

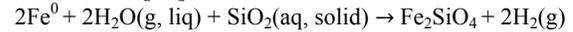
EXPERIMENTAL HYDROTHERMAL ALTERATION OF AMORPHOUS MATERIALS: INSIGHTS INTO EARLY FLUID-ASSISTED HYDRATION PROCESSES ON ASTEROIDS. E. Dobrică¹, J. A. Nuth² and A. J. Brearley¹, ¹Department of Earth and Planetary Sciences, MSC03-2040, 1 University of New Mexico, Albuquerque, NM 87131-0001, USA (edobrica@unm.edu); ²Solar System Exploration Division, Code 690, NASA Goddard Space Flight center, Greenbelt MD 20771 USA.

Introduction: Iron-rich olivine is one of the major minerals in the matrices of unequilibrated ordinary (UOCs) and carbonaceous (CV, CK, CO) chondrites whose petrologic type is >3.1 [1-3]. Additionally, FeO-rich olivine has been detected in cometary dust particles [4]. There has been an extensive discussion in the literature as to the formation mechanism of these olivines; however, their origin is poorly understood. Earlier studies argued that FeO-rich olivines were the products of gas-solid condensation in the solar nebula [5-6]; however, more recent studies disputed this argument based on mineralogic observations, thermodynamic considerations and the fact FeO-rich olivines are not present in very low petrologic type chondrites (<3.05). [7-9]. The formation of ferroan olivine during hydrothermal alteration has been demonstrated to be thermodynamically viable [10]. The stability of ferroan olivine is highly dependent on several variables, including temperature, water/rock (W/R) ratio, pressure, oxygen fugacity, and bulk rock composition. So far, hydrothermal alteration experiments have not been successful at forming FeO-rich olivines with the compositions and textures observed in the matrices of chondrites [11-13]. Therefore, unraveling the formation conditions of FeO-rich olivines remains a key problem to understanding the effects of hydrothermal alteration on chondrite matrices.

Methods and results: We performed three hydrothermal alteration experiments in an attempt to synthesize FeO-rich olivines. We used an amorphous silicate and iron powder as the starting material for the experiments. We chose amorphous silicates as the precursor material since they are ubiquitous fine-grained materials in almost all primitive solar system materials (chondritic meteorites and interplanetary dust particles) and in most astrophysical environments [14]. The amorphous silicate grains were synthesized experimentally by disequilibrium condensation [15]. The composition of the silicate grains, which condense from the SiO-H₂ vapor, is Si₂O₃ [16]. Additionally, we added iron metal powder (spherical particles, <10 μm) to the experiments, because previous studies [17] showed that fayalite forms from an iron-rich fluid that is SiO₂-poor and very reduced (log *f*(O₂) less than QFM conditions of -35.7 at 300°C).

In the experiments, we tried to reproduce the major chemical pathway of fayalite formation in chondrites inferred from equilibrium calculations [10-15, 17-18]. It has been suggested that under conditions too reducing to stabilize magnetite, fayalite can form through

oxidation of Fe metal in the presence of silica via the reaction below [18].



We used deionized water (18 megohms) from which we removed the dissolved oxygen using nitrogen purging. We loaded the samples in gold (Au) capsules (~3 mg - amorphous silicate, ~5.5 mg - iron powder and different amounts of water to simulate W:R ratios of 0.2 and 0.6) in a sealed glove compartment purged with N₂. We tested whether the experiments were successful or not (e.g. leaks) by weighing the capsules before and after the experiments. The capsules were placed in Parr bombs (reactor vessels) and heated in a low temperature furnace (Fisher Scientific, Isotemp 500 Series). Deionized water was added inside the Parr bombs as a pressure medium (the pressure during the experiments was ~2319.6 kPa).

In the first experiment, all the water was lost and so we consider that the effective W/R ratio for this experiment is 0. In a second experiment, the seal of the Au capsules containing the experiment failed and the water maintaining the pressure medium in the Parr bomb entered the capsule. In this experiment, the amount of water at the end was unknown; however, the W/R ratio was certainly higher than that calculated thermodynamically for the stability of ferroan olivine [10]. The last experiment at a W:R ratio of 0.6 was successful. We carried out experiments at a temperature of 220°C for periods of 6 (0.6 W/R ratio), 10 (1<W/R ratio) and 24 days (0 W/R ratio).

Four transmission electron microscopy (TEM) sections of the experimental run products were prepared using the FIB technique with a FEI Quanta 3D Dual-beam® FIB instrument. Each sample was studied using a variety of TEM techniques.

Our preliminary results suggest that in the dry experiments no reaction took place. However, in the presence of water, Fe and silica were mobile, forming new iron-rich, zoned amorphous materials (Fig. 2b), which are transformed into phyllosilicates at higher W/R ratio (Fig. 2c). Other new phases were formed such as euhedral iron oxides and fibrous phyllosilicates (Figs. 1-2) were also formed. However, no iron-rich olivine was formed.

Cronstedtite has been widely described in CM carbonaceous chondrites [19-22] and is also considered to be present on the surface of Ceres [19]. The formation of cronstedtite is probably related to aqueous oxidation of kamacite in the presence of dissolving silicates, which provides SiO₂ in solution [20, 23-24]. Cronsted-

tite is thermodynamically stable at $\sim 0^\circ\text{C}$ at moderately oxidizing aqueous conditions, at high W/R ratios [23], and at pH that evolves from an initial value of 7 to highly basic values (12–13) [25]. Our experiment suggests that the reaction rate to form cronstedtite is very rapid and occurs extensively at this temperature after several days (10 days). However, the thermodynamic calculation suggest that cronstedtite may not form at $T > \sim 120^\circ\text{C}$ at any $f\text{H}_2$ and $a\text{SiO}_2(\text{aq})$ [23].

Next experiments will be conducted in a reducing environment using oxalic acid ($\text{C}_2\text{O}_4\text{H}_2$) as starting material. At temperature above 443 K, oxalic acid decomposes as follows: $\text{C}_2\text{O}_4\text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{CO}$ [26]. The goal of the next experiments is to understand what is the water/rock ratio needed for the formation of FeO-rich olivine and what are the mechanisms and rates of hydrothermal alteration and fluid-assisted metamorphism reactions that form olivine.

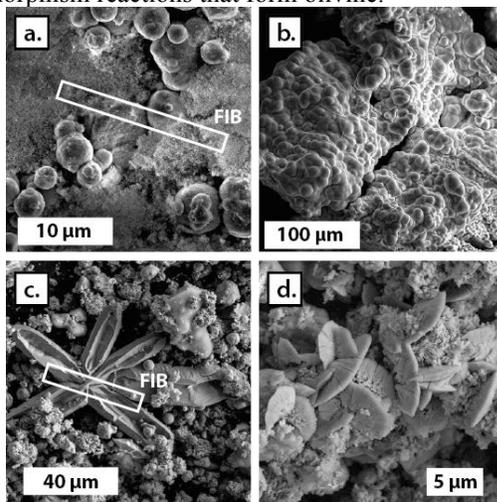


Figure 1. Secondary electron images of the experiment results for different W/R ratios: a) no water, b) 0.5 W/R ratio and c-d) W/R ratio unknown. The white rectangles show the region where the FIB sections were prepared for the TEM studies.

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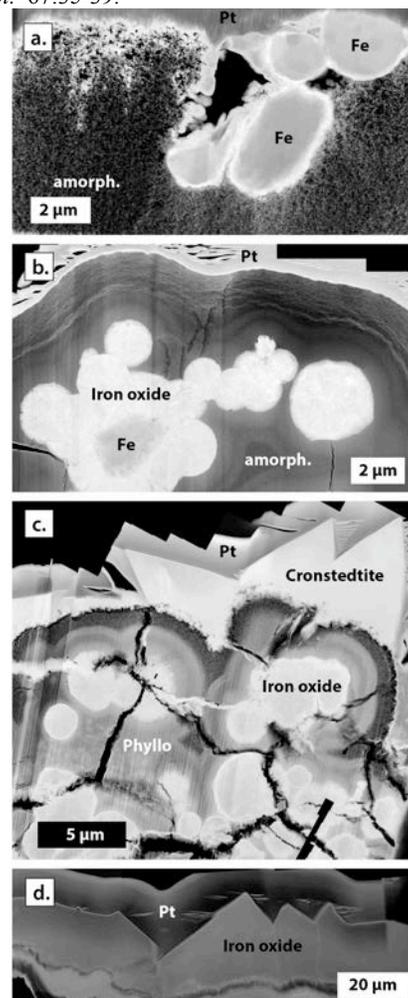


Figure 2. Dark-field STEM images of three experiments showing the mineralogy (phyllosilicates, iron oxide, cronstedtite) and the textural relationships between the reactant amorphous material and the new phases formed during the hydrothermal and fluid assisted metamorphism. Different W/R ratios and duration of the experiments: a) no water and 24 days - FIB section showed in Fig. 1a; b) 0.5 W/R ratio and 6 days and c-d) W/R ratio unknown and 10 days. Pt = platinum, Phyllo = phyllosilicate, amorph = amorphous silicate, Fe = iron metal.