EFFECT OF THE SALTING-OUT ON THE HABITABILITY OF PLANETARY AQUEOUS ENVIRONMENTS

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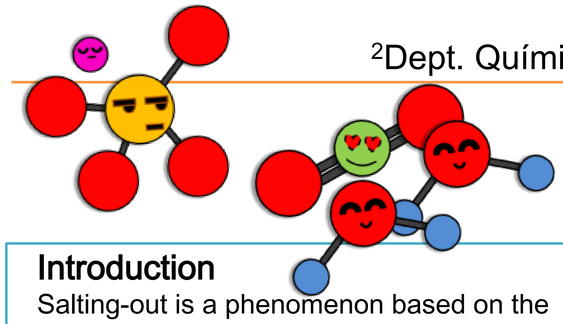


Introduction

Salting-out is a phenomenon based on the electrolyte-nonelectrolyte interaction, in which under certain conditions the solvent has a preferential interaction with one of them, decreasing the solubility of the contrary [1].

We suggest this phenomenon may occur within icy moons, such as Europa, during the evolution of aqueous fluids. A representative chemical system is constituted by H_2O-$MgSO_4$-CO_2 [2].

Figure 1. Europa moon.

Methodology

- Salting-out experiment is performed in a high pressure chamber equipped with a sapphire window, which allows monitoring runs by Raman spectroscopy.

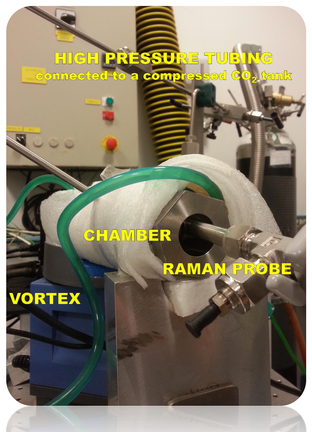
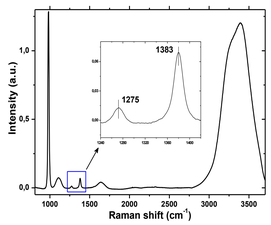


Figure 2. High pressure system (MPPC).

- Pressure and temperature are recorded during clathrate formation in the system H_2O-$MgSO_4$-CO_2. The initial composition of the aqueous solution is 17 wt% $MgSO_4$, saturated with CO_2.
- During the experiments, the system is subjected to different pressure and temperature regimes, which are relevant within the icy moons crusts.

Results

Raman bands, which are followed during the experiments.

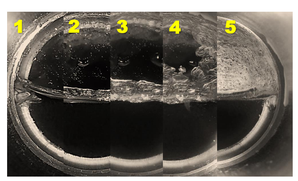


Vibration mode	Raman shift (cm^{-1})
v_1-SO_4^{2-}	981.9
Fermi doublet-CO_2 (g)	1285 and 1388
O-H stretching	3200-4000

Table 1. Frequencies of key bands.

Figure 3. Raman spectrum of liquid phase in the chamber at 2 ºC and 34 bar. Fermi doublet frequencies (inset) corresponds to CO_2(aq).

CO_2-clathrates crystallize from the liquid-gas interface toward the top of the chamber forming a layered structure.



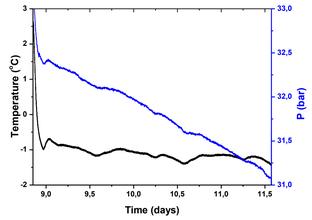


Figure 4. Interface evolution (left) and P-T – time diagram during one of the steps of CO_2 clathrates formation along the experiment (right). A drop in pressure is observed at constant temperature associated with gas entrapment.

As water molecules are removed from the solution, the salt concentration rises near to the interface. Then, the proximity becomes denser and tend to diffuse to the bottom, appearing a gradient of salt amount along the liquid. These facts are checked at 0 ºC and 35 bar by Raman spectroscopy (see table 2 and figure 5).

X-points	1	2	3	4
$A(SO_4)/A(H_2O)$	0.047	0.049	0.057	0.060
$[SO_4]$ (% w/w)	15.1	16.2	19.5	20.5

Table 2. Salt concentration at different depth X-points of the liquid phase.

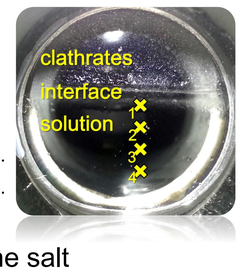


Figure 5. Measured X-points in the liquid phase.

The more clathrates are formed, the higher is the salt concentration. Then, aqueous solution can be supersaturated and sulphate hydrates precipitate (figure 6). This is followed by a drop in SO_4^{2-} concentration of the fluid.

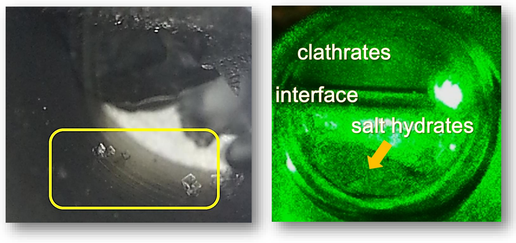


Figure 6. Picture of the chamber taken when salt precipitation starts (left). Image when the green laser impacts on the large amounts of solid at the bottom (right).

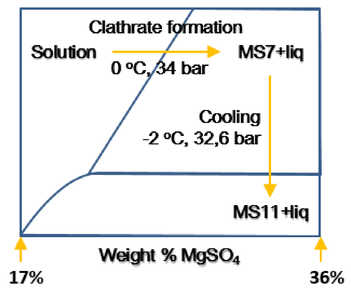


Figure 7. $MgSO_4$-H_2O phase diagram and P-T trajectory through stability regions of the formed salt hydrates.

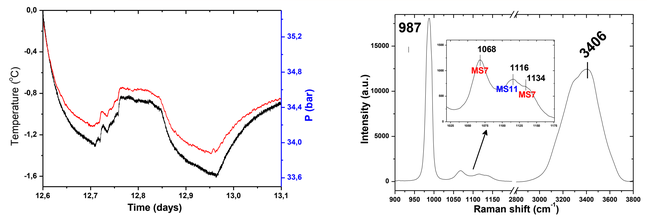


Figure 7. P-T-time transitions associated to sulphate hydrate precipitation which is exothermic (left). Raman spectrum which is registered at -2 ºC and 32.6 bar, after salts crystallization (right). Raman bands shows that, at these conditions, crystals are formed by a mixture of epsomite ($MgSO_4 \cdot 7H_2O$) and meridianiite ($MgSO_4 \cdot 11H_2O$) [3].

The system is heated for recording clathrate dissociation. When heating starts, temperature remains constant during the endothermic process of bonds rupture and then, a sharp increase in pressure is observed (figure 7).

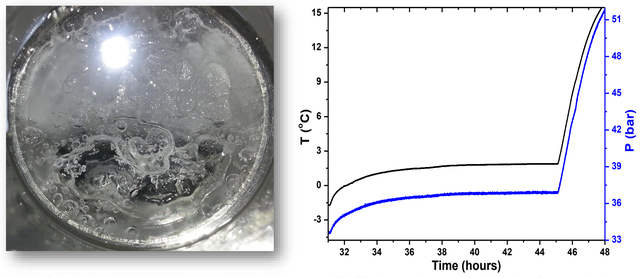


Figure 8. Bubbles ascend (left) and recorded P-T-time diagram (right) of the clathrate dissociation at high heating rate.

In order to follow the effects of clathrates formation in salty water, it is feasible to attend to salt concentration evolution along the experiments.

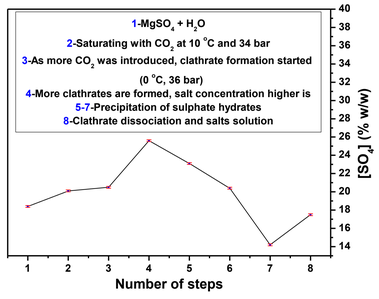


Figure 9. Variation in salt concentration during the salting-out experiment. In a great agreement with experimental error.

Conclusions

The salting-out process may has a great influence on fluid geochemistry of the icy moons and, consequently to the habitability because of its effects on chemicals solubility.
Nutrients can be concentrated near the interfaces.
Distribution of the hydrated phases during competitive crystallization has a direct impact on the nutrient exchange between deep liquid reservoirs and upper layers.
Fluid movement occurs when clathrates dissociate, which might be associated with tidal heating of the moon.

References

[1] Muñoz-Iglesias V. et al. (2014) *Geochim. Cosmochim. Acta*, 125, 466-475.
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