Composition and Habitability of Europa's Ocean Over Time.

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Introduction: Europa is proposed to host a global liquid water ocean that is in contact with a silicate interior [1]. Understanding the composition of this ocean and the underlying rock is crucial for evaluating the habitability of Europa. However, the presence of an ice shell impedes direct observation or analysis of the ocean and rock, leaving their compositions largely unknown. Previous modelling work has shown that, if Europa accreted entirely from CI or CM chondritic material, sufficient volatiles could be released during prograde metamorphism to account for the current size of the hydrosphere [2]. However, thermal models predict that temperatures in Europa's interior would gradually increase over billions of years [*e.g.* 3], where the progressive release of volatiles would change the ocean composition over time. In this study, possible ocean compositions were explored using computer modelling to simulate the thermal evolution of Europa's interior over its ~4.5 Gyr lifetime and assess the volatiles released from the starting material as it is heated.

Methods: The composition of Murchison (a CM chondrite) was chosen to represent the silicate material that accreted to form Europa because the CMs: formed close to early Jupiter (unlike the CIs [4]), contain sufficient water (largely held within hydrated silicates [5]), and can produce fluid compositions consistent with salts observed on Europa's surface [2, 6]. A 1-dimensional thermal evolution code was used to model the temperatures achieved within Europa's interior [3]. Temperature-depth profiles were then extracted at two points in time to reflect the formation of the proto-ocean (*i.e.* ~1600 Myr since the calcium-aluminium-rich inclusions (CAIs)) and the current-day ocean (~4568 Myr since the CAIs). Rcrust [7] and Perple_X [8] were used to predict the electrolytic fluid speciation from the starting material when heated to the temperatures predicted by the first temperature-depth profile (Stage 1; 4 – ~1600 Myr) and then the second (Stage 2; ~1600 – ~4568 Myr). Pyrrhotite was extracted from the starting material past the Fe-FeS eutectic temperature (which was also calculated using Rcrust and Perple_X) to approximate core formation. The volatiles forming the proto-ocean (*i.e.* those released in Stage 1) were then equilibrated using CHIM-XPT [9], where supersaturated gases were exsolved and minerals precipitated. The further volatiles (*i.e.* those released in Stage 2) were then added to the proto-ocean in CHIM-XPT, forming the current-day ocean.

Results and Discussion: Released volatiles for the proto-ocean are predicted to form a ~77.9 km deep layer around Europa. With the addition of the further volatiles, the current-day ocean would be ~84.8 km deep. The extraction of pyrrhotite, which occurs after proto-ocean formation, would form a metallic core of ~271.5 km radius by the current day. The current-day ocean depth and core radius predicted here agree with those inferred for current-day Europa based on observations [3]. The model predicts that both the proto- and current-day oceans would be rich in Na^+, Cl^-, and CO_3^{2-}, which may explain the recent observation of NaCl and CO_2 in geologically-disrupted regions of Europa's surface [10, 11]. Large concentrations of NH_3 and NH_4^+ are predicted for both the proto- and current-day oceans, despite the lack of any clear detection of nitrogen species on the surface. However, this abundance may be explained by the absence of thermodynamic data for solid nitrogen-bearing phases in the model resulting in an overestimation of nitrogen release during metamorphism (mainly as NH_3). A key difference between the proto- and current-day oceans is their HS^- concentration, where the current-day ocean has only ~0.2% that of the proto-ocean. This is due to the addition of the iron-rich Stage 2 volatiles to the proto-ocean causing the precipitation of pyrite (removing HS^- from solution).

Conclusion: We find that Europa's ocean composition would have varied over time as a result of continued prograde metamorphism, with particular changes in HS^- concentration. The significant decrease in HS^- content could affect the potential for energy generation by sulfide-oxidising microbes in the current-day ocean and, thus, would have implications for Europa's continuous habitability.

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