SEARCHING FOR CLATHRATE HYDRATES IN THE EUROPA SATELLITE. O. Prieto-Ballesteros[1] J. S. Kargel[2], F. Selsis[3], M. Fernández-Sampedro[1], E. Sebastián Martínez[1] and D. L. Hogenboom[4]. [1]Centro de Astrobiología. INTA-CSIC. Torrejón de Ardoz, 28850 Madrid. Spain. [2] Astrogeology Team. USGS. Flagstaff, Arizona, 86001. USA. [3] Centre de Recherche Astronomique de Lyon - Ecole Normale Supérieure (CRAL-ENS), 46 allée d'Italie, F-69364 Lyon Cedex 7, France. [4] Lafayette College, Easton, Pennsylvania, 18042. USA.

Introduction Several substances besides water ice, salts and/or acids have been detected on the surface of Europa, Ganymede and Callisto by spectroscopic sensors, including CO_2, SO_2 and H_2S [1, 2, 3, 4]. The spectral signal of CO_2 and SO_2, from stronger bands on Callisto than in Europa, have been attributed to exist as confined molecules within or attached to a host material [2, 4], so these materials might exist as clathrate hydrates instead ordinary ices or gases. Clathrate hydrates are crystalline compounds in which an expanded water ice lattice forms cages that contain gas molecules.The specific phase of these substances will depend on the system conditions where they occur.

Clathrate hydrates might be abundant in the solar system, as some authors have pointed out since the 1960's [5, 6, 7, 8, 9, 10, 11], but their volatility at low pressure usually restricts their present occurrence to below the surface for objects as warm as Europa or in the cold fringes of the Solar System as metastable surface condensates. If clathrate hydrates exist on Europa today, they have two possible origins: a) they might be primordial condensates from the Jovian subnebula, or b) they might be secondary minerals formed as a consequence of the geological evolution of the satellite. Primordial clathrate hydrates are not expected to have been preserved until now because of Europa's active geological history that is evidenced by many features on its surface. But dissociated gases from destroyed ancient clathrates may be added to volatiles from differentiation of both the chondritic rock precursor or reprocessing of cometary materials to make secondary clathrates that may be present today.

Remote searching for clathrate hydrates in Europa: Planetary subsurface gas hydrates may be abundant at shallow depths but be undetectable by spacecraft sensors. Direct remote sensing has not been useful for detecting these minerals until now. In principle, spectral reflectance of clathrate hydrates is expected to be different from water ice at some level of spectral resolution because the bond lengths are different from those of water ice; furthermore, the guest molecule will be spectroscopically different from the pure condensed guest phase because it will vibrate or rotate differently, and will interact with H_2O molecules instead of other guest molecules. In relation to this, the Galileo-NIMS observations of the SO_2 and CO_2 in the Jupiter satellites [2, 4] suggest a particular state of these molecules. However, so far, IR spectroscopy has shown clathrate to look very much like water ice. Results reported from the far infrared range show that ice and sI clathrate hydrates have similar spectra due to the same strength of the H bonds for both substances [12, 13].

On the other hand, their possible presence has been inferred indirectly by the evidence of their destruction and the associated catastrophic events.

Buried but exposed SO_2-clathrates: Spectral signals of SO_2 have been observed in both UV and NIR ranges. Although this volatile has to be buried to be stable as the clathrate hydrate phase, it just needs a few microns of ice over it [14] (table 1). So, the hypothesis that the observed SO_2-confined phase might be clathrate hydrate has been evaluated taking into acount the transparency of the ice in the mentioned spectral ranges.

In order to check the hypothesis that the absorption of SO_2 in Europa might be from subsurface gas molecules trapped within the ice or encaged in clathrates, we estimated the concentration of SO_2 within the ice required to produce a detectable absorption feature and we compared it to the maximum concentration of SO_2 that can be trapped in surface clathrate hydrate.

The penetration depth of the incoming radiation into the ice can be approximated by the depth $d(\lambda)$ of an ice layer having an extinction optical depth of 1 (extinction = absorption + scattering). The column density of SO_2 trapped along $d(\lambda)$ is $d(\lambda) \times [SO_2]$ where $[SO_2]$ is the concentration of SO_2 in the ice. At the surface conditions of Europa, the highest possible concentration of SO_2 in clathrates is $[SO_2]_{max} = 3.6 \times 10^{21}$ cm^{-3}, if we assume that the unit cell parameter for the sI structure of the SO_2 clathrates at 100 K is 11.85 Å and that while the small cages are empty due to the thermal contraction, all the larger ones are full . It can be seen on fig. 1 that this is enough to produce an SO_2 signature in the reflection spectrum. In the near-infrared, the penetration depth is only ~30 μm but at $[SO_2]_{max}$, the SO_2 contained in this thin upper layer still absorbs more than 10% of the radiation in its absorption band. In the UV, the penetration depth is much higher (5 cm in the snow, 25 cm in the ice) and, as the absorption coefficient of SO_2 is very high around 280 nm, a deep SO_2 feature is produced even at a concentration 4 orders of magnitude lower than $[SO_2]_{max}$. Considering the calculated transparency of ice at the absorption wavelengths of SO_2 and the stability ranges (table 1), it is conceivable that the observed signatures belong to the clathrate phases.

Geological evidence. Some geological features can be derived from the occurrence and destruction of clathrates in Europa such as explosive cryomagmatic deposits [8], or the signals of local retention of heat within or beneath clathrate-rich layers because of the low thermal conductivity of clathrate hydrates [15]. On the surface, destabilization of these minerals, triggered by fracture decompression or heating could result in formation of chaotic terrain morphologies, a mechanism that also has been proposed for some Martian chaotic [16, 17] areas. Conamara Chaos on Europa could be an example of the massive clathrate destruction associated with the depressurization via fractures.

The study of the evolution of the ice shell of Europa might take into account the presence of clathrate hydrates because if gases are vented from the silicate interior to the water ocean, they reach all the physical requirements first to dissolve in the ocean and then, if the gas concentrations are sufficient, to crystallize. If any methane releases occur in Europa by hydrothermalism or life activity, they also might form clathrates. Then, from both geological and astrobiological perspectives, future missions to Europa should carry instrumentation capable of clathrate hydrate detection.

Temperature of the surface(K)	Stability depth for clathrate hydrateswith several guest molecules (mm)			
	SO_2	CO_2	H_2S	CH_4
86	-	0.015	0.09	0.55
100	10^{-6}	0.065	0.4	3
128	6	200	80	3.5×10^{3}
132	7	220	93	1.4×10^{4}

Table 1. Depth at which the stability of several clathrate hydrate begins[14], assuming that the thermal gradient in the conductive part of the icy shell takes the indicated temperatures in the first column as the surface temperature[18].

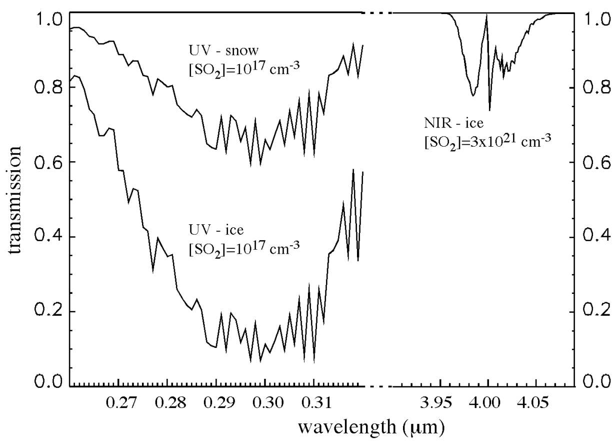

Figure 1 Absorption by SO_2 inside the ice. The curves give the transmission of a column density ρ of SO_2 along the typical penetration depth of ice (or snow). $\rho = [SO_2] \times d(\lambda)$ where $[SO_2]$ is the concentration of SO_2 molecules and d is the depth of ice (or snow) having an extinction opacity of 1 at the wavelength λ . The dashed curve is given for the near infrared band of SO_2 around 4 μm while the solid lines are for the UV band around 280 nm.

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