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MODELLING POSSIBLE CHEMICAL EVOLUTION PATHWAYS DURING FREEZING OF EUROPA'S ICE SHELL. M. G. Fox-Powell¹, N. S. Wolfenbarger², J. J. Buffo³, J. Semprich¹, N. K. Ramkissoon¹.
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Introduction: Constraining the chemical composition of Europa's ocean is a vital step in understanding the moon's evolution and potential habitability. Signatures of water-rock interaction in the form of sodium and magnesium chloride salts have been observed on the surface, promising a means to study ocean chemistry indirectly [1,2,3]. Models of water-rock interaction at Europa's seafloor predict that a sulfate-rich ocean should be expected [4,5], but recent telescope observations suggest that sodium and magnesium-chloride salts, not sulfates, dominate regions where geologically recent exchange with the subsurface may have taken place [1,2,3].

Reconciling these views requires a comprehensive understanding of the range of possible salt mineral assemblages produced by freezing, and of how chemical evolution pathways may interact with specific physical transport within Europa's ice to define ice shell composition.

Using a thermodynamic modelling approach, we explored the salt hydrate mineral assemblages produced from a comprehensive chemical parameter space of hypothetical ocean compositions. Our findings identify those ocean compositions that are compatible with current understanding of ice shell mineral assemblages, and provide a framework for interpreting improved estimates of ice shell mineralogy when available from upcoming missions. Furthermore, our results can be integrated with models of physical transport to predict the extent of transport-driven fractionation within Europa's ice.

Methods: We used Pitzer thermodynamic models implemented in the PHREEQC program [6] to investigate brine evolution and cryogenic mineral formation as a function of Europa's ice shell. As ocean composition is unknown, we considered a wide range of hypothetical oceans, in which the mole fractions (χ) of candidate major ions Na^+ , Cl^- , Mg^{2+} and SO_4^{2-} were independently varied over five orders of magnitude.

Calculations were performed in the program PHREEQC using the ColdChem.dat database [7]. The total salinities of the hypothetical oceans were kept constant (here reported at terrestrial seawater salinity; 34 g kg^{-1}), to allow direct comparison of solid phase formation temperatures as a function of fluid composition alone. Equilibrium (closed-system) crystallization scenarios were considered, in which solid

and liquid phases were allowed to remain in equilibrium at all stages of freezing. We also explored partially-open fractional crystallization cases, in which some non- H_2O material (solid salts and/or brine) was assumed to be lost before the brine volume decreases below a critical threshold. Once this threshold was crossed, fractional crystallization cases were assumed to evolve at equilibrium as above.

Results & Discussion: *Eutectic mineral assemblages.* In the Na-Mg-Cl- SO_4 system, there are only two stable eutectics, identified in our work as -33.67°C and -38.77°C . All brines compositionally evolve towards one of these two eutectics, reflecting two distinct mineral assemblages (Figure 1).

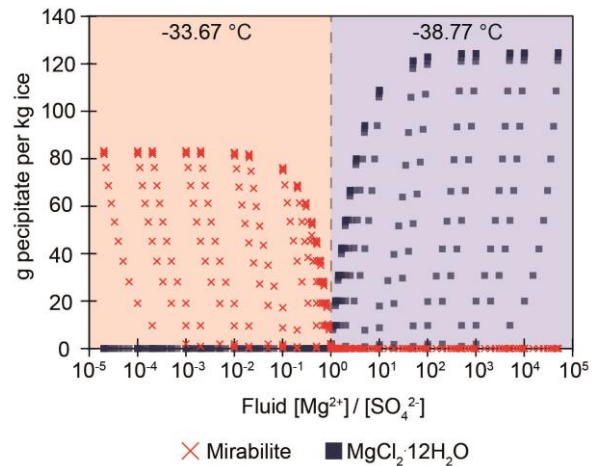


Figure 1. Abundances of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ as a function of $\text{Mg}^{2+} : \text{SO}_4^{2-}$ ratio formed in 529 individual freezing simulations. Temperatures are predicted eutectics.

Furthermore, we found that Mg-chlorides and Na-sulfates cannot co-precipitate under equilibrium conditions. If ocean-derived fluids are transported in a manner that allows residual brines to remain in equilibrium with precipitated phases, Mg-chloride minerals only form from oceans where initial $\chi\text{Mg}^{2+} > \chi\text{SO}_4^{2-}$, regardless of the initial concentration of other ions (Figure 1). From sulfate-rich oceans where $\chi\text{Mg}^{2+} \leq \chi\text{SO}_4^{2-}$, a Mg-sulfate mineral (in our models, meridianiite; $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$) is the sole sink for Mg^{2+} ions.

In sodium-rich cases where mirabilite saturation is reached early during freezing, as long as overall $[Mg^{2+}]:[SO_4^{2-}]$ of the system is > 1 , mirabilite is not present in the final mineral assemblage. In these cases, mirabilite forms at intermediate temperatures, but redissolves upon hydrohalite ($NaCl \cdot 2H_2O$) precipitation. This buffers residual brine with SO_4^{2-} , ultimately leading to Mg consumption via meridianiite precipitation. More complex fluids, such as terrestrial seawater, and Europa ocean compositions proposed from water-rock modelling [4,5], also obey this rule. These predictions are consistent with experimental evidence for mirabilite dissolution upon hydrohalite precipitation during freezing of terrestrial seawater [8].

Potentially endogenous Mg-chloride salts have been observed on Europa's surface [1,3]. Our models imply that these must form from an ocean where sulfate is less abundant than magnesium, provided that Europa's ice shell has not experienced significant fractionation. Importantly, our results indicate that the co-occurrence of mirabilite and Mg-chlorides on Europa, would provide evidence that the salt hydrate assemblages must not have formed through closed-system equilibrium freezing.

Potential for fractional crystallization. We also explored the possibility that salts precipitated within a high-porosity ice-ocean interface region of the ice shell may be flushed out, leading to fractional crystallization [9]. We imposed a percolation threshold of 6% brine volume fraction, based on the work of [10], and assumed that all salts precipitated before this volume threshold is reached are removed from the system. We found that oceans with lower initial $\chi_{SO_4^{2-}}$ do not precipitate sulfate minerals until relatively low temperatures; in many cases after the percolation threshold is reached. By contrast, those oceans which evolve into the $[Mg^{2+}]:[SO_4^{2-}] > 1$ regime before the percolation threshold is reached can form Mg-chloride, even if $[Mg^{2+}]:[SO_4^{2-}]$ is initially < 1 (Figure 2). Indeed, high sulfate oceans precipitate the majority of their SO_4^{2-} close to the ice/ocean interface, before the percolation threshold is reached, and thus would be most prone to switching from the mirabilite to the Mg-chloride regime. If such a process is involved in ice shell formation on Europa, it would offer the possibility of reconciling observations of Mg-chlorides on the surface with model predictions of sulfate-rich oceans [4,5].

Our ongoing work will consider five and six-ion systems and explore co-varying temperature and pressure. Accounting for the compositional evolution of brines within Europa's icy shell will allow better understanding of ice shell processes, and more accurate

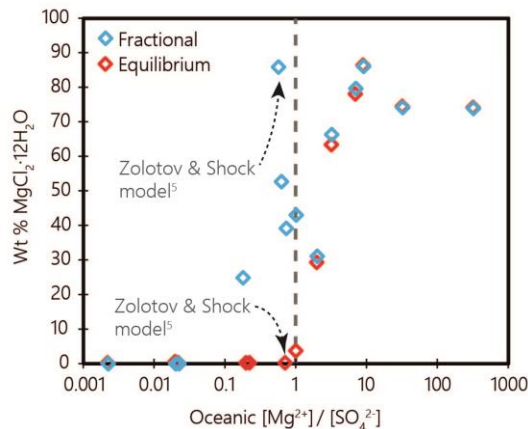


Figure 2. Abundance of $MgCl_2 \cdot 12H_2O$ formed in closed-system equilibrium models, and when subjected to a 6% brine volume fractional percolation threshold.

constraints on Europa's ocean chemistry that can continue to be refined in response to new observations.

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