

**SERPENTINIZATION OF AMORPHOUS SILICATE IN THE EARLY SOLAR SYSTEM : A NANOSCALE EXPERIMENTAL STUDY.** C. Le Guillou<sup>1</sup>, R. Dohmen<sup>1</sup>, T. Müller<sup>1</sup>, C. Vollmer<sup>2</sup>, D. Rogalla<sup>3</sup> and H. W. Becker<sup>3</sup>. <sup>1</sup>Ruhr-Universität Bochum, Inst. für Geologie, Mineralogie and Geophysik., 44780, Bochum, Germany, corentin.san@gmail.com. <sup>2</sup>Universität Münster, institut für Mineralogie, Corrensstraße 24, D-48149 Münster, Germany. <sup>3</sup>RUBION facility, Ruhr-Universität Bochum, Bochum, Germany.

**Introduction:** Serpentine is ubiquitous in carbonaceous chondrites [1] and reflects hydration episodes which may occur either in the solar nebula [2, 3] or in the asteroidal parent body [1]. The question of the location of aqueous alteration is also a key to understand how water was transported in the nebula, i.e. as ice, vapor or hydrated phases.

Amorphous silicates are observed in fine-grained matrices of the least aqueously altered chondrites. We have recently shown that this amorphous silicate was hydrated in MET00426 (CR3) and Renazzo (~ 10 wt.% H<sub>2</sub>O) and that they showed textural relationships with serpentine/saponite areas [4], indicating that the latter are formed from the former through hydration reactions. A limiting aspect of the analysis of this material is the size, which is usually below 1 µm. Amorphous silicates are also present in GEMS in IDPs [5] and are present in astronomical observation of protosolar disks [6]. This altogether indicates that amorphous silicates are important components of the solar nebula and that they might be the precursor materials that later accreted in chondrites.

There are at present no available experimental data on serpentinization below 200°C, and there are also no studies dealing with amorphous silicate as precursor. In order to constrain the locations and conditions of aqueous alteration (nebular vs. asteroidal), it is therefore mandatory to investigate the mechanisms and kinetics of amorphous silicate reactions relevant to the parent bodies conditions, and to compare them with observations in chondrites and IDPs.

**Experimental:** This experimental study of hydration/serpentinization is based on a novel experimental setup and coupled analytical techniques providing characterization of the products at the nanoscale. A micron-thick, homogeneous layer of amorphous silicate (~ Fayalite 50) is deposited on a Al<sub>2</sub>O<sub>3</sub> substrate by laser sputtering and plasma deposition using a pulsed laser deposition system under high vacuum (PLD) [7]. This starting material already contains some hydrogen (~ 5 at.%). The film is then heated (teflon bombs) in deionized water (60°C, 120°C, 150°C and 190°C, from 2 hours to 2 weeks and water to rock ratios between 300 and 1000). The thin film provides an ideal geometry to follow the evolution of the product as the reaction front progress by FIB/TEM and by Rutherford Back Scattering (RBS) and Nuclear Reaction Analysis (NRA) on a tandem linear accelerator at the RUBION

facility. Combined together, those techniques give access to depth resolved mineralogy (TEM), major elements composition (RBS), water content (NRA), thickness, and density of each layer. This enables to follow the kinetics of the alteration reaction, obtain mass budget at different advancement stages, as well as to look carefully at the interface between layers which are crucial to determine reaction mechanisms.

This new approach could also be applied to study all types of alteration reactions, including those related to continental or oceanic alteration, or to the durability study of nuclear waste glasses. In the latter cases, kinetics and reaction mechanisms remain highly debated [8]. In particular, whether or not dissolution is congruent (stoichiometric dissolution) or incongruent (non-stoichiometric dissolution) could be studied. In the first case, transport of elements would occur through nanochannels; while in the second one, solid-state diffusion and dissolution of cations occur followed by Si-O bonds hydrolysis and precipitation.

**Results:** At all temperatures, FIB/TEM/RBS reveal the formation of a sequence of amorphous layers with sharp fronts between them. SAED patterns show that all layers are completely amorphous. Their thickness and exact composition depend on temperature and duration of the experiments but the general pattern seems to be similar.

At 150°C and 190°C, the top layer is a hydrated silicon oxide (<50 nm) which covers only part of the surface of the film. Below, a fibrous and porous, but nevertheless amorphous layer with a composition close to Mg-serpentine is found. Below, a variable size iron-hydroxide layer occurs. It continues with a layer of Fe-rich serpentine-like composition. At 120°C, the iron-rich layer has a composition close to iron hydroxide but silicon is still present (Fig. 1). At 60°C, the top Mg-rich layer is barely visible (Fig. 2), and a thin iron-hydroxide layer is found below, followed by an iron-rich silicate. Unreacted material is still present only at 120°C and 60°C. Energy filtered TEM enables to map the compositional variations at the nanometer scale and do not reveal zonation at the interfaces which would result from diffusion profile. Hydrogen depth profile reveals that reacted layers are hydrated (Fig. 3), with values close to that of serpentine. Despite the lower resolution (30-50 nm), layer boundaries correspond to sharp H content variations.

**Discussion:** Using amorphous iron-rich silicates similar to those observed in chondrites, we demonstrate the possibility of studying hydration at low temperature with a new combination of experimental and analytical techniques. There is a consistent evolution, with fractionation of Fe/Mg between layers. Mg-rich layers tend to be porous and always occur on top of the film, maybe because it forms at a late stage. The intermediate iron-rich layers (silicate or oxide layers) are likely to be the first to form. The water content is close to that of serpentine (~ 14 mol.%). Further time series experiments and the analysis of the reaction products by irreversible thermodynamics should reveal if the reaction is limited by dissolution/precipitation or by the diffusive transport through the various layers. Diffusion of water does not seem to be a rate limiting process but the diffusion of solutes within nanoporous channels might be one. At this preliminary stage, we can show that amorphous silicates react faster than crystalline one, at conditions typical for aqueous alteration on parent bodies. At 60°C, micron sized particles could be completely altered in a timescale of months. However, the products remain amorphous (metastable, not seen in olivine serpentinization studies) and it is possible that time was missing to overcome the nucleation barrier. It contrasts with olivine serpentinization for which nucleation may be favored by topotactic transformation.

Thermodynamic models [9] show that the ratios of serpentine/brucite/magnetite/H<sub>2</sub> and the Fe-partitioning between serpentine and brucite depend on temperature and water to rock ratios. Our approach offers the possibility to compare those models to experimental data, and to predict the expected compositions to constrain the temperature and duration of the episodes in chondrites.

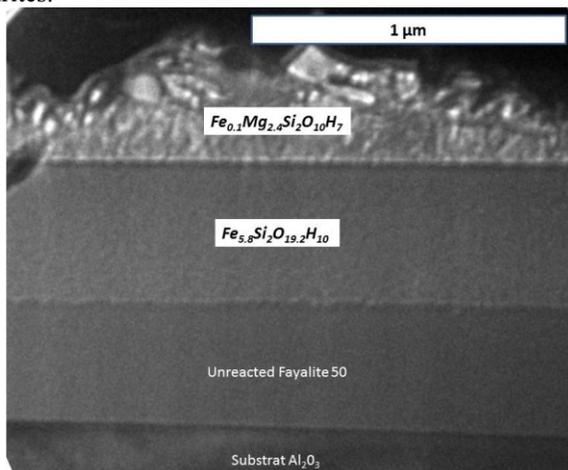


Fig. 1: TEM image of a FIB section from the thin film heated at 120°C (2 weeks, W:R = 300) together with composition deduced from RBS and TEM data.

We have shown that amorphous and hydrated iron-rich silicates of serpentine composition, similar to some degree to our observations in CR chondrites [4] can be produced by aqueous alteration. However, in the meantime, nebular hydration, which was thought to be kinetically inhibited, could be re-assessed based on the data showing fast transformation rate. We plan to study water vapor/silicate interaction in the future to constrain this specific mechanism.

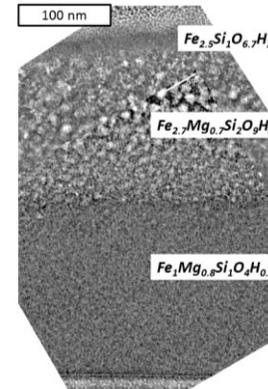


Fig. 2: TEM image of a FIB section from the thin film heated at 60°C (2 weeks, W:R = 300).

**References:** [1] Brearley A.J. (2006) *MESS II*, 587–624. [2] Ciesla et al. (2003) *Science* 299, 549–542 [3] Howard K.T., et al. (2011) *GCA*, 2735–2751 [4] Le Guillou et al. (2011) *Goldschmidt conference*, 1291 [5] Keller L.P. and Messenger S. (2011) *GCA* 75, 5336 [6] W. J. Forrest et al. (2004) *ApJS* 154, 443 [7] Dohmen R. et al. (2002) *Eur. J. Min.* 14, 1155 [8] Hellmann R. et al. (2012) *Chem. Geol.* 294, 203 [9] McCollom T. M. and Bach W. (2009) *GCA* 73, 856.

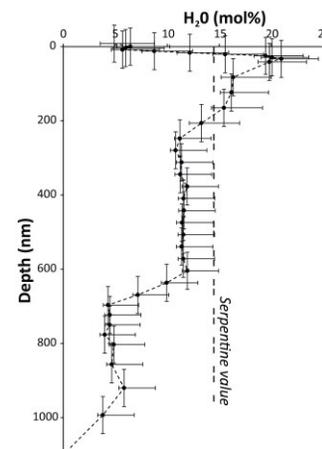


Fig. 3: Depth-resolved water content of the film (Fig. 1) - same scale - obtained by nuclear reaction analysis and showing a good match between layer boundaries and H-content variations.