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Clathrate formation and the volatile evolution of Europa'ocean

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Abstract

We used a statistical thermodynamic model to evaluate how clathrate formation could alter the composition of Europa's internal ocean. We ran calculations assuming an O_2 and CO_2 input from the icy crust (based on compounds present on the surface) and an input of either reduced or oxidized hydrothermal fluids. We found that the relative abundance of O_2, by promoting the formation of structure II clathrate, is an essential factor in the effect of clathrate trapping and this effect is readily seen on the ratios of noble gases (Ar, Kr, Xe) in the ocean. We also found clathrate formed in most cases is more likely to float up to the icy crust unless the ocean is salt-poor or the input of CO_2 is large compared with other compounds.

1. Introduction

The internal ocean of Europa could potentially harbor conditions favorable to life. Chemotrophic energy is the most likely way to sustain a biosphere under a thick icy crust, if the composition of the ocean presents a chemical disequilibrium on which life can feed [1,2,3,4]. Among the factors able to alter the ocean's composition, clathrate hydrate (hereafter clathrate) formation can affect the ratios of several volatiles of interest such as O_2, CO_2, CH_4, CO_2, H_2S and the noble gases Ar, Kr, and Xe. The conditions at the ice-ocean interface (cold temperature, high pressure, activity of water) are favorable to clathrate formation.

2. Model and assumptions

We used a statistical thermodynamic model [5] to predict the occupancy fraction of various volatiles in a multi-guest clathrate formed in Europa's ocean.

We assumed a flux into the ocean based on O_2 and CO_2 from the surface [6, 7] and a hydrothermal input that is either oxidized or reduced in nature (CO_2 + sulfates versus CH_4 + H_2S, with sulfates not involved in clathrate formation) [8]. The amount of volatiles added is based on estimates of the input rate to the ocean from the surface [7] and a range of estimates for hydrothermal production based on extrapolation of Earth values [8, 9, 10]. We considered "large" and "small" hydrothermal inputs, relative to the O_2 input from the icy crust. We introduced small quantities of Ar, Kr and Xe with ratios consistent with measurements at comet 67P [11, 12]. For each run we calculated the density of the clathrate produced assuming near-complete (90%) filling of the cages. The ocean's pH is assumed to be mildly acidic. A more basic pH would induce speciation of CO_2 and H_2S into carbonates and HS^-, respectively, which would not be trapped in clathrate. We calculated with SUPCRT 92 that SO_2 from the icy crust [6] is likely to speciate into sulfite species (non-clathrate forming) under conditions other than strongly acidic and we did not include it.

3. Results

In the case of a mostly oxidized hydrothermal input, our model only includes O_2 and CO_2 (+ noble gases) as clathrate-forming volatiles. A large CO_2 input promotes the formation of structure I (sI) clathrate along with structure II (sII), which maintains the O_2/CO_2 ratio in the ocean close to the total input (from the icy crust + hydrothermal fluid). A smaller CO_2 input results in O_2/CO_2 decreasing as O_2 is preferentially trapped in sII clathrate, with steady state not reached within the timeframe of our calculations (equivalent to 4 Gyr).

In the case of a reduced hydrothermal input (CH_4 + H_2S), a large input of methane promotes structure I formation, dramatically altering the fractions of volatiles in the mixture (**Figure 1**), depleting methane relative to other species. A smaller hydrothermal input lets O_2 drive sII clathrate formation with the most notable effect being O_2/CO_2 decrease. The calculated clathrate density ranges from 0.98 g/cc (methane-rich clathrate) to 1.037 g/cc (CO_2 –rich clathrate).

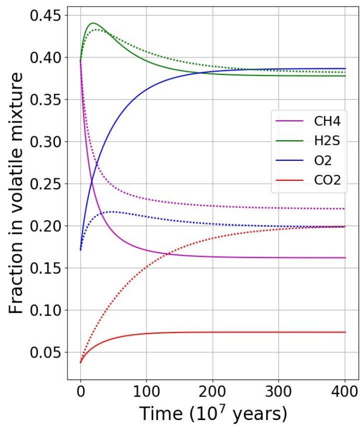

Figure 1: Evolution of the volatile mixture in the ocean in the case of a large input of reduced hydrothermal fluids. Full lines assume sI formation, dotted lines assume sII.

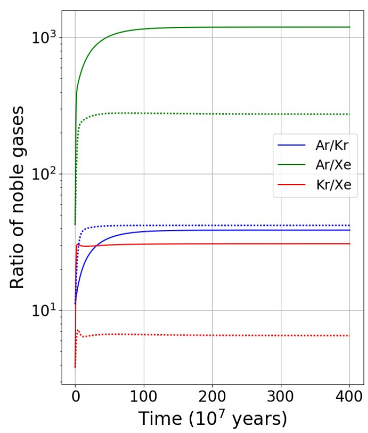

Figure 2: Evolution of the noble gas ratios in the ocean. Full lines assume sI formation, dotted lines assume sII

The effects on noble gas ratios are mostly decided by which clathrate structure forms (sI or sII) and an example is shown in Figure 2.

4. Discussion

The clathrate densities we calculate are generally lower than most estimates of Europa's ocean density [13], indicating clathrate is most likely to float and be integrated into the icy crust. CO_2-rich clathrate, though, could be dense enough to sink until it reaches depths where the high pressure fosters a higher seawater density.

Summary and Conclusions

We calculated occupancy fraction in clathrate formed in conditions relevant to Europa's ocean, considering possible inputs from both the icy crust and hydrothermal fluids, and we evaluated the effect of clathrate formation on Europa's ocean composition. We found differences in the evolution of the O_2/CO_2 ratio in the ocean depending on the relative size of the inputs (hydrothermal vs O_2 from the crust), and whether sI or sII clathrate is formed. The evolution of noble gas ratios is especially affected by the structure formed. The clathrate formed is most likely to float and become part of the icy crust. The exploitation of future measurements at Europa to deduce the ocean composition should take into account the effect of partitioning by clathrate formation on the mixture of volatiles that makes it to the surface.

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