

Methane Formation Catalyzed by Awaruite during Serpentinization on Planetary Bodies - J. Neto-Lima¹ (jlima@cab.inta-csic.es), M. Fernández-Sampedro¹ and O. Prieto-Ballesteros¹, ¹Centro de Astrobiología, INTA – CSIC, Ctra. Ajalvir km. 4. 28850 Madrid, Spain.

Introduction: The presence of olivine is confirmed in planetary bodies, asteroids and interstellar dust. Its widespread presence makes it a good starting material for the study of the evolution of rocky layers of planetary bodies throughout our Solar System's history.

The Nickel-iron alloy Awaruite (Ni₃Fe) is commonly associated with serpentinized ultramafic rocks. One possible origin of this mineral is by the reduction of the nickel-bearing silicates or sulfides during the serpentinization of peridotites [1]. In this process, awaruite is an important catalyst of methane synthesis [2], providing increased opportunities for starting Fischer-Tropsch Type (FTT) reactions. Without the presence of a catalyst, abiotic methane formation would be extremely slow, hence limiting the available energy for metabolic processes and with it limit the occurrence of life. Here we show the results of the experiment of Mg-rich olivine serpentinization in presence of awaruite. We suggest this process may occur in the rocky layer of Europa, releasing methane to the aqueous ocean.

Experimental Process: *Awaruite synthesis:* The awaruite used is synthesized via hydrazine hydrate reduction in an ethanol aqueous solution (2:3 ratio) [3]. Our main goal is to produce enough quantity of this alloy for the serpentinization simulation experiment; for this, perfect crystallization of the mineral is not needed, therefore we increase tenfold the amount of the salts used in the reaction. After collection of the highly magnetic particles, XRD and SEM coupled with EDS are used to confirm the presence of awaruite (Ni₃Fe) nanocrystals (Fig.1).

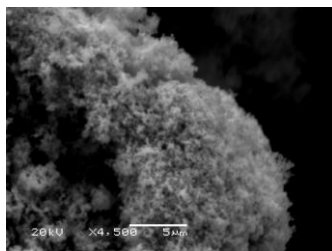


Fig.1 SEM image of the awaruite synthesized by Hydrazine reduction at 80°C

Serpentinization Simulation experiment: The synthesized awaruite is then used as a catalyst on a serpentinization simulation experiment. Natural olivine is pulverized into a fine powder, which composition is determined by XRD to be almost pure forsterite (Mg₂SiO₄). The experiment is assembled according to Table 1:

Reactant mass (gr)	Run					
	0	1	2	3	4	5
Olivine	-	1	1	1	2	-
Awaruite	-	-	0,005	0,010	0,005	0,005
CO₂	CO ₂ pellet [dry ice]					
Water	5ml [Water for ion chromatography]					

Table 1

These vials are heated up to 120°C, hermetically sealed with a vulcanized rubber cork and an aluminum cover. Some pressure inside each one is caused, firstly by the CO₂ and then by water vapor as the temperature rose. The vials are monitored daily for any weight variations and with infrared analysis detect the formation of methane. We selected relative low pressure conditions to simulate planetary surfaces/crust and also to understand which is the best olivine:awaruite:water ratio for methane formation catalysis. Once this ratio is obtained we will simulate this process under the constraints of the European seafloor.

Serpentinization on Europa: The discovery of several serpentine-hosted vent systems on Earth's seafloor coupled with fossil evidence supporting the sustainability of high-biomass communities by them, indicates the possibility that such systems may have played important roles in the emergence and evolution of life on Earth's primitive oceans. Hydrothermal vents are proposed to exist in the rock layer in contact with the global ocean of Europa [4] [5]. Some structures observed on the surface strongly support the notion that the liquid subsurface ocean exists and periodically, through different processes vents materials into Europa's surface (e.g. cracks on the icy shell or local melting episodes). These endogenous materials can be measured by future missions, including CH₄ from plumes, if they occur.

The C-S-Fe system is connected to the reduction/oxidation of carbon, thus forming and reacting methane [6]. Understanding methane catalysts becomes a priority to grasp the processes involved in carbon cycling under Europa conditions.

References: [1] (Krishnarao J. S. R., (1964) *Economic Geology*, 59, 443-448 [2] Horita J. and Berndt M. E. (1999) *Science*, 285, 1055-1057 [3] Abellán G. et al. (2014) *J Sol-Gel Sci Technol*, 70, 292-299 [4] McCollom T.M. (1999) *J. Geophysical Research*, 104-E12, 30.729-30.742 [5] Zolotov M.Y. and Shock E. L. (2003b) *J. Geophysical Research*, 108(E4), 5022 [6] Zolotov M.Y. and Shock E. L. (2004) *J. Geophysical Research*, 109, E6003