

BRINE EVOLUTION AND TRANSPORT-DRIVEN FRACTIONATION OF OCEAN FLUIDS WITHIN EUROPA'S ICY SHELL. M. G. Fox-Powell¹, J. Semprich¹, N. Ramkissoon¹, J. J. Buffo², S. D. Vance³, S. P. Schwenzer¹, V. K. Pearson¹. ¹AstrobiologyOU, Open University, Walton Hall, Milton Keynes, UK MK7 6AA, mark.fox-powell@open.ac.uk; ²Dartmouth College, Hanover, NH, USA; ³Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

Introduction: Constraining the composition of Europa's subsurface ocean is a vital step in understanding the moon's evolution and potential habitability. Models of water-rock interaction at Europa's seafloor indicate that a sulfate-rich ocean should be expected [1,2], but recent Earth-based telescope observations suggest that sodium and magnesium-chloride salts, not sulfates, dominate geologically young regions where exchange with the subsurface may have taken place [3,4]. Fractional crystallization of ocean fluids during freezing can act to enrich chlorides within ice, even from sulfate-dominated fluids [5], offering the possibility to reconcile these views. However, determining whether this mechanism is occurring at Europa, or whether surface chlorides directly represent ocean composition, requires a deeper understanding of how chemical evolution pathways interact with physical transport mechanisms within the icy shell.

We used thermodynamic models to explore potential for fractionation across a wide range of hypothetical ocean compositions. By integrating our findings with geophysical models of ice shell structure, the role of transport in driving subsurface brine evolution on Europa can be addressed. Our findings identify those ocean compositions compatible with both models and observations and provide new constraints on the degree of possible freezing-induced fractionation in Europa's icy shell.

Methods: We employed Pitzer equations to explore brine evolution and the formation of solid phases (ices and salt minerals) during equilibrium and fractional freezing of many hypothetical ocean compositions. Equilibrium cases assume that freezing brine remains in equilibrium with all solid phases at all stages of freezing, whereas fractional cases do not allow precipitated solid phases to further interact with the residual brine. Calculations were performed in the program FREZCHEM (v. 13.3) [5] and using the frezchem.dat database within PHREEQC (v. 3.0) [6]. Hypothetical ocean compositions were systematically varied across a broad chemical parameter space to identify those ocean compositions that produce mineral assemblages consistent with observations. We considered Na-Mg-K-Cl-SO₄ and Na-Mg-Ca-K-Cl-SO₄ systems, where the mole fractions (χ) of sulfate and

magnesium were systematically varied independently between 0.001 and 0.499. The relative abundances of all other ions were kept constant, fixed according to the model of [1]. The total salinities of the hypothetical oceans were also kept constant (here reported at terrestrial sea water salinity; 34 g kg⁻¹), to allow direct comparison of solid phase formation temperatures as a function of fluid composition alone.

Results & Discussion: Equilibrium freezing. If ocean-derived fluids are transported in a manner that allows residual brines to remain in equilibrium with precipitated phases, MgCl₂ minerals only form from oceans where initial $\chi_{\text{Mg}^{2+}} > \chi_{\text{SO}_4^{2-}}$, regardless of the initial concentration of other ions (Fig. 1). From sulfate-rich oceans where $\chi_{\text{Mg}^{2+}} \leq \chi_{\text{SO}_4^{2-}}$, a Mg-sulfate mineral (in our models, meridianiite; MgSO₄·1H₂O) is the sole sink for Mg²⁺ ions. Given that potentially endogenous MgCl₂ salts have been observed on Europa's surface [3], our models imply that these must form from an ocean where sulfate is less abundant than magnesium, similar to Earth's oceans; provided that Europa's ice shell has not experienced significant fractionation.

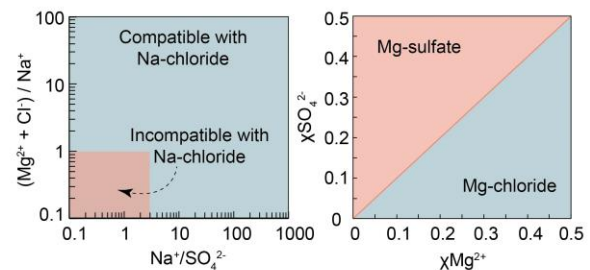


Figure 1. Constraints provided by equilibrium freezing simulations. Left: Initial ocean compositions compatible with NaCl (*i.e.*, hydrohalite) precipitation. Right: Mg²⁺ minerals formed as a function of initial oceanic mole fractions of SO₄²⁻ and Mg²⁺. All runs included Na, K, Ca, Mg, Cl, SO₄.

Furthermore, although all hypothetical ocean compositions contain Na⁺ and Cl⁻ ions, NaCl (hydrohalite, NaCl·2H₂O, in our models) does not always precipitate. In some limited cases, the formation of mirabilite (Na₂SO₄·10H₂O) maintains Na⁺ levels below hydrohalite saturation throughout freezing. This only occurs in sodium and sulfate-rich cases where both

χ_{Cl} and $\chi_{\text{Mg}^{2+}}$ are low (Fig. 1). In these cases, the formation of other sulfates such as gypsum or meridianiite do not occur until late in the sequence, thus allowing SO_4^{2-} to remain relatively high in the residual brine. Endogenous NaCl on Europa's surface, for which the observational case continues to strengthen [4,8], would therefore rule out such ocean compositions.

Transport-driven fractionation. We find that even extremely sulfate-rich oceans, where $\text{Cl}/\text{SO}_4 < 0.001$, tend to evolve towards a chloride-dominated composition as freezing progresses. However, the temperature at which sulfate minerals precipitate is a function of initial oceanic $\chi_{\text{SO}_4^{2-}}$ (Fig. 2). High-sulfate oceans lose most of their aqueous SO_4^{2-} to gypsum, mirabilite or meridianiite precipitation at relatively high temperatures. Oceans with lower $\chi_{\text{SO}_4^{2-}}$ achieve much lower temperatures before saturation with respect to these phases is reached.

Because ice shells can exhibit dynamic multi-layered structure [9,10], this finding has implications for the degree to which ascending brines can become fractionated away from original ocean composition. Figure 2 indicates the approximate positions of the ocean/ice interface (defined by the initial formation of ice in our runs) and the estimated region of ice I_h solid state convection (predicted by [10]), relative to the temperatures of sulfate precipitation, for a subset of our runs. The largest changes in temperature, and hence in brine composition, occur either above or below the region of solid-state convection. Thus, understanding how packets of brine are transported into and out of this region will be critical to understanding the potential for fractionation. High sulfate oceans precipitate the majority of their SO_4^{2-} close to the ice/ocean interface, and below the initiation of solid-state convection. This region of the ice shell can remain hydraulically connected to the ocean [9], thus we consider the possibility that phases that form here may not become entrained into the convecting region of the shell, and therefore are not delivered to shallower depths. High-sulfate oceans would be the most prone to this form of transport-driven fractionation.

By contrast, oceans with low $\chi_{\text{SO}_4^{2-}}$ do not precipitate sulfate minerals until much lower temperatures are reached; in many cases above the region of solid-state convection. In the context of these findings, endogenous sulfates on the surface could counterintuitively imply a relatively sulfate-poor ocean. However, as the thickness of the basal porous layer and the region of solid-state convection are affected by brine composition and concentration, our findings must be integrated with transport models to test this theory.

Our ongoing work will consider the implications of transport-driven fractionation and identify those hypothetical ocean compositions consistent both with observed surface minerals and existing models of Europa ocean chemistry. Accounting for the compositional evolution of brines within Europa's icy shell will allow better understanding of ice shell processes, and more accurate constraints on Europa's ocean chemistry that can continue to be refined in response to new observations.

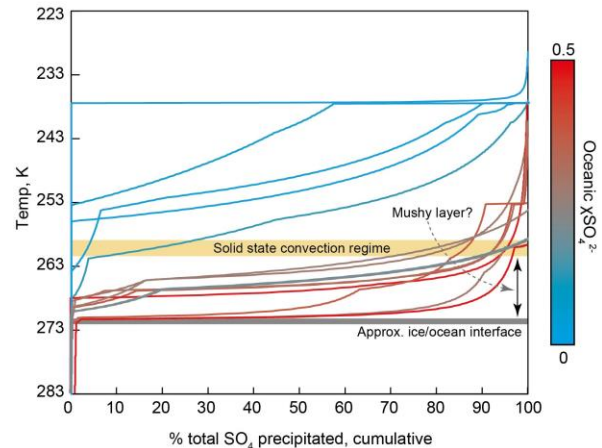


Figure 2. Precipitated sulfate minerals as a function of temperature and initial oceanic $\chi_{\text{SO}_4^{2-}}$ (indicated by the color scale). Apart from sulfate, all runs also included Na, K, Ca, Mg, Cl. The temperature range of the solid-state convection regime for a thick ice shell containing 34 g kg^{-1} NaCl is reproduced from [10].

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