model is based on the original work of Van der Waals (1959), following the method described by Lunine & Stevenson (1985) and Thomas et al. (2007). It determines the occupancy fractions in the clathrate by describing trapping of guest molecules as a three-dimensional adsorption (see Mousis et al. (2013) for a detailed description). We considered the amount of gas coming into the ocean from the icy crust based on the estimates of Hand et al. (2006) and Greenberg (2010) for O_2 and CO_2. We add a volatile input due to hydrothermal fluids, either reduced (H_2S and CH_4) or oxidized (CO_2), in quantities within published estimates (Hand et al. 2007). We also consider the presence of noble gases argon, krypton and xenon to evaluate the evolution of their ratios in the ocean caused by clathrate formation. When considering a reduced hydrothermal input, we consider the fast oxidation of H_2S by O_2 (Millero et al. 1987) to eliminate the limiting reactant.

We calculated the amount of dissolved volatiles necessary to reach a fugacity to start clathrate formation (Mousis et al. 2013)and found that with the input we consider the ocean starts producing clathrate in less than a billion year. In every case we consider the two usual clathrate structures (sI and sII).

3 Results

The results are shown in Figures 1 and 2 for two cases: an input dominated by O_2 and CO_2 from the surface, and one dominated by CH_4 and H_2S from hydrothermal fluid.

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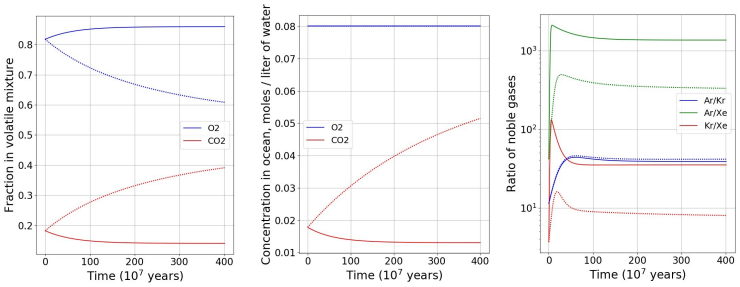

Fig. 1. Evolution of O_2 and CO_2 mole fraction (left) and concentration (center) in the ocean, and noble gases ratios (right), in the case of a O_2-CO_2 input mostly from the icy crust. Full lines represent the formation of sI clathrate, dotted lines the formation of sII (more likely due to the prevalence of O_2).

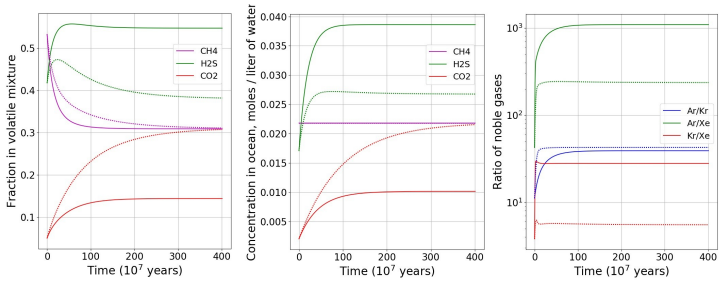

Fig. 2. Same as Figure 1 but with a large reduced input of CH_4 and H_2S. The reduction of O_2 by H_2S is sufficient to eliminate O_2. Due to the large input of CH_4, formation of sI (full lines) is the most likely outcome.

4 Conclusions

Clathrate formation may influence the abundance of several species in Europa's ocean, in particular the noble gas ratios evolution depends on what clathrate structure (sI or sII) is formed. When CH_4 and H_2S are present, their abundance in the ocean become less representative of the hydrothermal input due to preferential trapping of CH_4 over H_2S. We find the clathrate density to be lower than that of seawater, indicating it would be incorporated into the icy crust and its volatile content possibly measurable by future missions such as Europa Clipper and JUICE.

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