HYDROGEN CONTENT IN CHONDRULES OF CM CHONDRITES: INFLUENCE OF AQUEOUS ALTERATION OR PREACCRETIONAL HERITAGE? S. Azevedo-Vannson<sup>1</sup>, L. Remusat<sup>1</sup>, L. Piani<sup>2</sup>, S. Pont<sup>1</sup>, M. Roskosz<sup>1</sup>. <sup>1</sup> Muséum National d'Histoire Naturelle, Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), UMR CNRS 7590, Sorbonne Université, <sup>2</sup> Université de Lorraine, CNRS, CRPG, F-54000 Nancy, France.

Introduction: Chondrites were formed during the early ages of the Solar System hence they witnessed this era. Hydrogen contents and isotopic compositions of these objects bring some constraints about the hydrogen accretion. Two main reservoirs of hydrogen, with distinct isotopic compositions, occurred in the early Solar System: the molecular gas of the protosolar nebula with a low D/H [1] and water ice. Water ice may have a presolar origin with a high D/H or solar origin, resulting from an exchange between presolar ice and molecular hydrogen (H<sub>2</sub>) [2]. Water ice was likely accreted on the parent body of hydrated meteorites like carbonaceous chondrites, mostly in the matrices. When it melted, water then percolated into the matrices resulting in the aqueous alteration of its components. The aqueous alteration could have affected mineral components of both matrices and chondrules.

origin The of the chondrules remains misunderstood<sup>[3]</sup>. in part because they present a diversity of mineralogy and textures. Among this diversity, one typically distinguishes two main types of chondrules with different textures exist, type I (FeOpoor) and type II (FeO-rich), which were formed in a reducing and oxidizing environment, respectively, in the early Solar System when H2 was still abundant of the protoplanetary disk. Stephant et al.<sup>[4]</sup> reported large hydrogen content in olivine in chondrules of carbonaceous chondrites. However, few studies have investigated hydrogen content in chondrules and this observation remains debatted<sup>[5]</sup>. The aim of this study is to constrain the origin of hydrogen contained in chondrule olivines of CM chondrites and to assess the influence of aqueous alteration on hydrogen content and isotopic signature in these emblematic constituents of chondrites.

**Samples and Methods:** Two carbonaceous chondrites showing different alteration degrees were investigated: Paris (CM2.7 to CM2.9) and Aguas Zarcas (CM2). Two polished sections were prepared in epoxy and were carbon coated. Olivines of chondrules of both type I (FeO-poor) and type II (Feo-rich) were analyzed.

Hydrogen abundance and isotopic composition were measured with a CAMECA 1280 HR2 SIMS at the CRPG in Nancy, France. A liquid nitrogen cold trap was used to reduce the  $H_2O$  background and maintain the vacuum below  $2 \times 10^{-8}$  mbar in the analytical chamber. We used a 10 keV  $O^-$  primary ion beam produced by a

Hyperion radio-frequency plasma source<sup>[6]</sup>. Prior to analysis, 180s of presputtering with a 15 nA current was applied over an area 10  $\mu$ m  $\times$  10  $\mu$ m to remove the carbon coating and reach the sputtering steady state. The samples were then analyzed with a 15 nA current rastered over the 10  $\mu$ m  $\times$  10  $\mu$ m area. A high magnification (M. Area = 60), a small field aperture (3000  $\mu$ m) and 60% electronic gate were used to eliminate hydrogen contamination from the crater edges. Secondary ions of  $^{1}$ H $^{+}$ , D $^{+}$ , and  $^{30}$ Si $^{+}$  were collected sequentially in monocollection mode, using an electron multiplier for H and D and a faraday cup equipped with a  $10^{12}$ -ohm resistor for Si. The mass resolution (M/ $\Delta$ M) was set to 4,000 to avoid interferences of H $^{2+}$  on  $^{2}$ H $^{+}$  and  $^{29}$ SiH $^{+}$  on  $^{30}$ Si $^{+}$ .

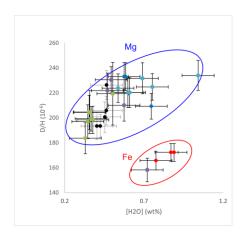


Figure 1: D/H ratio as a function of water concentration in olivines of Paris chondrules. Two populations can be distinguished with type I chondrules rich in magnesium and D and type II chondrules rich in iron and poor in D

**Results and Discussion:** The hydrogen concentration, expressed as water concentration, in olivine of the Paris chondrite varies between 0.24 and 1.04 wt% H<sub>2</sub>O, whereas the water concentration of olivine in Aguas Zarcas varies between 0.20 and 1.18 wt% H<sub>2</sub>O (Fig. 1 and 2). The D/H ratio in olivine of Paris chondrules ranges between 158.10<sup>-6</sup> and 234.10<sup>-6</sup>, whereas in Aguas Zarcas the D/H ratio ranges between 119.10<sup>-6</sup> and 247.10<sup>-6</sup>. Moreover, there is a correlation between the iron-content of these olivine crystals, the

water concentration and the D/H ratio. The Paris olivines are divided into two populations, with a D-rich magnesian pole and a D-poor iron-rich (Ferroan might works here) pole. On the other hand, in Aguas Zarcas, iron-rich and D-poor olivines are water enriched.

Unlike Paris, a clear trend can be observed for the Aguas Zarcas dataset (Fig. 2). These values are less dispersed and tend towards larger water concentrations with a lower D/H ratio. Moreover, this D-poor signature is present in iron-rich olivine but also at the edge of some zoned olivines in Aguas Zarcas, (Fig. 3). Furthermore, according to Piani et al.<sup>[7]</sup> the matrix of CM chondrites, which surrounds these chondrules, was altered by D-poor water and then records this D-poor signature. Thus, the signature at the mineral edge could be interpreted as a chondrule-fluid interaction during aqueous alteration, by isotope exchange or diffusion. Hydrogen and iron would migrate and the D/H ratios would converge toward the matrix values. So, the aqueous alteration could constitute a viable process to account for the composition of iron-rich olivines.

However, some data seem inconsistent with this hypothesis. Indeed, the section of Paris analyzed here exhibits type II chondrules, which are not significantly altered. It seems difficult to explain their composition solely by aqueous alteration. These chondrules are not zoned and Paris is one of the least altered meteorites found so far. Secondly, in Aguas Zarcas some zoned chondrules are only a few microns away (e.g. Fig. 3) from magnesian olivines. It is difficult to explain the zonation of these chondrules by aqueous alteration that should likely affect chondrules and isolated olivines over microns. Thus, although the effect of aqueous alteration on the composition of iron-rich olivines cannot be excluded, it seems unlikely considering the textural context of the chondrules studied here. Therefore, zonations as well as the trends in hydrogen composition of these iron-rich olivines seems to be of preaccretional origin.

Iron-poor olivines could originate from precursor having lower hydrogen concentration and higher D/H ratio than iron-rich olivines. These iron-poor olivines, which could be precursor of iron-rich olivines would have been oxidized (as a consequence of transportation in an oxidized zone or simply upon cooling). Thus, during this oxidation, these olivines would have assimilated water and acquired their isotopic signature with lower D/H ratios.

However, these scenario does not account for the anomalously large water content in nominally anhydrous minerals. Fine scale characterization of the mineralogy of these olivine crystals are planned in order to interpret the large water concentrations in these chondrules.

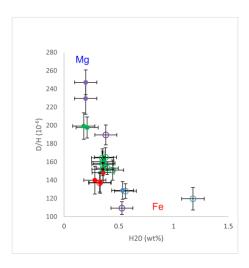


Figure 2: D/H ratio as a function of water concentration at the center (filled circle) or at the edge (open circle) in olivines of Aguas Zarcas chondrules.

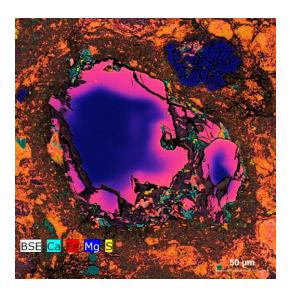


Figure 3: SEM-EDS chemical map of a zoned chondrule within a few micrometers from non-zoned Mg-rich olivines in Aguas Zarcas meteorite.

**References:** [1] Mahaffy, P.R. et al. (1998) *Space Science Reviews*, 84, 251-263. [2] Cleeves, I. et al. (2014) *Science*, 345, 1590-1593. [3] Connolly, H.C. and Jones, R.H. (2016) *J. Geophys. Res. Planets*, 121, 1885-1889. [4] Stephant, A. et al. (2017) *GCA*, 199, 75-90. [5] Shimizu, K. et al (2019) *LPSC*, 2132. [6] Piani, L. et al. (2020) *Science*, 369, 1110-1113. [7] Piani, L. et al. (2018) *Nature Astronomy*, 2, 317–323.