AWARUITE, SERPENTINIZATION AND ICY MOONS. J. Neto-Lima[1], M. Fernández-Sampedro[1] and O. Prieto-Ballesteros[1], [1]Centro de Astrobiología, INTA-CSIC, Carretera de Torrejón a Ajalvir, km4, 28850 Torrejón de Ardoz – Madrid Spain (jlima@cab.inta-csic.es).

Introduction: Recent observations on the icy moon Enceladus point towards the existence of ongoing hydrothermal activity in its silicate mantle that heats a recently discovered global ocean beneath the moon's ice shell. This global ocean beneath Enceladus is assumed to be the source of the chemical species detected by Cassini's INMS (Ion and Neutral Mass Spectrometer) [1]. Using this data, some constrains for the ocean can be set in order to understand the geochemical processes that occurred and can still be at work in this icy moon of Saturn [2].

Europa's internal structure of the upper layers is proposed to be similar to this Saturn moon, supporting material and energy exchanges between the rocky and aqueous layers.

Serpentinization is a geological process that can still be occurring in environments such as the ones beneath the icy shells of these icy moons. It consists in the aqueous alteration of olivine to form minerals of the serpentinite group. The oxidation of the ferrous iron present on this mineral to form magnetite results in the release of dihydrogen gas. When the fluids, released during serpentinization, contact with carbon dioxide bearing water, under certain constraints it leads to the formation of methane and other hydrocarbons:

$$(Mg,Fe)_2SiO_4 + H_2O + CO_2 + Ni_3Fe \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2 + CH_4 \quad \text{(eq. 1)}$$

Geochemical processes such as serpentinization, that reduce carbon in hydrothermal systems, like the Lost City Field, represent the same energy releasing chemical reactions thought to be the origin of the first lifeforms that appereared on Earth's primitive oceans. Methane is thought to be the first hydrocarbon to be "harnessed" as a source of energy [3].Therefore understanding the mechanisms and catalysts behind the formation of this hydrocarbon is paramount to comprehend the mechanisms that allow a planetary body habitable.

Being an exothermic reaction, serpentinization is potentially a source of heat in both moons, also causing further silicate mantle differentiation and chemical evolution. This geological process occurs under a wide range of temperature and pressure conditions, fluid pH values are more restrictive, the values must range between 9-11, otherwise serpentinization is inhibited [4]. Under the icy moons temperature constraints expected for their seafloors, and without the presence of catalysts, the formation of methane would be painstakingly slow. Two naturally occurring serpentinization products that can act as catalysts for the formation of abiotic methane are iron-oxides (Fe_3O_4, magnetite) and a nickel-iron alloy awaruite (with chemical composition ranging from Ni_2Fe to Ni_3Fe). Since magnetite can suffer further alteration to awaruite, when in contact with dihydrogen, and in the presence of nickel-bearing olivine, we selected this mineral alloy as the catalyst to be used in this experiment. Because awaruite formation is usually connected to low temperature serpentinization processes, during which it acts as a surface catalyst for the series of reactions that ultimately lead to the formation of methane, from inorganic carbon, we believe this alloy is of paramount importance to the environments suggested to exist in various planetary scenarios [5].

Here we describe the experiments we are running, which objective is to understand how the catalytic action of the nickel-iron alloy awaruite affects the dynamics of the serpentinization process, with special focus on the formation of methane through Sabatier and FTT reactions. These experiments are used to simulate what could be observed in possible planetary scenarios where the formation of plumes occur, and learn how materials are captured in ices in contact with hot plumes rising from hydrothermal vents existing in icy moons seafloors [6, 7]. Combining the data collected by Cassini's instruments with our experimental results we expect to shed light in what processes still occur in Enceladus and Europa.

Serpentinization Simulation Experiment: The experiments reported here are carried under low pressure, so the presence and catalytic influence of awaruite alloy is observed, quantified and measured.

M*ethods*: Fayalite olivine is incubated for 500 days, with 20ml of 20mM $NaCO_3$ solution at 90ºC in 27ml borosilicate vials.

Awaruite used is synthesized via hydrazine hydrate reduction in an ethanol solution [8]. Characterization is obtained through Scanning Electron Microscope (SEM) coupled with EDS microanalysis system, X-ray powder diffraction and FTIR spectroscopy.

The vials are hermetically sealed with a PTFE/Silicone seal and a metallic crimp, inside an inert atmosphere chamber (N_2). The experimental setup is prepared for 6 different runs, to be collected at pre-established moments (after 30, 120, 240, 365 and 500 days).

Sample Analysis: After the established incubation period, the concentration of methane is measured by Raman spectroscopy on the vials headspace and the dissolved materials on the liquid. Gas and liquid samples are collected using a Luer syringe. FTR-IR is performed using liquid and gas cells. The vials are frozen and RAMAN spectroscopy is performed on the formed solid to observe the ice structures and the materials that are captured [2]. After that, X-ray Powder Diffraction and FTR-IR is performed on the resulting solid fraction to determine mineral assemblage and presence of serpentinization products.

Discussion: Measurements from the cooling experiment are used to model how silicate materials associated to hydrothermal alteration are dragged, captured in ices, and released from the interior by a possible planetary plume formed in Enceladus or Europa.

References:

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