High Pressure Serpentinization Catalysed by Awaruite in Planetary Bodies

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Abstract. Recent discoveries from planetary missions show that serpentinization process may act significantly on the geological evolution and potential habitability of the icy bodies of the Solar System, like Enceladus or Europa. Here we review the available experimental data so far about methane formation occurring during serpentinization, which is potentially relevant to icy moons, and present our results using awaruite as a catalyst of this process. The efficiency of awaruite and high pressure in the Fischer-Tropsch and Sabatier Type reactions are evaluated here when olivine is incubated.

1. Introduction
Olivine is ubiquitous throughout the Solar System, its presence is detected in a wide range of planetary surfaces, from planets to asteroids, meteorites and interstellar dust. Therefore, it is a good mineral to study the evolution of silicate-rich materials throughout our Solar system’s history.

Serpentinization consists in the aqueous alteration of olivine to form minerals of the serpentinite group. In the Earth, they are part of rocks from the ultramafic upper mantle and mafic oceanic crust. Serpentinization is proposed to be an important geological process that affects the cycle of bio-essential elements not only in the Earth but in other planetary bodies of the Solar system. Oxidation of the ferrous iron of olivine to magnetite results in the release of dihydrogen (H₂) and precipitation of secondary minerals. When this serpentinization-derived fluids contact with CO₂ rich water, under certain constraints it leads to the formation of methane and other phases, as shown in the equation:

\[
(Mg,Fe)\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + \text{CO}_2 + \text{Ni}_2\text{Fe} \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg(OH)}_2 + \text{Fe}_3\text{O}_4 + \text{H}_2 + \text{CH}_4
\]

The most popular environments for serpentinization on Earth are hydrothermal systems such as those found in Lost City, the alkaline hydrothermal field discovered in 2000, at the mid-Atlantic ocean.

Serpentinization occurs under a wide range of conditions of pressure and temperature (from 40°C to 500°C), pH values have to be between 9-11, otherwise serpentinization is inhibited. Temperature is rate controlling, meaning higher the temperature faster the olivine hydrolysis; and pressure assists the diffusion rates of water through olivine and serpentinized rocks, not enough water at the serpentinite-olivine interface limits the rate of the reaction [1].

Under the temperature constraints expected for the icy moons seafloor, and without the presence of a catalyst, abiotic CH₄ formation would be extremely slow. Such catalyst has to have a reliable and
constant source, and to remain stable under these conditions. Two naturally occurring, serpentinization products that can act as methane catalysts are, iron-oxides (such as magnetite (Fe₃O₄)) and awaruite. Magnetite can further react with dihydrogen, producing ferrous iron that can produce a nickel-iron alloy, like awaruite, if nickel is present in the olivine that was serpentinized.

Awaruite is a nickel-iron alloy with a composition varying from Ni₂Fe to Ni₃Fe. It was first discovered embedded in black grains of sand collected from the West Coast of the South Island of New Zealand associated with a subduction context and the occurrence of serpentinites [2]. Since then, awaruite is usually connected to low temperature serpentinization processes of ultramafic and mafic rocks. During this alteration process, awaruite acts as a surface catalyst for the series of reactions that lead to the formation of methane, from inorganic carbon [3].

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 rocky layer in contact with the global ocean of Europa [4] [5], 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. Understanding serpentinization is paramount to grasp how methane behaves beneath the icy moons ice shell and how it can originate redox gradients that can be used by chemotrophic communities.

2. Materials and Methods
The experiments we report are carried under relatively low pressure so the influence of the presence of awaruite could be observed and quantified. To simulate the hydrothermal environment in which methane can be formed, a constant temperature of 120ºC is maintained.

Although iron is the main driver for methane formation, forsterite is selected as the olivine phase in these experiments because of Galileo’s Near Infrared Mapping Spectrometer (NIMS) detection of Mg-hydrated materials on Europa’s icy shell [6]. In addition to that, forsterite is detected in many meteorites, thus is suggested to be a primary condensate of the solar nebula [7].

Natural forsterite is used, which XRD patterns are compared to reference samples (Joint Committee on Powder Diffraction Standards file nº. 34-189). Composition is determined to be almost pure forsterite (Mg₂SiO₄) and enstatite (MgSiO₃).

Our experiments are run in order to understand the best olivine:awaruite:water ratio for CH₄ catalysis reactions.

3. Results
3.1. Awaruite Synthesis
The awaruite crystals used throughout our experimental assemblages are synthesized via hydrazine hydrate reduction in an ethanol solution (2:3 ratio) [8].

$$3\text{Ni}^{2+} + \text{Fe}^{2+} + 2\text{N}_2\text{H}_4\text{H}^+8\text{OH}^- \rightarrow \text{Ni}_3\text{Fe} + 2\text{N}_2\text{H}_8\text{O}$$

Our main goal being the production of enough amount of this alloy for the serpentinization simulation experiments, the perfect crystallization became secondary, therefore the amount of the iron and nickel salts used in the reaction is increased tenfold. Collection of the highly magnetic particles is carried using a magnet, thus limiting impurities. The collected particles are first washed with a solution of ultrapure water and absolute alcohol (4:1 ratio), and then placed in an oven to dry. Characterization of the awaruite is obtained through Scanning Electron Microscope (SEM) coupled with EDS microanalysis system and X-ray powder diffraction (Fig. 1).
Figure 1. Awaruite SEM image with EDS microanalysis results. The impurities detected result from the initial metallic salts, and NaOH used during synthesis. X-Ray diffraction pattern of resultant powder synthesized by hydrazine reduction, in an ethanol solution (2:3 ratio). XRD patterns obtained are compared to natural awaruite from Awarua Bay, New Zealand (Joint Committee on Powder Diffraction Standards).

3.2 Serpentinization Runs
The synthesized awaruite together with natural pulverized forsterite into a fine grain powder, are used in this serpentinization simulation experiment under relatively low pressures. The experiment is assembled according to Table 1:

Table 1. Experimental setup for the low pressure experiment

| Reactant | mass (gr) | Run 0 | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 |
|----------|-----------|-------|-------|-------|-------|-------|-------|
| Olivine   | -         | 1     | 1     | 1     | 2     | -     |
| Awaruite  | -         | -005  | 0010  | 0005  | 0005  | -     |
| CO₂      | -         | -     | -     | -     | -     | -     | -     |
| Water    | 5ml       | [ion chromatography purity] | |

Glass vials hermetically sealed with a vulcanized rubber cork, Teflon and an aluminium cover, are heated up to 120°C.

The pressure inside each one, which is slightly higher than 1bar, is the result of the release of CO₂ by the dry ice pellets and the increasing water vapor as the temperature rose.

After 34 days at 120°C, the solid fractions are analyzed with XRD to verify the alterations suffered by awaruite and olivine.
A mixture of forsterite olivine and awaruite, respecting the ratios used on the low pressure experiments is loaded into twin high pressure chambers. In it, a constant temperature is maintained using external heating and 300bar of pressure are kept using a RUSKA hydraulic system. The carbon dioxide for this serpentinization run is added from a pressurized bottle, 2mol of CO₂ were injected into the twin chambers before pressurizing them at 300bar.

Figure 2. High Pressure Experimental Assembly (1.CO₂ bottle; 2.Pressure Sensor; 3.Valves; 4.High volume high pressure chambers; 5.Temperature sensors)

4. Results
The use of CO₂ pellets in our experiments allows a faster dissolution of the gas in the water and consequently the acidification of the aqueous system. Serpentinization can only occur under alkaline conditions, with pH values between 9-11, therefore new experiments are planned for the near future in which a redox/carbon-source buffer will be used, in this case a sodium carbonate. Sodium is chosen because it is detected in Europa’s atmosphere by Galileo’s Near Infrared Mapping Spectrometer (NIMS)[9] and is proposed to originate from the global liquid ocean bellow Europa’s ice-shell.

Subtle changes in the crystallinity of the solid samples are evident in the diffractograms of the products.

At low pressures, hydrogen formation is favoured, and it is more thermodynamically favourable than methane, as pressure increases methane concentration in the system becomes comparable to hydrogen. Higher the pressure, higher the concentration of methane compared to hydrogen. According to experimental data, the high pressure conditions observed on Earth’s upper mantle favour the formation of methane. [10] Combining high pressure, with the presence of a nickel-iron alloy such as awaruite, the rate of abiogenic formation of methane raises considerably [3].

5. Summary and Conclusions
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.

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