

Petrographic/thermodynamic study of mineral assemblages of the H₂O-MgSO₄-CO₂ system

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Abstract

We investigate some petrographic and thermodynamic characteristics occurring during formation of clathrate hydrates from salty solutions. It is already suggested that the salting out effect has a great influence in the structure and composition of the icy satellites [1]. Here we show the textural evolution of the mineral assemblages formed when the H₂O-MgSO₄-CO₂ fluid is cooled under pressure and temperature conditions of Europa. Mineral formation/dissociation is recorded during pressure and temperature trajectories in order to determine how salting-out operates on the distribution of materials in icy crust of the icy moons. Detailed characterization of the involved mineral phases is carried out by Raman spectroscopy.

1. Introduction

Clathrate hydrates may have a starring role in planetary science due to their ability to act as efficient reservoirs of gases like CH₄ or CO₂. Some clathrate-forming volatiles, hydrated salts and water ice have been already detected on Europa's surface by remote spectroscopy [2, 3]. The formation of CO₂ clathrates is feasible under the conditions of Europa's internal ocean [4]. The presence of salts in the aqueous solutions affects clathrate hydrate stability by lowering the dissociation temperature [1]. However, under certain conditions, the gas exhibits more favoured interactions with water molecules than salts removing those from the system in order to form clathrates. When this process takes place, salinity increases in the remnant solution, which is known as salting-out phenomenon. We uphold that salting-out might has high impact on the icy moon geology and habitability.

Combining textural and thermodynamic characterization of the forming minerals, we should find signatures useful for the interpretation of some ambiguous remote data regarding endogenous processes and materials.

2. Methodology

Methods of experimental petrography are applied here to investigate the geochemistry and phase relationship of the interior of icy moons.

We run a salting-out experiment in a thermostated high pressure chamber equipped with a sapphire window ($\varnothing=2.5$ cm), which allows both, optical examination and Raman spectroscopy analysis. We evaluate mineral transformations and record thermodynamic changes of the system H₂O-MgSO₄-CO₂ using a personalized Labview program. The initial composition of the aqueous solution is 17 wt% MgSO₄, saturated with CO₂. All relevant processes and phases that occur during the variation of pressure and temperature are monitored, photographed and filmed.

3. Results

The experiment starts at room temperature and around 30 bar. At these conditions, the sample is shaken in order to force the formation of CO₂-clathrates.

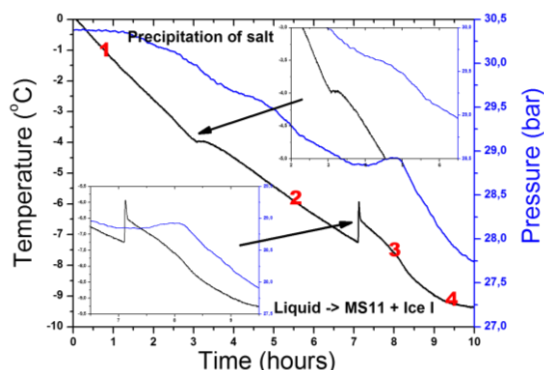


Figure 1: P-T-time diagram registered during cooling. Numbers indicate stages where some textural changes of the process occurred.

Figure 1 shows some phase changes when the temperature is decreasing. Upon cooling at 1°C/h, two main exothermic transformations are registered

in the T curve. The first one takes place as an inflexion at -4°C , in which some salt precipitates because of the salting-out. The second positive peak in temperature corresponds to salt formation after crossing the eutectic. Crystallization of meridianite (MS11) + ice I presents a significant ΔV , which is observed with an abrupt change in pressure [4].

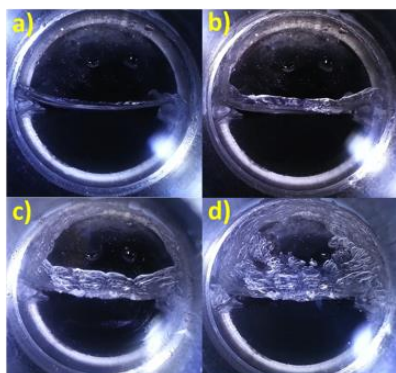


Figure 2: CO_2 -clathrates formation during the primary laminar growth at 2°C and 32 bar.

Some interesting macroscopic features are observed during the T-P evolution. In Figure 2, the laminar growth of clathrate hydrates before cooling is observed. The formation of these primary clathrates occurs between the fluids interface and in contact with the cold surface of the chamber walls and window. They present a significant grain size and are rather transparent. After that, when clathrates occupy all the room left by the liquid, they progressively recrystallize to form a massive texture until the original layering disappear (Fig. 3a and 3b).

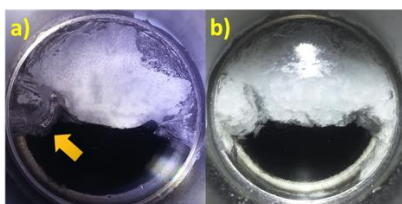


Figure 3: Changes in the crystal texture after primary clathrates crystallization. Note that the original layering pointed by the arrow (a), disappears (b).

Since the experiment starts with a CO_2 -supersaturated solution, some bubbles of CO_2 (g) appear in the liquid (Fig. 4-1) [5]. As mentioned before, clathrates crystallize taking advantage of available interfaces, like the bubbles' surface (Fig. 4-2), producing a spherical clathrate coating.

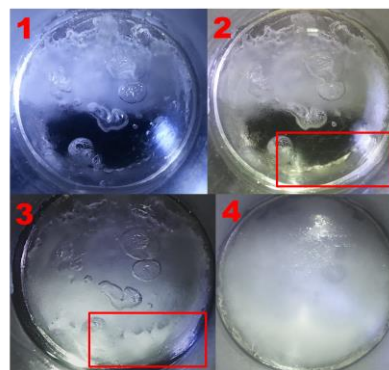


Figure 4: Observations at different points labeled in figure 1. Sulfates potentially crystallizing as consequence of the salting-out are in the red box.

4. Summary

Petrographic and thermodynamic information are used here to follow the evolution of salt-gas-rich fluids during cooling. Several features are observed, e.g. crystal layering and bubble coating, which are associated with change processes in the system. Some of these processes may be expressed on the surface as geological structures, which will be explored by future space missions to the icy moons.

References

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