

## EXPERIMENTAL STUDY OF THE INTERACTION BETWEEN AMORPHOUS SILICATES AND WATER VAPOR.

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**Introduction:** Chondrites are chemically undifferentiated rocks and are witnesses to the early stages of the formation of Solar System. For the most primitive of them, the matrix which cements chondrules and CAIs contains abundant amorphous silicates finely mixed with crystalline silicates, Fe-sulfides and organic matter [1]. Amorphous silicates are frequently partially altered, into phyllosilicates.

The main scenario for phyllosilicates formation is that they have grown within the parent bodies due to the action of liquid water [2]. However, it is also possible that the hydration of silicates takes place, at least partially, before the accretion of parent bodies by interaction between water vapor and silicates in the proto-planetary disk. In this context, early studies considered the hydration of forsterite in canonical condition [3]. This scenario was found kinetically limited i.e. the activation energy was too high. Several studies have now shown that the matrix of the most primitive chondrites contains abundant amorphous silicates [4]. This led [5] to consider the much lower activation energy determined from experimental hydration of basaltic glasses. It opened the possibility to form phyllosilicates in the chemical lifetime of the proto-planetary disk. [6] also showed that the local physical conditions associated to a shock wave, which locally involve a significant increase of temperature and partial pressure of water, could lead to the formation of hydrated phases in the protoplanetary dust. Finally, regarding the kinetics of transformations, recent experimental studies showed that, for silicates glasses, the atmospheric alteration can be faster than the aqueous alteration [7].

In our study, we develop an experimental approach to study the interaction of water vapor with amorphous silicates. We present the first results obtained with an amorphous silicates of pyroxene composition. The main objectives are the identification of the alteration products, their comparison with the alteration phases in chondrites and the determination of the activation energy and kinetics of the observed phase transitions.

**Experimental setup:** Our experimental setup aims to simulate interactions between thin films of amorphous silicates of pyroxene composition and water vapor, in closed hydrothermal bomb. The thin films are synthesized by pulsed-laser deposition [8]. The chosen composition of the silicate is close to that of the amor-

phous silicates of primitive chondrites [9]. Our experiments run at different pressures (6 bar and 13 bar) controlled by the initial amount of water introduced in the hydrothermal bomb. These closed systems are heated at 443 K, 503 K and 563 K over durations that extend from 12 days to 1 year. The experimental products are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to extract the textural, structural, and chemical characteristics. TEM samples are prepared by focused ion beam (FIB).

**Results:** A 12 days and a 60 days experiment were performed at 503 K and 13 bar. The SEM study shows a rough surface on the two experimental products. The 60 days sample shows a more widespread and porous structure than the 12 days experiment. A low-voltage SEM map performed on 60 days experiment allowed to show variation of the Mg/Fe ratio with a magnesium-rich region and an iron-rich region (Fig 1).

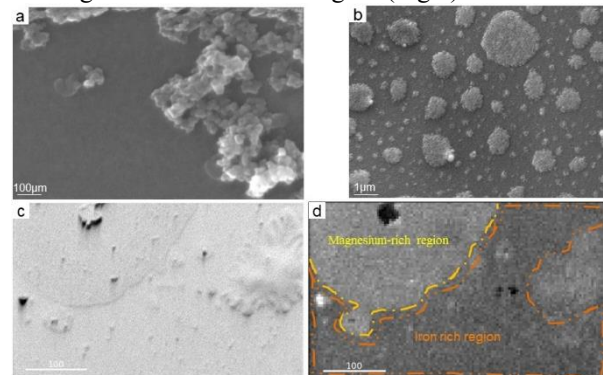


Fig 1: (a) SEM image of a rough surface of a 12 days/6 bar/503 K experiment. (b) SEM image on a rough surface on a 60 days/6 bar/503 K experiment (c,d) Mg/Fe ratio intensity map of a 60 days/6 bar/503 K Sample showing lateral heterogeneity.

The TEM study of the 12 days experiment shows altered layers in the experimental product. The top of the sample consists of 40 nm thick iron-rich layer (around 16 at.% compared to the 10 at.% of the starting composition). Below this layer, we observe a porous magnesium-rich layer (30 nm thick). For the 60 days experiment, thin iron-rich layer is also present in contact with a magnesium-rich phyllosilicates layer 160 nm thick (12 at.% of magnesium) (Fig 2)

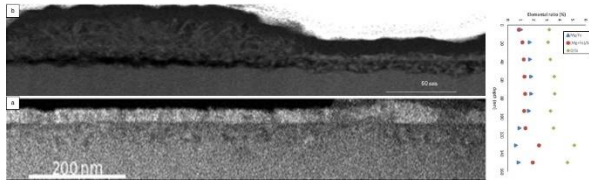


Fig 2 : TEM images and analyze of the experimental products. (a) TEM image of an experimental product at 503°K and 6 bars during 12 day (a) and 60 days (b). The image (2) shows an iron oxidized layer who can be observed in the image (1) too.

**Discussion :** These first results allow us to draw up a first assessment of the first stages of alteration of an amorphous silicate in the presence of water vapor. The first conclusion is the formation of a layer rich in iron on the surface of the samples. This testifies to a significant mobility of iron within the altered amorphous silicate. We also show that Mg-rich phyllosilicates can form in the presence of water vapor. These are formed in a second step. The separation and the mobility of these elements is revealed by the chemical map at the SEM scale and the TEM study showed that the Mg-rich phyllosilicates are in contact with the Fe-rich region. From these observations, we deduce that iron cations tend to move towards the surface and form a Fe-rich layer. This process leads to iron depletion in the underlying region in which we also observed porosity. It is in this Mg-rich region that the crystallization of phyllosilicates takes place, as revealed by the fibrous texture both at the SEM and TEM scale. Several hypotheses can be put forward to explain the mobility of the element.

- (1) Solid-state diffusion: This process involves a diffusion in the amorphous network. It was identified on the context of alteration with liquid water and requires the formation of a gel layer [10].
- (2) Interfacial dissolution-precipitation: For this mechanism, a thin film of water forms when water molecules are in contact with the sample surface which can be partially dissolved causing an enhanced mobility of cations. These cations reprecipitates at the surface to form an altered layer [11].
- (3) Hydroxyls pathways: When a water molecule hit the amorphous silicate, the molecule reacts to form two hydroxyls by breaking a Si-O-Si bond. These hydroxyls can provide a preferential way for the water molecule to circulate through the amorphous network as well as enhance the mobility of cation network modifiers and Mg in the amorphous network [12].

At this stage of our study, all these hypotheses are still open. Future experiments should make it possible to identify the dominant mechanisms responsible for the observed modifications.

The kinetics of the hydration of amorphous silicates in the experiment seems to be lower than expected from. [7]. This can be explain by the influence of the glass composition on the alteration kinetics. Indeed [13]

found that the presence of Alkali-Earth elements seems to make the glass more reactive. These elements actively participate to the formation and the kinetics of secondary phases during the alteration process. Our sample does not contain such elements which might explain its slower reactivity.

Finally, the microstructure that we observe are quite close to those present in some chondrites, in which an association of phyllosilicates and iron oxide is identified [e.g., 14] (Fig 3). Further experiments are in progress to consolidate the understanding of the alteration mechanisms and to extract the kinetic law and the activation energy.

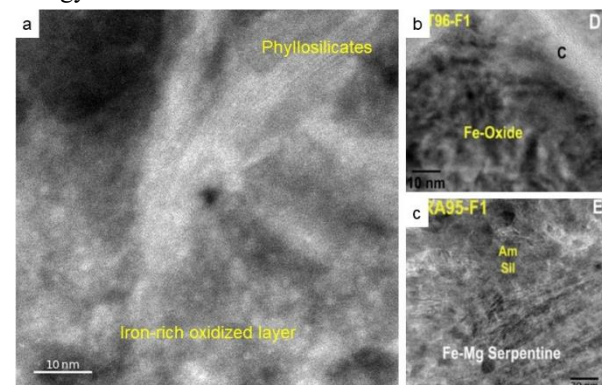


Fig 3 : TEM images of altered phases. (a) experimental product at 503 K, 6 bar during 60 days. (b) Fe-Oxide in CR chondrites[14]. (c) Fe-Mg Serpentine in CR chondrites[14]. These structures look similar between the experimental products and the natural object.

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**References:** [1] Le Guillou C. et al. (2015) Earth Planet. Sci. Lett., 420, 162-173. [2] McSween H. Y. (1979) Rev. Geophys., 17, 1059. [3] Fegley B. Jr. (2000) Space Science Reviews, 92, 177-200. [4] Brearley A. J. (1993) GCA, 57,1521-1550. [5] Ganguly J. and Bose K. (1995) LPSC XXVI, 441. [6] Ciesla F. J. (2003) Science, 299, 549-552. [7] Alloteau F. (2017) Corrosion Science, 122, 12-25. [8] Lowndes D. H. et al. (1996) The Astrophysical Journal, 699, 35-38. [9] Tomeoka K. Buseck P. R. (1985) GCA, 49, 2149-2163. [10] Valle N. et al. (2010) GCA, 525, 53-71. [11] Hellman R. et al. (2012) GCA, 71, 2361-2382. [12] Kuroda M. et al. (2018) American Mineralogist, 103, 412-417. [13] Narayanasami S. (2019) Journal of Nuclear Material, 525, 53-71. [14] Abreu N. M. (2016) GCA, 194, 91-122.