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Assemblages of hydrated minerals within Europa from the system H_2O-$MgSO_4$-CO_2

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Abstract

Some geophysical and geochemical data of Europa suggest the presence of gas clathrates and hydrated salts in the interior of the satellite. In this study, the experimental crystallization and dissociation of CO_2-clathrates in presence of solid phases formed from supersaturated $MgSO_4$ aqueous solutions, at liquid CO_2 stability field, is reported from the Raman spectroscopy analysis of the system CO_2-$MgSO_4$-H_2O. We show how crystallization of gas clathrates is affected by the presence some hydrated sulfate phases

1. Introduction

Attending to the data available about Europa's surface composition, and its self-induced magnetic field, which suggests the presence of liquid water and electrolytic salts [1], we can assume that the ingredients to form gas clathrates and salt hydrates are present inside the moon. It is known that surface is mainly formed by water ice, but reddish materials have been also detected in some lineaments and chaos regions. These non-water ice compounds are interpreted as $MgSO_4$-rich hydrated minerals [2]. In addition, UV spectral signatures indicate the presence of volatiles such as CO_2, H_2S and SO_2 [3]. On the other hand, relatively high pressure and low temperature in the crust and the ocean are propitious conditions to gas clathrate stabilization. Previous work demonstrates the possible formation of $MgSO_4$ hydrated minerals at Europa interior conditions, starting from supersaturated solutions [4]. Since few data exist about the CO_2-clathrate behavior in the field where CO_2 is liquid, and in presence of supersaturated $MgSO_4$ solutions and, considering that stability regions of some solid phases overlap, we study their co-existence, the effect of the salt on the temperature dissociation of the CO_2-clathrate, and the implications of our results to the satellite's evolution.

2. Equipment and procedure

Experiments are performed using a high pressure cell equipped with a sapphire window and temperature-pressure sensors [4]. Formation of hydrated sulfates followed by CO_2-clathrate stabilization is carried out at 268 K, at several $MgSO_4$ concentration (5, 17 and 30 wt %) and pressures up to 60 bar. In order to do the experiments, CO_2 gas is injected to the solutions, which are previously frozen and powdered. Once gas clathrate stabilization is confirmed by Raman signatures, the system is compressed with liquid CO_2 and then it is heated in order to record the dissociation point from the variation of both, pressure-temperature data and the spectroscopic signatures.

3. Results

A drop in the dissociation temperature of the CO_2-clathrate occurs when it is formed from frozen powdered solutions at 5 and 17 wt % of $MgSO_4$, compared to the pure solution. This result agrees with preceding theoretical estimations [5]. Experiments start at 268 K from frozen solutions with 5 and 17 wt %, under enough pressure to liquefy the CO_2 gas . At the initial temperature, CO_2-clathrate co-exists with an assemblage of water ice (I) and meridianiite (MS11) in several proportions. When the system with 5 wt % of salt is heated from 269 K to 272 K, water ice and gas clathrate are stable with a remaining liquid (L), while starting with the 17 wt % frozen solution, the eutectic solid previously formed melts at 269 K without the formation of another salt or water ice phase. Raman spectra of the system with 5 wt % of salt are shown in Fig. 1 at three different situations: once the clathrate is stabilized (269 K, 31 bar), when gas clathrate begins to dissociate and liquid CO_2 is observed (268 K, 33 bar), and after its complete dissociation (293 K, 58 bar). When the gas clathrate is present in the system, the salt concentration in the remainder aqueous solution is higher than in the original solution, since the gas clathrate cage removes most of the H_2O molecules from the environment. Besides, CO_2 peaks are slightly closer and increase in intensity respect to the moment when the molecule is dissolved in the liquid solution.

If the run is performed with 30 wt % of salt, gas clathrate is formed in presence of MS11+I. The dissociation point depends on both, the ratio between sulfate/clathrate formed, and in the heating rate. Thus, when the system is heated from 269 K at 0.5 K/h, incongruent melting occurs to form H+MS11+L. This assemblage is later transformed to H+MS7 (epsomite)+L, when the system is above 275 K. MS7 is stable beyond 300 K but not the hydrate. The stabilization of MS7 decreases the SO_4^{2-} ion content in the residual solution, which results in the dissociation of the gas clathrate at higher temperature than expected (Fig. 2). Nevertheless, when the heating is faster (at 3 K/h), epsomite is not formed. Then, in this case the global effect observed is an increase in the salt concentration in the solution respect to the initial (inset Fig. 2), obtaining a decrease in the gas clathrate dissociation temperature.

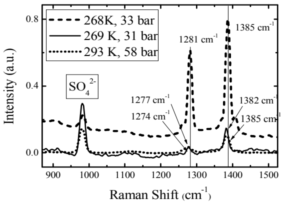

Figure 1: Raman spectra of the aqueous solution with 5 wt % $MgSO_4$ and saturated in CO_2 at several states: CO_2 in the clathrate structure (solid line), in liquid state (dashed line) and dissolved (dotted line).

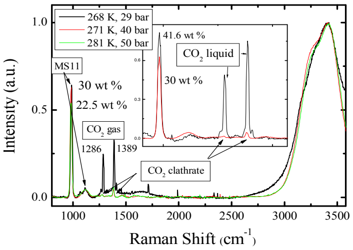

Figure 2: Raman spectra of the system at 30 wt % $MgSO_4$ during the experiment at slow heating; MS7 precipitation promotes the drop of SO_4 ion concentration from 30 to 22 wt %. Raman spectra of the system during the fast heating experiment, without MS7 precipitation, is in the inset; final sulfate concentration results 42 wt %.

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