

TEXTURAL EVOLUTION OF CLATHRATE-SALT HYDRATES-WATER ICE ASSEMBLAGE AND THE INDUCED GEOLOGICAL ACTIVITY IN ICY MOONS. A. S. J. Méndez¹, F. Izquierdo-Ruiz^{1,3}, O. Prieto-Ballesteros¹, ¹Centro de Astrobiología-INTA-CSIC (Ctra. Ajalvir km. 4. 28850 Madrid. Spain. E-mail: asanjo-se@cab.inta-csic.es), ³Universidad de Oviedo (Dept. Química Física y Analítica, Julián Clavería, 8, 33006 Oviedo, Spain).

Introduction: Mineral textures and crystallization patterns hold valuable thermodynamic information about the origin and formation conditions of geological materials. Textures registered in water-related minerals, which result from endogenous geological processes such as cryomagmatism, may have relevance in terms of structure and habitability of icy moons. We are performing a macroscopic textural study of the mineral assemblage resulting from the crystallization of potential cryomagmas in order to find a correlation between mineral fabric experimentally obtained and formation parameters such as pressure, temperature, concentration and solubility of different components, or diffusion phenomena.

$\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ chemical system is proposed as an approach of Europa's aqueous layers composition [1]. In this particular system, CO_2 may form clathrate hydrates when it is under pressure and low temperature. If clathrate hydrates form from Europa's ocean-waterice crust interface, water molecules would be removed from the liquid phase promoting the formation of concentrated brines locally under the crust. Alternatively, if they form into the icy crust, brines would accumulate within interstitial spaces. As consequence, both kinds of brine accumulations could reach a grade of supersaturation that would trigger the precipitation of hydrated salts [2]. This phenomenon is known as salting-out.

Salting-out and clathrates dissociation are two opposite processes in the $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system that activate the exchange of energy and materials between Europa's interior and the surface. Several simulation experiments are carried out at high pressure following textural evolution of $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system under proper P-T conditions for clathrate formation. Mineral evolution is followed by Raman spectroscopy which allows the recognition of all involved phases.

Methodology: A thermostated high pressure chamber equipped with a sapphire window which allows both optical examination and Raman spectroscopy analysis is used in these experiments. Thermodynamical evolution of the system during the formation/dissociation of clathrate hydrates is recorded with a personalized Labview program. Pressure and temperature data is plotted on P-T-time diagrams to identify all involved thermal transformations.

Although Europa's aqueous layers distribution is uncertain yet, it is suggested that a global ocean lays between 20-100 km (24-120 MPa, considering that gravity is $1.314 \text{ m}\cdot\text{s}^{-2}$ and crust composition is dominated by water ice Ih). On this basis, the pressure at Europa's ocean-icy crust interface would correspond to CO_2 (l) stability region.

The initial composition of the aqueous solution is assumed here as 17 wt% MgSO_4 , which is the eutectic point of $\text{MgSO}_4\text{-H}_2\text{O}$ system. The solution is saturated with CO_2 at 283 K and then it is brought to 273 K in order to form clathrate hydrates.

Here report several textures of the different mineral phases crystallized from $\text{MgSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system at clathrate formation conditions and during salting-out event.

Results: Examples of the textures registered in the mineral assemblage during the crystallization/dissociation processes are:

- Layered texture. When clathrate hydrates initially forms from the solution, it is possible to observe a clear laminar growth of transparent CO_2 -clathrates (Fig. 1a) mostly in the closest regions to the interface. CO_2 -clathrates are detected since CO_2 Fermi diad shifts to lower frequencies in relation to CO_2 (g) Raman bands (Fig. 1). This crystallization pattern is remarkable at points where a sudden change in components diffusion takes place [4].

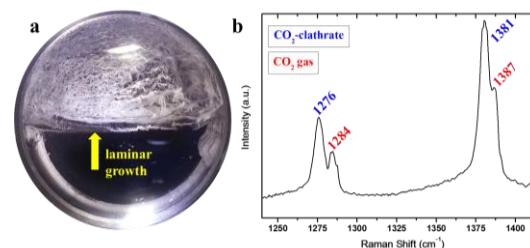


Figure 1. **a)** Clathrate layers in liquid-gas interface, which shows a clear laminar growth pattern. **b)** Raman spectrum of CO_2 (g) and CO_2 -clathrates obtained in the same point on the clathrate layer.

- Massive texture. Transparent clathrate layers turns into a white and opaque mass with time (compare figures 1a vs. 2a). It also shows high porosity homogeneously distributed.

- Blocky texture. At pressure conditions of liquid CO₂ but higher temperatures than the solidus of the system, an interface between phases with different texture is visibly arched probably due to diffusion phenomena (Fig. 2b). Additionally, large blocks of clathrates form as a result of a favourable temperature of crystallization.

- Mousse texture (Figure 2b). A mousse-like texture is observed in a secondary crystallization of clathrates, as it occurs in terrestrial sediments disturbed by the ancient presence of clathrates [5]. In Fig. 2b it is also distinguishable the shape of crystals which could have formed during the release of dense interstitial fluids.

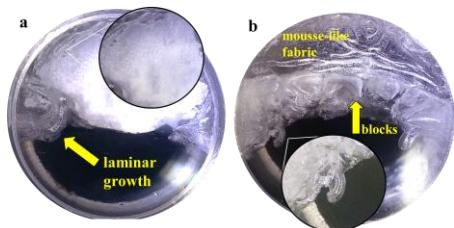


Figure 2. a) Laminar and massive textures of clathrates (274 K and 3.3 MPa). b) Mousse and blocky textures formed from liquid CO₂ (274 K and 3.65 MPa).

- Idiomorphic textures. After crystallization of large amounts of clathrates, salt concentration raises, favouring the subsequent precipitation of a mixture of meridianiite ($MgSO_4 \cdot 11H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$), which is easily recognizable by Raman spectroscopy (Fig. 3). Anhedral crystals indicate high supersaturation rates [6] so these ones are the first crystallized while euhedral crystals indicate lower supersaturation rate. Both types of crystals are heterogeneously distributed along the chamber, likely due to the salt concentration gradient related to the clathrates previously formed. Figure 4 shows some examples of salt crystals of different experimental runs.

If the system is heated again, clathrate hydrates dissociate, and salts dissolve, which results in derived cryomagmatic fluid. It is interesting to notice how these fluids ascend through two adjacent blocks of clathrates while they are dissociating. (Fig. 5).

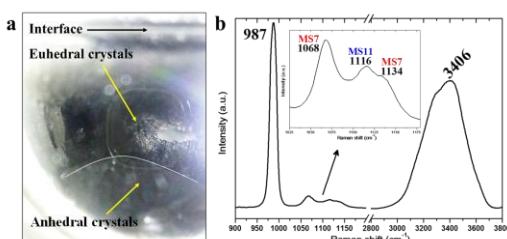


Figure 3. a) Salt crystals after salting-out. b) Raman spectrum of the mixture at 271 K and 3.3 MPa.

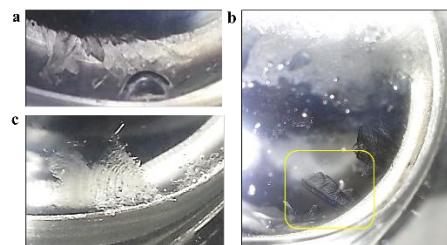


Figure 4. a) Crystals of sulfates shaped as needles (274 K, 3.6 MPa). b) Twin crystals (yellow square) appear at 274 K and 2.9 MPa. c) Crystals freeze the movement of fluids (273.5 K, 2.85 MPa).



Figure 5. Ascent of fluids in analogy to the rise of cryomagmas through Europa's icy crust.

Discussion: We follow the fabric evolution of the mineral assemblage resulting from the MgSO₄-CO₂-H₂O system while pressure/temperature/time variables change. CO₂ clathrates recrystallize from their first primary transparent crystals during the experiment, in which salting out effect occurs. There are textures that depend on CO₂ state in the original fluid system, hence it would indicate the depth at which the reported crystallization processes take place (e.g. blocky texture). Salts crystallize here stimulated by clathrates formation. We observed salt crystals shaped as needles with a common direction of growth, likely related to thermal and salt concentration gradients.

Some fabrics could be associated with geological activity in the ice crust of Europa, e.g. the layered texture registered during the primary formation of clathrates near 3 MPa might promote shearing events of ice inside Europa. Future experiments will be orientated to quantify texture characteristics for modelling the growth of these mineral phases and their role on geology of the icy moons.

References: [1] Muñoz-Iglesias V. et al. (2012) *Spectrosc. Lett.* 45, 407-412. [2] Lombardi S. et al. (2006) *Advances in the Geological Storage of Carbon Dioxide* (Netherlands: Springer) p. 111-126. [3] Muñoz-Iglesias V. et al. (2014) *Geochim. Cosmochim. Acta* 125, 466-475. [4] Samyn D. et al. (2005) *J. Glaciol.* 51, 611-619. [5] Pinero E. et al. (2007) *Geo-Mar. Lett.* 27, 279-288. [6] Rodriguez-Navarro C. and Doehne E. (1999) *Earth Surf. Process. Landforms* 24, 191-209.