EVALUATION OF THE POSSIBLE PRESENCE OF CO₂-CLATHRATES IN EUROPA’S ICY SHELL OR SEAFLOOR. O. Prieto-Ballesteros¹, J. S. Kargel², M. Fernández-Sampedro¹ and D. L. Hogenboom³. ¹Centro de Astrobiología, INTA-CSIC. Torrejón de Ardoz, 28850 Madrid. Spain (prietobo@inta.es). ²Astrogeology Team. USGS. Flagstaff, Arizona. USA (jkargel@usgs.es). Lafayette College, Easton Pennsylvania, USA (hogenbod@mail.lafayette.edu)

Introduction.
The mineralogy of Europa's crust has been partly revealed by reflectance spectroscopy and geochemical modeling using available sources of data from space missions and earth-based remote sensing. The exact chemical composition of the non-ice components is still under discussion because the infrared spectra can be interpreted as three different candidates: a) salt hydrates, b) hydrates of sulfuric acid, c) H₃O⁺. Infrared data from the noisy mid-IR region obtained by Galileo has detect additional substances on the surfaces of Europa, Ganymede and Callisto. A peak at 4.25 µm, for example has been interpreted as CO₂ [1]. However, CO₂ ice is unstable at the surface (ultravacuum and low temperatures) of Europa or Callisto. Thus, they have proposed the possibility that this signal comes from clathrates, so we have study the stability of CO₂ clathrates along the crust and the ocean.

The ultraviolet sensor of Galileo also provides data about CO₂ and other volatile materials like SO₂. Recent studies about the distribution of CO₂ determined that it is correlated to the H₂O₂ distribution [2, 3]; both are concentrated near the equator on the leading hemisphere. Carlson (2004) proposes that the CO₂ is the radiolytic product of exogenous meteoritic carbonaceous material. Another possibility is that both H₂O₂ and CO₂ comes from the radiolytic destruction of clathrates and other ices. Contrarily, an endogeneous source for CO₂ has been supported by some geochemical studies [4, 5]. Gases from the interior, therefore, would be involved in the evolution of the ocean and the icy crust. Degassing has occurred during the evolution of the terrestrial planets, Io, Titan, Triton, comets, and some evolved asteroids. Some of these, including Earth, Titan, and Io, continue to outgas. It would not be surprising if Europa similarly outgasses into its ocean and icy crust, as though it is an ice- and brine-covered Io-like object. However, having an ocean, the fate of gases vented from Europa's deep interior would be different from the situation on Io; clathrates likely would form.

Stable zones for clathrates in Europa.
The stability of clathrates in the crust and the possible ocean of Europa depends on the P-T regimes derived from the thermal gradient in the interior of the satellite, and hence the thickness model of the ice crust. Assuming different thermal gradients, one for a thick crust [7, 8] and other for a thin one [9, 10], stable zones for CO₂ clathrates can be traced (Fig.1). First we consider conditions required for clathrate formation and stability, and then gravitational stability.

Using the data from [11] to extrapolate the experimental data, the surface regime of Europa is obtained. Both thermal gradients from different models cross the dissociation curve of CO₂-clathrate in the range from 6.08-0.60 µbar CO₂ partial pressure. On Europa, this pressure range corresponds to a depth range of about 50-500 µm. Below this range the CO₂ clathrates are stable all along the icy shell and could form given a supply of CO₂. At shallower depths the clathrate would not form, but if formed at the required pressure but then erosionally unburied by some process, it might survive metastably or exist stably in inclusions contained in ice crystals due to the elastic strength of the crystal. The clathrates could also be stable in the ocean for both models. If the ocean is convective and isothermal, clathrates would be stable to the seafloor.
Bouyancy of CO$_2$-clathrates in Europa’s crust and ocean.

To model whether the CO$_2$-clathrates sink or float in the crust and the ocean, density data are needed. The density of a clathrate depends on both the lattice parameters and the composition. CO$_2$ clathrate has sI crystallographic structure, with 6 larger cavities and 2 smaller per unit cell. The unit cell dimension of CO$_2$ sI structure as function of the temperature has been calculated by Udachin et al. [12] as:

\[
a(T)/\text{Å} = 11.81945 - (9.08711 \cdot 10^{-5} \cdot T) + (4.59676 \cdot 10^{-6} \cdot T^2) - (8.35548 \cdot 10^{-9} \cdot T^3)
\]

As these authors pointed out, thermal expansion of the clathrate crystal lattice is much greater than the ice one. The guest specie fills bigger cells more comfortably. The occupancy of the crystal lattice is critical for the final density value, and it is dependent on pressure and temperature. A clathrate with sI structure and no guest molecules in the cages has a density of 0.8 g cm$^{-3}$ [13] (a concept only, because with no guest molecules this structure would collapse), while if all the cages are filled the density rises to 1.09 g cm$^{-3}$ (Fig. 2). On the other hand, studies by raman microspectroscopy about pressure dependence of the occupancy of sI cages by cyclopropane hydrate [14] result in an increase of the occupancy at higher pressures. Therefore, density will be greater at higher pressure while in the upper crust there would be an increase of the empty cavities. In any case, the clathrate could be either float in the brine (if the brine has, for example, a eutectic Mg-Na-sulfate or eutectic chloride composition [15]), or it might sink.

Conclusions.

CO$_2$-clathrate is stable in most of the crust and the ocean of Europa's satellite. Cryostatic pressure from the icy shell will result in the complete filling of the sI structural cavities of these clathrates, and thus in bigger densities. Depending on the final concentration of the salts in the ocean, clathrates should sink or float into the ocean. In contrast, in the upper levels of the icy shell, a decrease in pressure causes a fraction of the cavities to be empty, starting with the smaller ones. Subsequently, clathrates could be bouyant in these levels of the crust.

There are genetic differences between clathrates formed in the ocean, from the liquid water and from the crust. In the first case, the clathrates would be igneous minerals because they crystallize from the aqueous cryomagma, while the clathrates formed from ice would be formed by metamorphism of the water ice.

The radiation environment on the surface of Europa would affect CO$_2$ clathrate as it does to water ice. Depending on the penetration depth of the radiations, clathrates would be reached and destabilized. Then, the CO$_2$ signal detected by the Galileo sensors in the most affected hemisphere by radiation could be due to clathrates. Laboratory simulations of this are in progress.

References: