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Salting-out phenomenon induced by the clathrate hydrates formation at high-pressure

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Abstract. Here we show the salting out phenomenon assessment occurring on MgSO₄-CO₂-H₂O system due to the presence of clathrate hydrates under temperature and pressure conditions of the ocean of Jupiter's icy moon Europa. In order to form clathrate hydrates, water molecules are removed from the aqueous solution. This fact causes great impact on solutes concentration, including available nutrients in solution so habitability is directly affected. Both, thermodynamical history recorded in the experiments and visual features following of the system help to understand the truly effect of salting-out on geology and its expression on Europa's surface in application to space exploration.

1. Introduction

Salting-out is the chemical response of a system in which electrolyte and non-electrolyte compounds compete with each other for their dissolution in an aqueous environment. Commonly, when any salt and gas are dissolved in water, gas solubility goes down if the ionic strength increases, which is directly proportional to salt concentration. However, under certain conditions, a similar phenomenon takes places in the opposite way.

One example of geological feature from salting out phenomenon in terrestrial environments is the called brinicle [1]. They are tubular formations, which form in polar regions. Beneath the icy crust of these regions, two-dimensional crystals of water ice known as platelets crystallize from seawater. This process implies salt exclusion, and therefore the formation of brines in interstitial spaces between platelets. As water freezes in the brine inclusions, it generates a volume expansion and the crystal lattice undergoes an increment of internal pressure. This fact may provoke cracks in the ice pack causing release of trapped brine. This dense, cold brine drains downwards from sea ice freezing the water that is in direct contact with and forming a tube of ice.

MgSO₄-CO₂-H₂O system is proposed as an approach of Europa's ocean composition [2]. In this particular system, CO₂ may form clathrate hydrates under the properly conditions. Clathrate hydrates are ice-like crystalline structures, which trap individual gas molecules in cages. This fact makes these minerals to have a starring role in planetary science due to their ability to act as efficient reservoirs of carbon-bearing species like CH₄ and CO₂ [3]. In order to form clathrate hydrates, water molecules are removed from the liquid phase. As a consequence, salt concentration increases and whether this situation continues long enough, hydrated salts may precipitate [4].



Several simulation experiments are carried out at high pressure followed by Raman spectroscopy analysis, which characterize involved chemical species in formation-dissociation of clathrate hydrates from salty water. Here we evaluate how Europa's geochemistry and even habitability could be conditioned by this phenomenon.

2. Materials and methods

In order to characterize the salting out process, $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system is studied under pressure. Reagents used to perform the experiments are $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ($\geq 99.5\%$ purity, Sigma-Aldrich, USA), CO_2 gas (99.998% of purity, Praxair, USA) and Milli-Q water with total organic carbon (TOC) lower than 5 ppb. To run the salting-out experiment it is used a thermostated high pressure chamber. The chamber is equipped with a sapphire window, which allows both optical examination and Raman spectroscopy analysis to follow all changes involved in the evolution of the system. Circulation Thermostat Unistat 815 w (Huber, Germany) is used to control sample temperature, while the cell is connected to a tank of CO_2 (g) by high pressure tubing. A Nd:YAG solid state laser with a wavelength of 532 nm non polarized is used for Raman analysis. After focusing onto a monochromator (Horiba JobinYvon HRi550, 550 mm optical length), with a diffraction grating of 1800 grooves/mm, the scattered light is detected with a Charge Coupled Device (CCD) with 1024x256 pixels cooled to 203 K for thermal-noise reduction. Pixel resolution of the equipment is $2.16 \text{ cm}^{-1}/\text{pixel}$ (binning factor=1). Spectral resolution, with a width slit of 50 μm , results better than 10 cm^{-1} .

Thermodynamical history of the ternary system is recorded to identify all involved transformations. For this purpose, pressure and temperature data are monitored and saved using a personalized Labview program.

Salting-out induced by clathrate hydrate formation is proposed to occur in the aqueous ocean of Europa [5]. Although its distribution is uncertain yet, it is suggested that lays between 20-100 km (24-120 MPa, considering that gravity is $1.314 \text{ m}\cdot\text{s}^{-2}$ and crust composition is dominated by water ice Ih). On this basis, the pressure at Europa's ocean-icy crust interphase would correspond to CO_2 (l) stability region thus P-T conditions of the experiment should respect this constrain.

For convenience, the initial composition of the aqueous solution is 17 wt% MgSO_4 , which is the composition of $\text{MgSO}_4\text{-H}_2\text{O}$ system eutectic point. Employed volume of sample is around 30 mL, which is the half of the total volume of the chamber in order to differentiate gas-liquid interphase at half height of the sapphire window. The system is saturated with CO_2 at about 283 K and 3.3 MPa during few days and then it is brought to 273 K in order to form clathrates. The pressure is maintained in the CO_2 (l) stability region of $\text{H}_2\text{O-CO}_2$ phase diagram. The system is periodically refilled with CO_2 for maintaining the formation rate nearly constant. Liquid phase is immediately homogenised by shaking the chamber after every gas replenishment in order to avoid the presence of gradients.

2.1. Chemical system characterization by Raman spectroscopy

All phases and chemical changes in the ternary system are studied by Raman spectroscopy.

In solution, sulphate ion has a Raman band at 982 cm^{-1} , which is quite strong and narrow (figure 1). Raman shift increases as hydration does for the hydrated salts (Table 1): hexahydrate ($\text{MgSO}_4\cdot 6\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4\cdot 7\text{H}_2\text{O}$) and meridianiite ($\text{MgSO}_4\cdot 12\text{H}_2\text{O}$) respectively. CO_2 occurs as a diad in the spectrum due to Fermi resonance. Raman shift and band shape of the diad is modified for different CO_2 states. Water Raman band may show different shapes regarding alterations such as concentration or dilution of salt in solution, thus it allows to discriminate between clathrates and water ice as well.

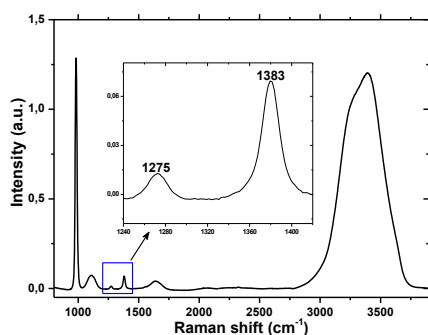


Figure 1. Raman spectrum of liquid phase in the chamber.

Vibration mode	Raman shift (cm ⁻¹)
$\nu_1\text{-SO}_4^{2-}$	981.9 (aqueous)
	983 (MgSO ₄ ·6H ₂ O)
	986 (MgSO ₄ ·7H ₂ O)
	990 (MgSO ₄ ·12H ₂ O)
Fermi doublet-CO ₂	1285/1388 (gas)
	1280/1286 (liquid)
	1275/1383 (aqueous)
	1276/1381 (clathrate)
OH-stretching	2900-3900

Table 1. Frequencies of key bands.

2.2 Calibration.

In order to quantify salt concentration, the spectrometer is calibrated with 5 aqueous solutions 5, 10, 20, 25 and 30 wt% MgSO₄. The ratio between sulphate and water molecules vibration band areas, i.e. $a = A(\text{SO}_4^{2-}) \cdot [A(\text{H}_2\text{O})]^{-1}$, are related to salt concentration by a second order polynomial (1), after spectrum normalization using Raman isosbestic point from liquid water [6].

$$\text{wt}\% = (-10,67 \pm 0,45) + (6,7E2 \pm 1,7E1) \cdot a + (2E3 \pm 1E2) \cdot a^2 \quad (1)$$

3. Results and discussion

Thermodynamical evolution of the system during the formation/dissociation of clathrate hydrates is recorded continuously and plotted on a P-T-time diagram, while spectral changes are followed at discrete points (figure 2). The most relevant points are labeled from 1 to 6 and they are also pointed on H₂O-CO₂ phase diagram in figure 3. Involved thermal transformations as eutectic and peritectic points of MgSO₄-H₂O binary system are labeled as well.

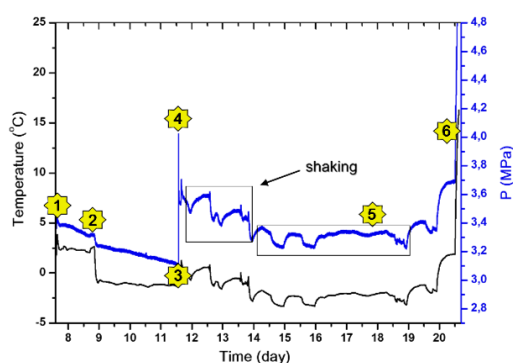


Figure 2. P (upper line)-T (bottom line)-time diagram registered along the salting-out experiment.

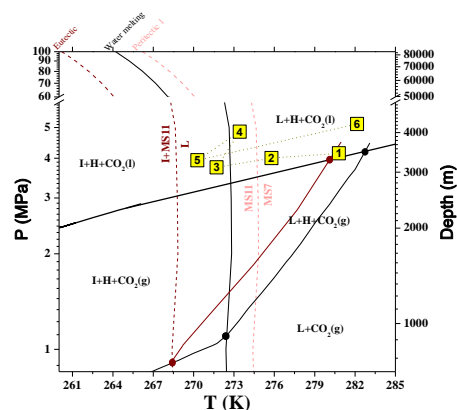


Figure 3. Phase diagram of H₂O-CO₂ system. Numbers correspond to explored points along one run experiment (as in figure 2).

The onset of clathrate hydrate formation occurs at the turbidity time [7], which denotes the first appearance of stable clathrate crystals (see figure 4). The crystals growth upwards from the liquid-gas interphase, therefore clathrate formation requires starting mainly from aqueous CO₂. This stage

corresponds to point 1 on the P-T-time diagram. When clathrate hydrates start to grow, several drops in pressure at constant temperature are observed (points 1-2-3 on the P-T-time diagram).



Figure 4. Pictures showing the liquid-gas interphase through the sapphire window. **(a)** Progress of a turbid front in the liquid phase at the turbidity time. **(b)** Clathrate hydrate layer over liquid-gas interphase.

When clathrate hydrates layer form, Raman spectrum of the Fermi diad of CO₂ (g) is observed (figure 5). In spite of maintaining the pressure into the stability region of liquid CO₂, the explored points along the experiment are very close to the limit between the stability regions of both liquid CO₂ and gas, thus it is explained that there is CO₂ (g) in the upper part of the chamber. Entrapment of CO₂ molecules in cages of clathrates modifies the vibration frequency of molecular bonds and therefore Fermi doublet is shifted to lower frequencies (figure 5). Shape of hydroxyl stretching band evolves as well, showing a new broad peak around 3200 cm⁻¹.

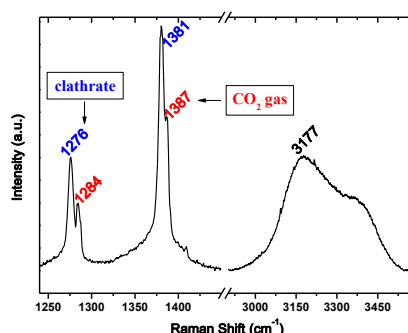


Figure 5. Raman spectrum of CO₂ (g) and CO₂-clathrates. A clear displacement of CO₂-clathrates Fermi diad is observed upon clathrate formation.



Figure 6. Measured points as a function of depth.

X-points	1	2	3	4
$A(\text{SO}_4^{2-}) \cdot [A(\text{H}_2\text{O})]^{-1}$	0.047	0.049	0.057	0.060
$[\text{SO}_4^{2-}]$ (% w/w)	15.1	16.2	19.5	20.5

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

Point 4 on P-T-time diagram corresponds to a refilling step that helps CO₂ to diffuse throughout the clathrate layer and replenish the quantity of CO₂ in solution and maintain the clathrate growth almost constant. After that, chamber is shaking assisting clathrates to nucleate. As more clathrates form, more water molecules are removed from the solution and salt concentration raises near the interphase. Then, the proximity becomes denser and tends to diffuse to the bottom, appearing a gradient of salt along the liquid phase (Table 2). This gradient varies from 15 wt% to 20 wt% MgSO₄. If salt concentration goes

on to increase, aqueous solution can be supersaturated until hydrated sulphate precipitate and it implies registering wide variations in pressure due to the volume expansion caused mostly by meridianiite ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$) precipitation than that of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). That step corresponds to the P-T-time diagram region labeled as point 5. Large amounts of solids at the bottom of chamber are visually detectable but also by Raman spectroscopy (figure 7) which shows a mixture of both salts. Finally, point 6 corresponds to a heating step when clathrate dissociation occurs. This is an endothermic process which is recorded at around 282 K.

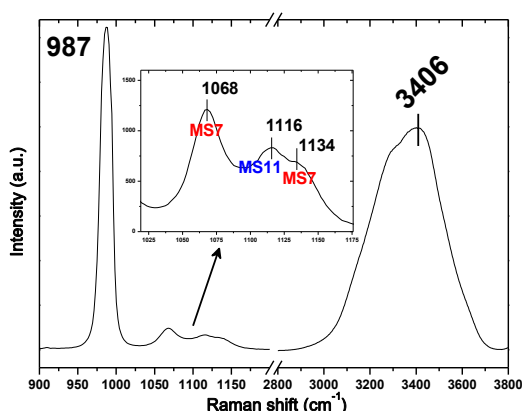


Figure 7. Raman spectrum of the solids at 271 K and 3.3 MPa shows a mixture of epsomite and meridianiite, as it is expected attending to the phase diagram.

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 8). For this assessment, measures are taken with the Raman laser focused on the middle of the liquid phase. It is clear that first, salt concentration raises due to clathrate formation, then it decreases due to salt precipitation and after clathrate dissociation salt concentration recovers its initial value.

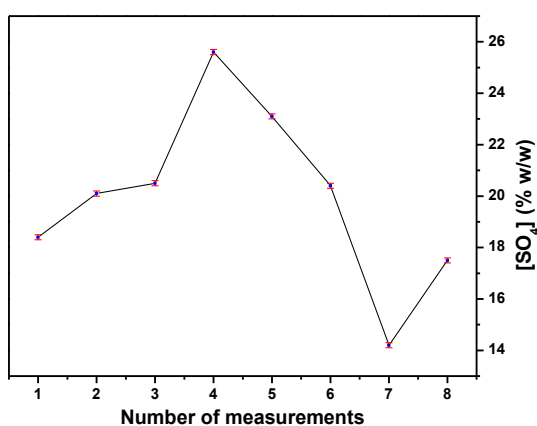


Figure 8. Variation in salt concentration according to the number of the most representative measurements along the salting-out experiment. It is in a great agreement with experimental error.

4. Conclusion

Raman spectroscopy analysis and thermodynamical information are used here to follow the evolution of salt-gas-rich fluids during cooling. It allows detecting clathrate hydrate formation/dissociation processes and precipitation of minerals involved in $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system.

Salting-out takes places in $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system after clathrate hydrates formed appearing a gradient of mineral density which drives fluid convection. Besides, gradients in salt concentration may derive to transient stratification before fluid convects. Salting-out associated to the presence of clathrates may have a great influence on Europa's geological activity due to changes in several physical properties of the system (e.g. total volume, density, or thermal properties).

It is assumed that Ganymedes' fluids have a similar chemistry to Europa, but they are distributed in deeper layers up to 1.3 GPa. Fluids are sandwiched between different high pressure phases of water ice instead of being in direct contact with rock, like occurs in Europa [8]. We predict that formation of CO_2 high pressure clathrate hydrates may have different consequences on salting-out and therefore on remnant brines density. HP-clathrates require lower amount of water dictated by their stoichiometry so salting –out impact would be less pronounced at the bottom of the ocean.

Salting-out effects may be expressed on surfaces of the icy moons as geological structures, which will be explored by future space missions to the icy moons.

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