OLIVINE AQUEOUS ALTERATION UNDER LOW TEMPERATURE CONDITIONS IN THE PRESENCE OF AMMONIA – A CASE FOR THE ICY MOONS. J. Neto-Lima[1,] , O. Prieto-Ballesteros[1] , M.Fernández-Sampedro[1],[1]Centro de Astrobiologia, CSIC-INTA. Carreteta de Torrejón a Ajalvir, Km 4, 28550 Torrejón de Ardoz - Madrid, Spain (jlima@cab.inta-csic.es)

Introduction: We report the results from laboratory experiments in which hortonolite (a Fe and Mg olivine) is reacted with anoxic basic carbonate saturated solution and ammonia in the presence of different amounts of laboratory synthesized Fe-Ni catalyst (awaruite) at the constant temperature of 363,15K. Then, the mineral alterations of the hortonolite olivine, were monitored using XRD, IR and SEM.

Serpentinization as geological driver of key chemical elements. This geological process, discovered in 2000, is the aqueous alteration of olivine, giving origin to minerals of the serpentine group, along with seconday minerals consisting of iron oxides (goethite and magnetite p.e.). This process usually occurs under a wide range of conditions of pressure and temperature (from 315,15K to 773,15K), but pH conditions are more strict, the aqueous solution has to be basic [1], otherwise serpentinization does not occur.

The icy moons, far from the sun, rely mainly on the energy from tidal heating stress while orbiting their main planet, so the high temperatures registered in some Earth serpentinization scenarios can hardly be expected. Methane production has been detected on serpentinization locations where temperatures as low as 363,15K are registered, and because we use awaruite, a surface catalyst for methane formation, usualy connected to low temperature serpentinization of mafic and ultramafic rocks [2].

These are the first results from hydrothermal alteration simulation experiments being run for over 300 days (we expect to conduct this experiment for at least 500 days) which main objectives are: a) to understand the catalytic action of awaruite and its influence on the serpentinization process itself; b) the behavior and cycling of ammonia under this conditions and its influence on the serpentinization products; c) to understand and quantify the formation of methane through Sabatier and FFT reactions under these conditions.

Serpentinization process in icy satellites: The hydrothermal alteration study under the proposed constraints is of paramount importance for the experimental validation and characterization of geochemical models suggesting the existence of a liquid water ocean and the presence of active hydrothermal vents on the seafloors beneath the icy shell of moons such as Europa and Enceladus [3, 4]. Recent discoveries and spacecraft-based observations point to ongoing hydrothermal activity on Enceladus [5, 6] and the presence of such activity is also proposed for Europa, through the observations of some structures observed on its surface and due to its internal structure. The chemical species detected by the INMS (Ion and Neutral Mass Spectrometer) instrument aboard Cassini support the hydrothermally active scenario [5, 6], the internal structure of Jupiter's moon, Europa, is proposed to be similar to Enceladus, therefore on our serpentinization simulation experiments we will focus on how material and energy exchanges between the rocky and aqueous layers.

According to INMS data, collected during fly-bys of of the Cassini spacecraft over Saturn's moon Enceladus, ammonia was detectedin planetary plumes detected on the moon's South Pole terrain[6]. The detection of ammonia provides yet another evidence supporting the existence of liquid water beneath the icy shell, allowing the preservation of aqueous alteration processes in the water/rock interface. The detection of methane and other hydrocarbons, together with ammonia also supports the models that propose a hot interior.

Serpentinization Simulation Experiment: The widespread distribution of olivine throughout the Solar System, confirmed by spacecraft that visited and analyzed a wide variety of planetary surfaces, ranging from planets to asteroids, makes it a good reference-mineral to help the study of the evolution of silicate-bearing materials in planetary surfaces, under a wide range of conditions. The magnesium-rich end member, forsterite was identified in many meteorites suggesting that this mineral is a primary condensate of the solar nebula that gave origin to our Solar System [7], because of this we started our incubation experiments with forsterite. But due to our interest in methane formation, through Sabatier and FTT reactions, we opted to use for this new batch of experiments an olivine with higher iron content. The release of dihydrogen (H_2) that will be used for the formation of methane comes from the oxidation of the iron from the olivine to iron oxides (magnetite, goethite p.e.), hence the importance of an olivine with iron in its composition. When serpentinization fluids contact with CO_2 rich water, under certain constraints, it leads to the formation of hydrocarbons, such as methane, as shown in the following equation:

$(Mg, Fe)_2SiO_4 + H_2O + CO_2 + Ni_3Fe \rightarrow (Mg, Fe)_3Si_2O_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2 + CH_4$

The experiments are conducted under low pressure (0,1 MPa) and low temperature (363,15K). Ten distinct series were prepared and incubated in 27 ml borosilicate vials, gassed with N_2 and placed in a sealed oven, Series 1 to 7 are prepared according to Table 1; Series 8 to 10 are prepared to observe and compare (in order): a mixture of forsterite and hortonolite (Reference to last year abstract), the effect of intermittent agitation, and the effect of crescent concentrations of ammonia.

Table 1 Experimental Setup for Series 1 through 7

Run / Reactants	Hortonolite	Ni_3Fe	$NaCO_3$(aq)	NH_3
Ni_3Fe Blank	5g	X	20ml	X
$NaCO_3$(aq) Blank	5g	20mg	X	X
Hortonolite Blank	X	20mg	20ml	X
Vial 1	5g	20mg	20ml	X
Vial 2	5g	50mg	20ml	X
Vial 3	5g	100mg	20ml	X
Vial 4	5g	20mg	20ml	0,4ml
Vial 5	5g	50mg	20ml	0,4ml
Vial 6	5g	100mg	20ml	0,4ml

Preliminary results: With the complete analysis of the series incubated for 125 days, using XRD, IR and SEM-EDS, we could observe the formation of rosette-like structures, as shown on Figure 1. The growth and complexation of these structures accompanies the adition of higher quantities of awaruite catalyst to the system; we could also observe substantial visual differences between the rosettes grown with and without ammonia present, as shown on Figure 1.

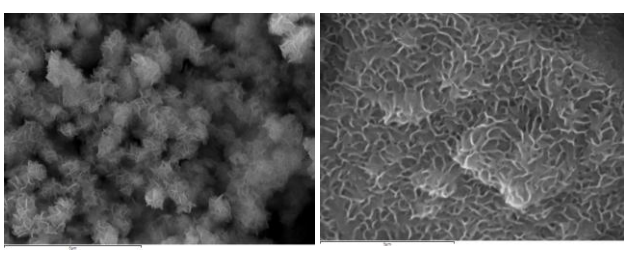

Figure 1 - Vial 2 (left) and Vial 4 (right) – After 125 days of incubation (SEM photos obtained with JEOL 6400, image magnification of 10.000x)

Throughout the incubation period, the vials containing ammonia (Vials 4,5,6), present a blue taint in the solution. After less than 30 days, blue plates start to form and precipitate (this is specially visible in Series 10, on vials that contain the highest concentration of ammonia). These plates are very fragile and are collected separately, even without using magnification, blue spherical structures can be easily observed on the surface. The results of the EDS analysis performed on the samples ar currently under study.

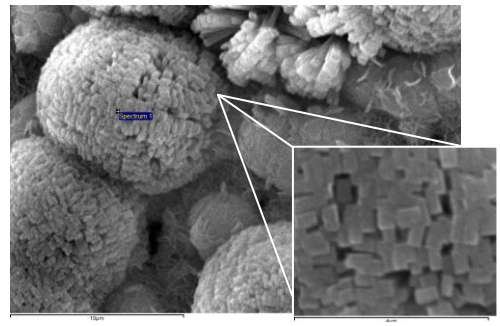

Figure 2 SEM image of the structures formed in blue plates formed on vials 4,5 and 6. (Image magnification of 5.000x, insert magnification 14.000x)

In the following series we expect to measure directly the amount of methane and dihydrogen produced during our incubation and relate it with the presence of the awaruite catalyst in the system. We also expect to take our serpentinization simulation experiment to a high pressure environmental chamber, so we can better simulate the proposed conditions at the seafloor of icy moons like Europa and Enceladus, study the mineralogy and the effects of pressure on the secondary minerals formed compared to a low pressure forming environment.

References: [1] Macdonald A.H. and Fyfe W.S. (1985) *Tecnophysics*, 116, 123-135 [2] Horita J. and Berndt M.E. (1999) *Science*, 285, 1055-1057 [3] MCCollom T.M. (1999) *J.G.R.*, 104-E12, 30.729-30.742 [4] Zolotov M.Y. and Shock E.L. (2003b), *J.G.R.*, 108 (E4), 5022 [5] Hsu H.W. et al. (2015) *Nature*, 519, 207-210 [6] Waite Jr. J.H. et al. (2009) *Nature*, 460, 487-490 [7] Weinbruch S. et al. (1998) *Meteorites and Planetary Science*, 35, 161-171