CLATHRATE HYDRATES IN JUPITER'S SATELLITE EUROPA AND THEIR GEOLOGICAL EFFECTS. O. Prieto-Ballesteros[1], J. S. Kargel[2], M. Fernández-Sampedro[1] and D. L. Hogenboom[3] . [1]Centro de Astrobiología. INTA-CSIC. Torrejon de Ardoz, 28850 Madrid. Spain (prietobo@inta.es). [2] Astrogeology Team. USGS. Flagstaff, Arizona. USA (jkargel@usgs.es). Lafayette College, Easton Pensylvania, USA (hogenbod@mail.lafayette.edu)

Introduction: The crust of Europa is dominated by water ice, but some contaminants have been detected on the surface. Several hydrates have been mentioned as part of the composition of the mineralogy of the surface of Europa such as sulfuric acid hydrates [1, 2] and salt hydrates [3, 4, 5, 6]. Clathrate hydrates are also minerals to be considered to be formed in the crust and the possible ocean of Europa.

Physical chemical properties of the hydrates are sometimes substantially different from water ice, so they could locally regulate the final state of the crust and the ocean. Parameters such as thermal conductivity, density and low melting points of these materials are useful to incorporate in the physical geological models of Europa.

Clathrates from brines.

Electrolytes in solution are usually taken as clathrate formation inhibitors. Ions in solution affect the formation of the clathrates in two ways: a) the strong attraction of the water to the electrolytes, and b) the salting-out effect, or the decreasing solubility of the gas molecules into the salty water due to the clustering of the water with the ions. The effects of some chlorides such as NaCl or $CaCl_2$ in the clathrate formation are already quantitatively known. These systems have been extensively studied experimentally and theoretically because they are frequent in the Earth seawater and in many fluid inclusions of terrestrial rocks.

The composition of water reservoirs in Europa have been proposed to be salty from magnetic data analysis and geochemistry modelling [7, 8, 9]. Sulfate-enriched brines for Europa's water reservoirs have been supported by some studies. Since planetary objects generally also contain and release gases from their solid interiors, various gases are also likely constituents of Europa's ocean and floating icy shell. Unlike most planetary objects, which release their gases onto their surfaces, where they form atmospheres or surface condensates, or else escape into space, Europa's ocean is likely to contain vented gases up to the limit of high-pressure saturation. Free fluid phases can form and then may be vented as gases through the icy shell. However, ocean saturation of small apolar gas molecules generally should result in formation of clathrate hydrate phases.

Candidate guest molecules to form clathrates in Europa are CO_2 and SO_2, both observed on the surfaces of some Galilean satellites [10, 11] and are geochemically plausible [5, 12]. Other likely clathrate-forming guest molecules in Europa's ocean and icy shell may include N_2 and perhaps O_2 (the latter from radiolytic processes), and possibly CO and CH_4. CO_2 is especially likely and probably abundant, because it is observed and abundant from Venus to the most distant realms of the Solar System, including comets. SO_2 may be abundant on Europa if Europa's rocky interior and the geochemical processing there is anything like that of Io.

We use a modification of the Hammerschmidt equation (eq. 1) [13, 14] to calculate an approximation of the effect of the magnesium sulfate to the formation of CO_2 clathrates at constant pressure as an example of how salts may affect clathrate stability in Europa:

$$\left(\frac{1}{T_d^0}-\frac{1}{T_d}\right)=\frac{n\cdot\Delta H_{FUS(I)}}{\Delta H_{DIS}}\left(\frac{1}{T_f^0}-\frac{1}{T_f}\right) \qquad \text{(eq. 1)}$$

where: T_d^0 and T_d are the temperatures at which CO_2 dissociates in pure water and in the solution, ΔH_{DIS} is the enthalpy of dissociation of CO_2 clathrate, n is the number of water molecules in hydrate formula, $\Delta H_{FUS(I)}$ is the enthalpy of fusion for pure ice and T_f^0 and T_f are the melting temperatures of ice and the electrolyte solution.

The result (Fig. 1) indicates that dissolved magnesium sulfate decreases the crystallization point of the clathrate in a similar manner to the way the salt itself reduces the melting point of water ice.

Geological implications: The presence of large amounts of hydrates (clathrates, sulfuric acid or salt hydrates) produce some effects on the geology of Europa. Clathrate and salt hydrates have low thermal conductivities, as some experimental analyses indicate [15, 16]. If they are present in the icy crust they would produce zones of high thermal gradient and perhaps enhanced geological activity of several types.

As has been theoretically predicted, CO_2 clathrates may crystallize from salty water reservoirs at lower temperatures than from pure water. The inhibition of formation only amounts to about 2 K at the eutectic proportions og $MgSO_4$ (17%). On one hand, this means that insofar as clathrates are concerned, the salts do not have a large effect. On the other hand, the introduction of clathrate-forming gases into a salt-saturated or undersaturated ocean may have a large effect on the salts. Formation of clathrates removes water from the solution, so there will be a higher concentration in ions as soon as the clathrates are formed. This property has been used to desalinate terrestrial seawater. If this process occurs in an aqueous magmatic chamber in the crust of Europa, clathration could result in a cryomagmatic differentiation. The formation of clathrates would separate the crystals from the more concentrated brine magma by density. If the destruction of the clathrate layer occurred by any movement or fracturation, clean water ice could ascend through the brine to higher levels.

Destruction of clathrate layers near the surface could produce catastrophic processes because of the fast liberation of gases, and the large negative volume change of the solid phases upon dissociation and loss of the free gas phase. Fracturing and gravitational collapse of terrain could ensue. It could be an autocatalytic, even catastrophic process if fracturing and depressurization causes more clathrate to dissociate and especially if gas-saturated brine from the ocean jets through fractures and erosionally widens them. Chaotic terrain on Europa could conceivably be related to this process, as it may also on Mars, Earth, and Triton [17]. That also could be responsible for explosive cryovolcanic events, as some authors have already pointed out [17, 18, 19].

The transition from a condensed phase (such as clathrate) to a multiphase system containing a free vapor phase is always endothermic if chemical reactivity is not involved (as with clathrate dissociation forming a free vapor phase). Therefore, cooling and crystallization of ice (possibly also salts if the system is already salt-saturated) will occur during dissociation of ice-equilibrated clathrates (as Europa's are expected to be). However, the system includes a negative volume change of the condensed phase assemblage if the free vapor phase is vented; therefore, a continuing fracturing process and collapse of the system can occur in a runaway process of chaotic terrain formation. Energy for the process can be supplied by effervescing oceanic brine gushing through and widening the fractures.

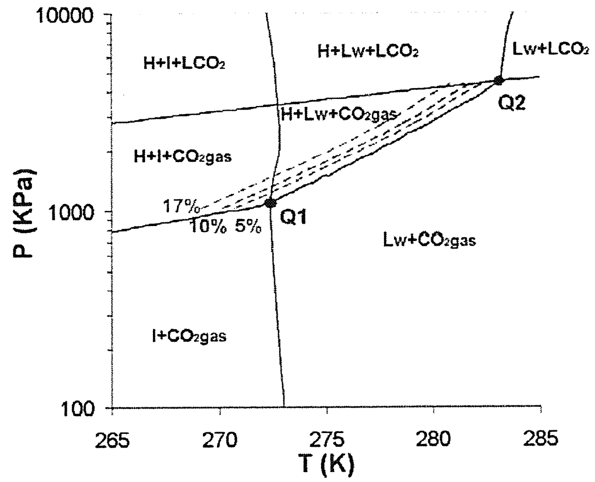

Figure 1. Phase transition diagram of CO2 clathrate. Colors show thedisplacement of the stability line of clathrates, if the indicated proportions of MgSO4 are added to the aqueous solution. H= clathrate hydrate, I = water ice Lw=liquid water, LCO_2= liquid CO_2, Q1 and Q2 are the quadruple points.

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