CHARACTERIZATION OF THE DIFFERENTIATION PROCESS BY CLATHRATION IN EUROPA SATELLITE USING RAMAN SPECTROSCOPY.

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Introduction: Clathrate hydrates are solid crystal structures of water, with cavities inside containing gas molecules, which form at low temperature and high pressure. In icy satellites of the outer solar system, such as Europa, have been detected the clathate-forming compounds and also exist the conditions required for their formation. Based on this, we can assume that gas clathrates may be present in those satellites, although they have not been detected yet.

In the present work, we crystallize and dissociate CO_2-clathrates from an aqueous solution of $MgSO_4$ and CO_2. 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 endogeneous and composed by salt hydrates [1]. Our results confirms the theoretical models which predict that clathrates are stable from the icy crust to the potential salty ocean that may exist below the icy crust [2, 3].

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_2O-CO_2-$MgSO_4$. We have analyzed the clathrate kinetic formation with the iH550 Spectrometer (Horiba Jobin Ybon,), by using a 1200/1800/2400 grooves/mm diffraction grating and a solid state laser Nd:YAG 532 nm.

Results: In Figure 1 we compare the two Fermi dyad peaks (≈1280 and 1380 cm^{-1}) of CO_2 molecule in different states: gas, dissolved and enclathrated, respectively. We observe that it is possible to differentiate between each state of the molecules by Raman spectroscopy, despite the Raman shift difference is very small (≈1 cm^{-1}) between the dissolved and the clathrated CO_2 . It should be note that the peak area around 980 cm^{-1} corresponding to the $MgSO_4$ decreases after the crystallization (see the lowest spectra in Fig. 1). This could be due to the fact that sulfate (and all salts) is 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 about 980 cm^{-1}.

Conclusions: These results are of a deep planetologic importance because it can explain satellite internal differentiation and cryovolcanism processes which may occur in the satellite. Features explained previously in the Fig. 1 can be associated to different stages of the differentiation process (Fig. 2). Figure 2 shows schematically the evolution of a cryomagma trough the time: (Fig. 2.A) Cryomagmatic chamber with H_2O, salts y volatiles, (Fig. 2.B) Clathrate formation and concentration of the salt in the remaining solution (with or without precipitation), (Fig. 2.C) Differentiated chamber by clathration and (Fig. 2.D) Cryomagma ascent after depressurization and clathrate destabilization, which produce the positive buoyancy of the liquid respect to the icy crust. Hydrated salts observed by Galileo's probe on the surface support this theory because it appear as extrusions from the inner in the geologic accidents mentioned [1].

Similar experiments will be performed in the future with other salts (Na_2SO_4 and mixtures) and volatiles (SO_2, H_2S) also detected in Europa. From the obtained data, we will propose a compositional model for Europe to support Raman spectroscopy as a potential instrument for the next missions to the satellite.

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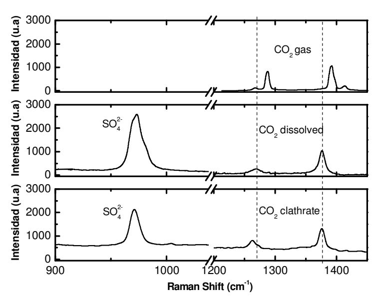

Figure 1. Spectra of the CO_2 gas, CO_2 dissolved in an aquous solution of $MgSO_4$ and spectra of the same compounds after clathration.

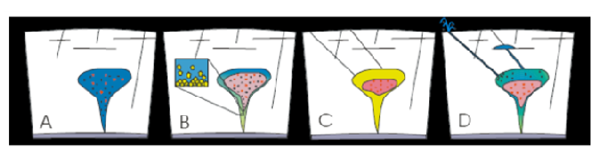

Figure 2. Magmatic differenciation by clathration and subsequent cryovolcanism process

References: [1] Dalton J. B. et al. (2005) *Icarus, 177*, 472-490. [2] Prieto-Ballesteros O. et al. (2005) *Icarus, 177*, 491-505. [3] Kivelson M. G. et al. (2000) *Science, 289*, 1340-1343.