Insights into Europa’s frozen brines via chemical divide modelling and experiments

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Abstract

Here we present results of chemical divide modelling combined with Raman and X-ray diffraction experiments to examine the freezing of a four ionic component (Na, Mg, SO₄, Cl) solution. We have quantitatively identified the minerals that are formed upon freezing as a function of relative ionic concentration and freezing rate. In performing this exercise, we begin making links between observations of the Europa’s surface chemistry and the chemical environment of the internal ocean.

1. Introduction

The global ocean believed to exist beneath Europa’s thick ice shell is often cited as one of the most likely places in the solar system to find evidence of extraterrestrial habitable environments or even extant life. The potential habitability of the ocean is primarily driven by its chemical composition. Apart from the possibility of sampling periodic active plumes [1] in future missions, constraints on the ocean composition currently will need to rely on analysis of the expressed surface ice. In this work, we combine Raman and X-ray diffraction experiments on a relatively simple putative brine system with chemical divide modeling to assess the effectiveness of such approach in inferring the ocean’s chemical composition. This in turn can provide guidance as to whether future missions should focus on direct analysis of plume materials, or should look to explore other terrains such as diapirs in order to gain the most insights into the ocean.

2. Methods

Chemical Divide Modeling: This approach predicts the sequence of precipitation of salts based on their solubility and relative ionic concentrations in solution [2]. In the case of putative Europan brines with pH ≤ 8.4 containing the four components Na, Mg, Cl and SO₄, chemical divide modeling for thermodynamic freezing yields the flowchart in Figure 1 [3].

![Figure 1: Mineral crystallization sequence for brine systems containing Na⁺, Cl⁻, Mg²⁺, and SO₄²⁻ with pH ≤ 8.4.](image)

Experimental Techniques: In this work, we examine a greatly simplified brine system where the concentrations of Na and Cl are exactly twice those of Mg and SO₄, thus only mirabilite (Na₂SO₄•10H₂O) and MgCl₂•12H₂O are expected as products. We studied two freezing scenarios (flash vs slow freezing) as well as two concentration regimes (molar vs tenths of molar) using complementary Raman (surface) and cryogenic X-ray diffraction (XRD, bulk) techniques. The latter is a unique facility for investigating planetary ices that has recently been developed at JPL.

3. Results

In all cases, the XRD experiments detected only the two products as predicted by the chemical divide model. The Raman results are more complex, where the two expected salts were detected in only 2 scenarios. In the case where the molar brines were...
slowly frozen, epsomite and hydrohalite also formed along with mirabilite and MgCl$_2$$\cdot$12H$_2$O. In addition, flash freezing of the diluted brine often produces water ice together with MgCl$_2$ glass, greatly hindering detection. A summary of the Raman results is shown in Table 1.

Table 1: Summary of the mineral phases observed by Raman upon freezing of molar (Na = Cl = 2Mg = 2SO$_4$ = 4M) and sub-molar brines (10× diluted).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flash Freeze</th>
<th>Slow Freeze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar brine</td>
<td>2 salts</td>
<td>4 salts</td>
</tr>
<tr>
<td>Diluted brine</td>
<td>Ice + glass</td>
<td>2 salts</td>
</tr>
</tbody>
</table>

These results hold important implications for both instrument as well as landing site selection for a potential Europa lander. Specifically, the Raman payload needs to be accompanied by a complimentary instrument that can detect salts in low-concentration brines, especially for the plumes where brines are likely to be flash frozen. In addition, terrains such as diapirs where brines are more likely to freeze slowly and closer to thermodynamic equilibrium should be considered for exploration in order to gather more comprehensive chemical information from the subsurface ocean.

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**References**

