

THE VALENCY OF IRON IN THE SILICATES OF CR CHONDRITE MATRICES: OBSERVATIONS AND EXPERIMENTS. C. Le Guillou¹, H. G. Changela², R. Dohmen¹, T. Müller¹, A. J. Brearley², C. Vollmer³, D. Rogalla⁴, and H-W. Becker⁴. ¹Ruhr-Universität Bochum, Inst. für Geologie, Mineralogie and Geophysik., 44780, Bochum, Germany, corentin.san@gmail.com. ²University of New Mexico, Dept. Earth & Planetary Sciences. ³Universität Münster, Institut Für Mineralogie, Corrensstraße 24, D-48149 Münster, Germany. ⁴RUBION facility, Ruhr-Universität Bochum, Bochum, Germany.

Introduction: Aqueously altered carbonaceous chondrites (CCs) record the history of water in the early solar system [1]. The CR chondrites have experienced overall lesser alteration than other CC groups such as the CM and CI chondrites. Iron-rich amorphous silicates have been shown to be progressively altered into fine-grained phyllosilicates in the CR3 and CR2s [2, 3], and are completely replaced by serpentine / saponite in the CR1 chondrites. To constrain the conditions of aqueous alteration (temperature, timescale, water to rock ratio (w/r), oxygen fugacity), it is important to understand the mechanisms and kinetics of the reactions between amorphous silicate and water by both experiment and observation. Iron oxidation and serpentinization reactions are coupled and iron redox state is an important diagnostic of the conditions of formation [4].

At present, experimental data on hydration / serpentinization below 200°C using an Fe-rich amorphous silicate as a precursor are lacking. We have therefore conducted experiments, and have characterized the reaction products including the oxidation state of iron. We have also measured *in situ* the valence state of iron in amorphous and crystalline silicates from the matrices of multiple CR chondrites.

Experimental: Our study is based on a novel experimental setup combined with analytical techniques, providing characterization of the reaction products at the nanoscale. A micron-thick layer of amorphous silicate (composition : ~ fayalite 50) is deposited on a TiO₂ substrate by laser sputtering and plasma deposition (pulsed laser deposition) [5]. This precursor contains some hydrogen (~ 4 at. %). The sample is then sealed in a gold capsule with deionized water (under nitrogen atmosphere) and then heated in teflon bombs. Several runs at 90°C (4 hours, 4 days, 2 weeks, 1.5 months, 6 months) and runs at 50°C and 150°C were performed (w/r ~ 250). The thin film geometry in this experiment is ideal to follow the evolution of the reaction front between the water and the amorphous silicate. Rutherford Back Scattering (RBS), Nuclear Reaction Analysis (NRA) (using a tandem accelerator at the RUBION facility, Bochum) and FIB/TEM, are combined. X-ray Absorption Near Edge Spectra (XANES) at the Fe L_{2,3}-edge were also obtained by scanning transmission X-ray microscopy (STXM) at the Canadian Light Source (SM beamline, 10 ID-1). These

techniques give access to depth resolved mineralogy (TEM), major element concentrations (RBS), water content (NRA), as well the valence state of iron.

In parallel, several FIB sections from 8 different CR chondrites spanning the complete alteration sequence (from type 3 to 1) were studied by STXM and TEM. Following [6], a calibration has been established to quantify the Fe³⁺/ΣFe ratios by Fe L-edge XANES.

Results: Experiments: In all of the experiments, TEM analysis shows a sequence of formation of amorphous layers with sharp boundaries between them (Fig. 1, left). At the reaction front, a compact and homogeneous amorphous layer is found which has a Fe-rich serpentine composition. On the outer part of the film an amorphous Mg-rich layer forms with a fibrous and porous texture. With increasing temperature and run duration, the thicknesses of the layers increase. The Fe-Mg fractionation between them increases as well. Some crystalline serpentine only appears within the Mg-layer in the “90°C, 6 months” experiment.

The reacted layer reached a thickness of 150 nm at 50°C-3 months. At 90°C, 500 nm reacted after 2 weeks, and after 6 months, the entire 1.5 μm film was transformed. The precursor contains only Fe²⁺. After reaction, the Fe-layer has a Fe³⁺/ΣFe ratio of ~60-70% (Fig. 1), always higher than the Mg-layer (~ 40-50%). At 90°C, the Fe³⁺/ΣFe ratio of the Fe-layer increases with duration, from 55% (4 days) to 70% (6 months).

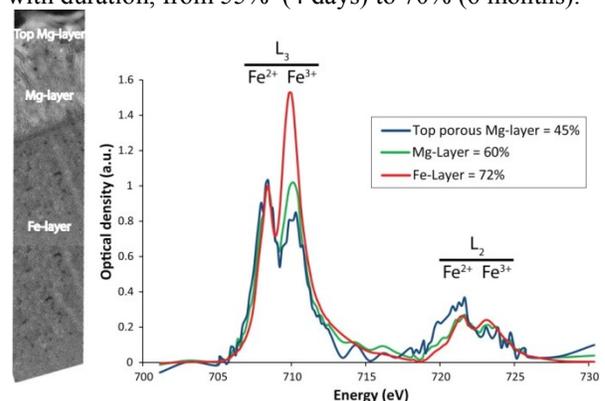


Fig. 1 : TEM image of a FIB cross section across the reaction fronts (run at 90°C, 6 months). Chemical fractionation occurs between the Fe-layer and the Mg-layer. XANES spectra at the Fe-L_{2,3}-edge of the layers.

Chondrites. Texturally, the CR chondrite matrices can be divided into 2 groups based on their matrix miner-

alogy: i) the types 3 and 2 CRs contain hydrated amorphous silicates mixed to various degrees with phyllosilicates and ii) GRO 95577 and Al Rais, are fully altered into phyllosilicates of various grain sizes. The fine grained material is more Fe-rich (Fig. 2), and has a higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio ($\sim 70\%$) than the coarser grained serpentine/saponite ($\sim 50\%$) (Fig. 3). Renazzo is intermediate - it has amorphous silicates but some areas clearly have a lower Fe^{3+} content.

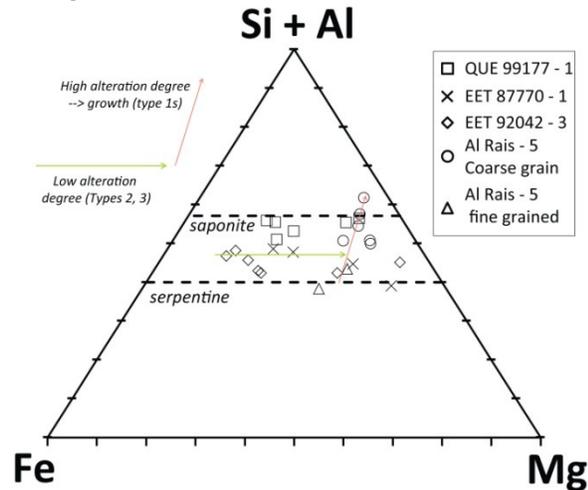


Fig. 2 : Fe-Mg-Si+Al ternary diagram (at. %) of the matrix silicates in CR chondrites showing decreasing Fe and increasing Si content with increasing alteration.

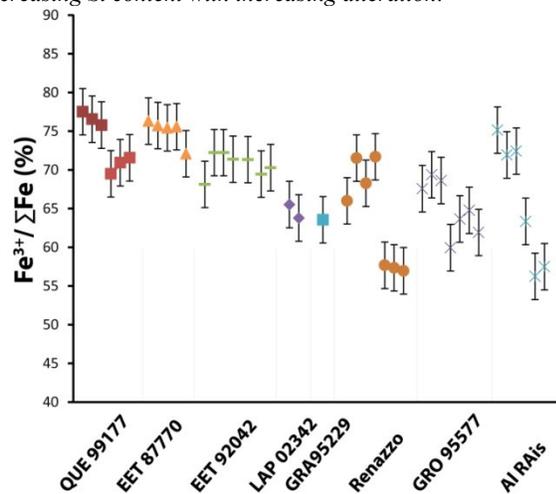


Fig. 3 : $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of matrix silicates in CR chondrites plotted as a function of their alteration degree from [8].

Discussion: The textures of the experimental products suggest that the distinctive Fe and Mg-rich layers formed by different mechanisms. The lowermost Fe-layer may form by a reactive transport through the bulk film, either by transport of liquid water through nanometer-sized channels or by diffusion through the amorphous silicate. This transport is coupled with hydrolysis and the preferential transfer of Mg^{2+} which is

more soluble in the fluid. This results in a hydrated and highly oxidized material. It is currently not clear whether the coexistence of the two types of serpentines is the result of a chemical gradient in the system or is a reflection of the final equilibrium assemblage. In contrast, the outermost fibrous Mg-rich layer may have formed by precipitation/growth from the Mg-saturated fluid and has a lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio.

In the CRs, the phyllosilicates have a bimodal composition with both Fe and Mg-rich compositions (Fig. 2). Chondrites and experiments are somewhat similar; the finer-grained materials are more Fe-rich and more oxidized. These heterogeneities might be explained by kinetically-controlled reactions if the hydrolysis/oxidation rate was higher than the nucleation rate of stable crystalline phases. This would result in metastable products, which do not record the oxygen fugacity at equilibrium. A single alteration event could therefore yield two different serpentine-like phases of different redox states. It does not necessarily imply that the oxygen fugacity has changed with time or that several different alteration episodes are required [7]. The slightly decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio with increasing aqueous alteration (Fig. 3) may reflect the evolution towards equilibrium. The decreasing iron content and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in the coarser grained phyllosilicates may have been the result of increasing content of Fe^{3+} in magnetite, as re-equilibration progressed.

Thermodynamic modeling [4] shows that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in serpentine should mainly depend on the w/r. It is therefore striking that our experiments performed at a w/r ~ 250 produced $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios similar to those observed in the CCs for which the w/r is usually considered to be close to 1. Whether or not this discrepancy is due to the inaccurate thermodynamic database, kinetically-controlled transformations or underestimated w/r ratios remains to be determined.

We can estimate the timescale of alteration of amorphous Fe-silicates at low temperatures. Assuming an initial grain size of ~ 100 nm for the dust that accreted to form the matrix, it would take from \sim months at 50°C , to days or hours at 90°C to form the hydrated/oxidized fine-grained phyllosilicates. However, the coarser-grained material in the CRs are not reproduced at 90°C and may require higher temperatures or longer timescales.

References: [1] Brearley A. J. (2006) *MESS II*, 587–624. [2] Le Guillou and Brearley. (2013) *GCA*, in press [3] Le Guillou et al. (2013) *GCA*, doi:10.1016/j.gca.2013.11.020 [4] Klein et al. (2009) *GCA*, 73, 6868–6893. [5] Dohmen R. et al. (2002) *Eur. J. Min.*, 14, 1155. [6] Bourdelle et al. (2013) *Contrib. Min. Pet.*, 166, 423–434. [7] Zega et al. (2003) *Am. Min.*, 88, 1169–1172. [8] Schrader et al. (2011) *GCA*, 75, 308–325.