

## Monitoring by Raman Spectroscopy of CO<sub>2</sub> Clathrate Formation from Electrolyte Solutions. The Performance to Icy Satellites

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### 1. Introduction

Clathrate hydrates are solid crystal structures of water, with cavities inside containing gas molecules, which form at low temperature and high pressure. These solids have not been detected in the outer solar system yet. However, their presence can be assumed because there are environments where both, the forming compounds and the required thermodynamic conditions coexist. The putative ocean of Europa may be an example.

In the present work, we crystallize and dissociate CO<sub>2</sub> clathrates from an aqueous solution of MgSO<sub>4</sub> and CO<sub>2</sub>. We assume that the aqueous magmas from the Europa interior are salt-rich. This assumption is based on the NIR Galileo observations of dark terrains, which seems to be endogenous and composed by salt hydrates [1].

### 2. Experimental apparatus and procedure

Experiments were carried out in the High Pressure Planetary Environment Chamber (HPPEC), a simulation chamber facility of Centro de Astrobiología, Madrid, Spain. Runs were done at several pressures to obtain the phase diagram of the system H<sub>2</sub>O-CO<sub>2</sub>-MgSO<sub>4</sub>. We have analyzed the clathrate kinetic formation with the iH550 Spectrometer (Horiba Jobin Yvon), by using a solid state laser Nd:YAG 532 nm.

### 3. Results and conclusions

Crystallization and dissociation cycles of CO<sub>2</sub> clathrates in MgSO<sub>4</sub> aqueous solution [2] at different

concentrations were monitoring by Raman spectroscopy. In Figure 1 we compare the two Fermi dyad peaks ( $\approx 1280$  and  $1380$  cm<sup>-1</sup>) of CO<sub>2</sub> molecule in different states: gas, dissolved and enclathrated, respectively. We highlight that it is possible to differentiate between each state of the molecules by Raman spectroscopy, despite the Raman shift difference is very small ( $\approx 1$  cm<sup>-1</sup>) between the dissolved and the clathrated CO<sub>2</sub>. Figure 2 shows the spectra of several solutions of MgSO<sub>4</sub> at different concentration with which the calibration has been done (left) and the use of it to study de variation of salt concentration during the clathrate formation (right) [3]; it should be note that the corresponding peak area of the SO<sub>4</sub><sup>-</sup> around 970 cm<sup>-1</sup>, decreases after the crystallization. This could be due to the fact that salts are expelled from the clathrates structure, increasing the concentration in the remaining aqueous solution. If the eutectic composition is exceeded, precipitation takes place, seeing a decrease of the sulfate peak.

Features explained previously in the Figures 1 and 2 can be associated to the evolution of a cryomagma trough the time. Therefore, these results are of a deep planetologic importance because it can explain satellite internal differentiation and cryovolcanism processes which may occur in the satellite. Furthermore, we support the Raman spectroscopy as an especially useful instrument for the detection of clathrates.

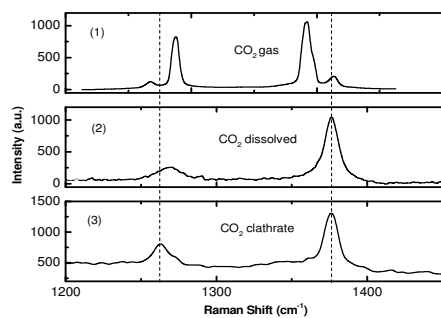


Figure 1. Raman spectra of the CO<sub>2</sub> gas (1), CO<sub>2</sub> dissolved (2) and the CO<sub>2</sub> inside the clathrate structure (3).

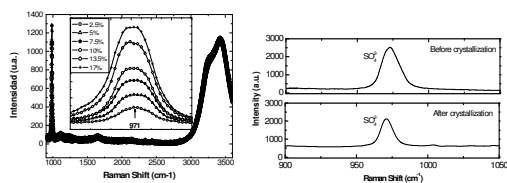


Figure 2. Raman spectra of several aqueous solution of MgSO<sub>4</sub> used for the calibration (left) and decrease of sulfate concentration after clathrate formation (right).

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## References

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