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Methane Formation Catalyzed by Awaruite during Forsterite Serpentinization on Seafloors of Planetary Bodies

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Abstract

Olivine is ubiquitous throughout the Solar System. Its presence in such different planetary surfaces that ranges from planets to asteroids makes it a good starting material for the study of the alteration of rocky layers through water activity. The aqueous alteration of olivine is called serpentinization, a process that in reduced environments may release methane, such as the suggested hydrothermal vents beneath Europa's icy shell. The nickel-iron alloy awaruite (Ni_3Fe), is usually connected to the serpentinization of ultramafic/mafic rocks. During this geologic process, awaruite acts as a surface catalyst promoting methane generation during Fischer-Tropsch Type (FTT) reactions, increasing the energy potentially available for metabolic processes. We carry out two different experiments to infer whether awaruite would catalyze the serpentinization process and if pressure is an important parameter that can influence the efficiency of the FTT reactions. One is performed under relatively low pressure and the other under the expected pressure on Europa's seafloor.

1. Introduction

The presence of olivine is confirmed on rocky planetary bodies, asteroids, meteorites and interstellar dust. Its widespread presence makes it a good starting material for the study of the evolution of silicate-rich layers of planetary bodies throughout our Solar System's history. The aqueous alteration of olivine in the presence of carbon dioxide, called serpentinization, may lead to the production of methane. In the case of Mg-olivine (forsterite, Mg_2SiO_4):

$$Mg_2SiO_4 + H_2O + CO_2 + Ni_3Fe \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + CH_4 + H_2 \quad (1)$$

The Nickel-Iron alloy awaruite (Ni_3Fe) commonly associated with serpentinized ultramafic/mafic rocks, may be originated 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]. The presence of a catalyst, accelerates the process of abiotic formation of methane and may expand the limits for the occurrence of life. Here we show the results of Mg-rich olivine serpentinization simulation experiments in the presence of awaruite. We suggest this process may occur in the rocky layer of Europa, releasing methane into the aqueous ocean.

2. Materials and methods

2.1. Awaruite Synthesis

The awaruite crystals used throughout our experimental assemblages are synthesized via hydrazine hydrate reduction in an ethanol solution (2:3 ratio) [3].

$$3Ni^{2+} + Fe^{2+} + 2N_2H_4 + 8OH^- \rightarrow Ni_3Fe + 2N_2 + 8H_2O \quad (2)$$

Our main goal being the production of enough amount of this alloy for the serpentinization simulation experiments, the perfect crystallization became secondary, therefore we increase tenfold the amount of the iron and nickel salts used in the reaction. After collection, the highly magnetic particles are analyzed with XRD and SEM coupled with EDS to confirm the presence of awaruite nanocrystals.

2.2 Olivine selection for Serpentinization

Forsterite is chosen for this serpentinization study, first because Galileo's Near Infrared Mapping Spectrometer (NIMS) detected the presence of Mghydrated materials on Europa's icy shell [4], and second, the forsterite detected in many meteorites is suggested to be a primary condensate of the solar nebula [5].

2.2.1 Low Pressure Experiment

The synthesized awaruite is used as a catalyst on a serpentinization simulation experiment under relatively low pressures, together with natural olivine pulverized into a fine grain powder, which composition is determined by XRD to be almost pure forsterite. 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
CO_2	CO_2 pellet [dry ice]					
Water	5ml [ion chromatography purity]					

These vials are heated up to 120ºC, hermetically sealed with a vulcanized rubber cork, Teflon and an aluminum cover. The pressure inside each one is caused, firstly by the CO_2 released by the pellets and then by the water vapor as the temperature rose. We select these conditions to simulate planetary surfaces/crusts and also to understand which is the best olivine:awaruite ratio for methane formation catalysis. After 34 days, the solid fractions are analyzed with XRD to verify the alterations suffered by awaruite and olivine.

2.2.2 High Pressure Experiment

A mixture of olivine and awaruite, respecting the ratio obtained by the low pressure experiments is loaded into a high pressure chamber. In it, we reproduce the expected conditions of a hydrothermal vent on Europa's seafloor.

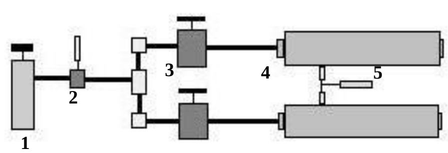

Figure 1: High Pressure Experimental Assembly (1.CO_2 bottle; 2.Pressure Sensor; 3.Valves; 4.Reaction chambers; 5.Temperature sensors)

At 120ºC and high pressure, serpentinization is monitored through the analysis of the composition of the solid fraction with XRD.

6. Summary and Conclusions

The discovery of serpentine-hosted vent systems on Earth's seafloor coupled with fossil records to support the sustainability of high-biomass communities by them, indicates the possibility that such systems may have played important roles in the emergence 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 [6][7], which was indirectly detected by the Galileo spacecraft. Some of the structures observed on the surface strongly point towards the idea that a liquid subsurface ocean exists and periodically, through different processes exchanges materials to and from Europa's surface (e.g. cracks on the icy shell or local melting or subduction episodes). These endogenous materials could be measured by future missions, including methane vented from plumes, if they occur.

The understanding of the action of methane catalysts such as the nickel-iron alloy awaruite, during the serpentinization process of the magnesium end-member of the olivine family, forsterite, becomes a priority in order to grasp the complex processes involved in the carbon cycling in Europa.

References

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