



# New experimental approach to study aqueous alteration of amorphous silicates at low reaction rates



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## ABSTRACT

Understanding the kinetics of silicate alteration in aqueous media is central to the study of oceanic hydrothermal systems, nuclear glass durability or carbonaceous asteroids from which chondrites are coming. We present a new experimental approach in combination with an integrated analytical protocol designed to study alteration processes at low temperatures (<200 °C) and slow reaction rates. We used pulsed laser deposition (PLD) to produce micrometer thick films of amorphous silicate of controlled chemical composition. After reacting with water in sealed capsules, the films consist of a succession of compositionally different layers. The initial planar geometry of the film allows a complete characterization of the transformed materials at the nanometer scale. By combining Rutherford back-scattering (RBS), nuclear reaction analysis (NRA), transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM), it is possible to constrain the propagation rate of the reaction fronts, the thicknesses of individual layers, spatial variations in composition, the nature of the interface between the layers, the iron redox state, the water content along depth profiles, as well as the porosity and the density. We investigated the serpentinization of amorphous silicate films with stoichiometry close to olivine (~Fe<sub>1.1</sub>Mg<sub>0.9</sub>SiO<sub>4.15</sub>H<sub>0.3</sub>) at 90 °C (2 weeks) and 200 °C (2 h). In both cases, ~500 nm of altered material is formed. At the reaction front, a hydrated, amorphous and oxidized Fe-rich layer forms. At the interface with the fluid, a more Mg-rich layer develops. The system evolves towards a biphasic assemblage of Fe-serpentine and Mg-saponite composition. Both layers remain amorphous. It is shown that water propagation is coupled to hydrolysis, iron oxidation (Fe<sup>3+</sup>/Σ Fe ratio > 50%) and H<sub>2</sub> formation, whose quantifications are crucial to understand terrestrial serpentinization processes. Interfacial precipitation–dissolution seems to be the rate controlling mechanisms. In addition, we investigated a crystallized film reacted at 190 °C (2 h), which transformation rate is ten times slower than that of the amorphous silicate but is nevertheless readily observable. This approach can be used to understand alteration in terrestrial and extraterrestrial samples. In particular, we reproduced several features observed in carbonaceous chondrites (amorphous and oxidized hydrated silicates) and show that, at 90 °C, alteration may be faster than usually considered. It should allow us in the future to constrain the temperatures and timescales of alteration in chondrites.

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## 1. Introduction

Alteration of silicates at low temperatures is a common process in geosciences and cosmochemistry. It occurs in many different environments such as continental surfaces (Hellmann et al., 2003; Godderis et al., 2010), oceanic floor (Berger et al., 1987; Crovisier et al., 2003; Schramm et al., 2005; Benzerara et al., 2007; Klein et al., 2009; Andreani et al., 2013), or meteorites and asteroids (Tomeoka and

Buseck, 1988; Brearley, 2006 and references therein; Morlok and Libourel, 2013). In addition, it is also a major topic of discussion in material sciences for purposes like alteration of glasses used for nuclear waste confinement (Frugier et al., 2008; Valle et al., 2010), alteration of archeological glasses (Dohmen et al., 2013), or silicate carbonation for CO<sub>2</sub> sequestration purposes (Knauss et al., 2005; Daval et al., 2009; Hövelmann et al., 2012). However, our understanding of the kinetic laws controlling such processes is limited. This is mainly due to difficulties in constraining the reaction mechanisms, especially at the relevant low temperature ranges (<100–150 °C) and because the physico-chemical models extrapolating the experimental results to natural

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environments are still debated (Hellmann et al., 2012; Daval et al., 2013; Malvoisin and Brunet, 2014).

Our long term goal is to constrain the temperature and timescales of hydrothermalism in asteroids, from which chondrites are formed. These meteorites carry a record of the earliest solar system processes, including water–silicate interactions. In particular, amorphous silicates are observed in the interstellar medium and protoplanetary disks (Dorschner and Henning, 1995; Kemper et al., 2004) and are also observed in primitive chondrites (Brearley, 1993). At the time of the formation of the solar system, asteroids have accreted water as ice, together with iron-rich amorphous silicates (Le Guillou and Brearley, 2014). The latter were likely condensed from the gas phase (Nuth et al., 2005; Pontopiddan and Brearley, 2010). Water and silicate have then reacted and the alteration products are now found in CI, CM or CR carbonaceous chondrites (Zolensky et al., 1989; Rubin et al., 2007; Chizmadia and Brearley, 2008; Abreu and Brearley, 2010; Zolotov, 2012). Alteration formed diverse minerals including hydrated amorphous silicates, serpentine-type phases (Mg-chrysotile or oxidized Fe-cronstedtite), and a suite of minor phases such as iron oxides and hydroxides, sulfides and carbonates (Tomeoka and Buseck, 1988; Brearley, 1993, 2006; Laretta et al., 2000; Rubin et al., 2007; Le Guillou et al., 2014, 2015). In particular, a hydrated amorphous iron-rich silicate and serpentine are found in all groups of carbonaceous chondrites. Unraveling their formation and hydration conditions is a key to understand the origin of matrices and their hydrothermalism history (Abreu and Brearley, 2010; Le Guillou and Brearley, 2014; Le Guillou et al., 2015). To that end, it is crucial to quantitatively constrain the kinetics and the operating mechanisms of amorphous silicate alteration. A few studies have experimentally investigated alteration in chondrites (Jones and Brearley, 2006; Ohnishi and Tomeoka, 2007), but they only addressed the alteration of crystalline material at temperatures above 150 °C. However, experiments focusing on the specificity of amorphous silicate and of low temperatures processes are required. Ultimately, this will enable estimating the timescales of hydrothermalism, and how water was consumed and/or degassed in asteroids.

Serpentinization reactions are very sluggish at temperatures below 200 °C, and are therefore not trivial to study within laboratory timescales, as the reacted volumes are typically limited (Malvoisin et al., 2012a,b). In fluid-mediated reactions (opposed to a solid-state transformation), dissolution is often a prerequisite to the formation of secondary phases, and kinetic competition occurs between various mechanisms such as dissolution, precipitation, hydrolysis and oxidation reactions, as well as water and cation transport through the porosity of the precipitated materials (O'Neil and Taylor, 1967; Berger et al., 1987; Banfield et al., 1995; Crovisier et al., 2003; Hellmann et al., 2003; Frugier et al., 2008; Daval et al., 2009, 2013; Mueller et al., 2010; Valle et al., 2010; Ruiz-Agudo et al., 2014).

Different types of experimental strategies have been used to study silicate alteration. Olivine serpentinization is often studied in closed system setups, using powders as starting materials (Marcaillou et al., 2011; Malvoisin et al., 2012a,b). The solid phases are then characterized by SEM, X-ray diffraction Mossbauer spectroscopy, XANES or magnetic monitoring, among others (Marcaillou et al., 2011; Malvoisin et al., 2012a, 2012b). One difficulty with powder experiments is that the grain size distribution changes during progressive alteration. Thus the specific rate of the chemical reactions requires integrating the evolution of the surface to volume ratio over time, which is not straightforward. Another issue arises from the fact that crystalline olivine is not reactive within laboratory timescales at temperatures below 200 °C, and that few data are available within the temperature range relevant for chondrites. Studies on glass alteration performed at lower temperatures are generally conducted in semi-open systems (fresh H<sub>2</sub>O continuously brought to the reaction cell at a slow rate) which consequently leads to a higher alteration rate, but do not adequately simulate chondritic environments (i.e. closed system and low fluid to rock ratio). Most studies use fluid analysis as the main analysis tool. It allows the determination

of the relative rates of dissolution of different elements, but it does not contain much information about the temporal evolution of the solid phase, which is rarely studied (Valle et al., 2010). In chondrites, only the solids are available and their study is required to understand the reaction mechanisms.

In order to investigate amorphous silicate alteration at low temperature, i.e. to precisely study their reaction mechanisms and kinetics, we designed a novel experimental protocol. Specific requirements have to be met for the study of chondritic amorphous silicate: 1) synthesizing amorphous iron-rich precursors of micrometer dimension, 2) running the experiments in closed system, and 3) being able to characterize the solid products with nanometer scale resolution. We used the pulsed laser deposition (PLD) technique to synthesize a starting material of desired composition (Dohmen et al., 2002). A one micron thick amorphous layer is deposited from a plasma on a polished surface substrate. During the alteration process, successive layers of altered materials form progressively from the surface down towards the depth of the film. The film can also be pre-annealed at high temperature prior the alteration experiment in order to obtain a fine-grained, polycrystalline film, allowing for direct comparison of reaction rates of amorphous and crystallized material of similar composition. The ideal, flat geometry allows combining complementary analytical techniques to fully characterize the products at the nanometer scale. The surface to volume ratio is also easily determined. We combined, in an integrated manner, Rutherford back-scattering (RBS), nuclear reaction analysis (NRA), focused ion beam (FIB) coupled with transmission electron microscopy (TEM) and scanning-transmission X-ray microscopy (STXM) in order to: study the reaction front advancement, determine the composition and physical properties (density, porosity) of each layer, characterize each layer boundaries, measuring the water content of different layers with tens of nanometer resolution, spatially determine the redox state of iron to assess the role of redox reactions, and establish a mass budget to discuss the transport processes within the materials.

In this paper, we describe our experimental setup, and discuss how to efficiently combine and optimize the outcome of each analytical technique. We then present examples of experiments comparing initially crystalline and amorphous materials to illustrate how this information can be successfully used to constrain the mechanism and rates of reaction. Finally, this new combination of experimental and analytical protocol is used to discuss the conditions of hydrothermalism of chondritic materials.

## 2. Experiments and characterization methods

### 2.1. Experimental setup

#### 2.1.1. Sample preparation: pulsed laser deposition and annealing

Pulsed laser deposition is a method which allows synthesizing various types of material of controlled composition in their amorphous state. An excimer laser is used to ablate a target of known composition, which results in a plasma (Fig. 1). The latter condenses on a substrate. Different deposition rates can be achieved depending on the laser intensity (laser fluence, energy per surface area of the target), wavelength and the target composition, which are typically in the range of 1 to 10 nm per minute for most silicates (Dohmen et al., 2002).

In the present study, we use a 193 nm wavelength laser (power around 300 mJ per pulse, operating at 20 kV, 10 Hz). After passing through the optics, the beam is focused on a mm large area with a power of ~40–50 mJ/pulse (Watson and Dohmen, 2010). We used a synthetic polycrystalline target composed of fayalitic olivine (fayalite 50) and the plasma condenses under high vacuum (~10<sup>-5</sup> Pa) on polished, 001 oriented 0.5 mm thick TiO<sub>2</sub> substrates (© Crystec), which were cut to cylinders with a diameter of approximately 5 mm. TiO<sub>2</sub> has very low solubility and dissolution rates at the present experimental conditions and is thus considered to be inert. The substrate is first heated to about 400 °C in order to degas and to clean its surface

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