

WATER CONTENT IN AMORPHOUS SILICATES OF CHONDRITE MATRICES DETERMINED BY ADVANCED TEM ANALYSIS - AND SCANNING TRANSMISSION X-RAY MICROSCOPY.

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Introduction: Water is mainly expressed in carbonate chondrites as phyllosilicates or amorphous silicates. These phases are most likely the result of the interaction between the accreted water ice and anhydrous phases during hydrothermal episodes [1]. In weakly altered chondrites, amorphous silicate is the main material, and it has now been identified in all chemical groups [2, 3, 4]. Being able to precisely quantify the water content of this material is crucial to understand the nature of the silicates that were originally accreted in the chondrite matrices, as well as to identify the alteration mechanism and conditions.

In contrast to crystalline phases which have “nominal” water content, there is no easy way to determine the water content of submicrometric domain of amorphous materials. In recent works [2], using TEM-EDS, we suggested that the observed oxygen excess could be due to the presence of hydroxyl groups allowing us to deduce the equivalent water content. Thanks to the new generation of EDS detectors (windowless, SDD technology), we have now a much better efficiency for the measurement of oxygen which should allow to precisely quantify the O/Si ratio, and, eventually, the water content of any material.

However, low energy X-rays (such as O-K or Fe-L lines) can be strongly re-absorbed within the sample and modify the quantified O/Si ratio up to 40%. This absorption is a function of three parameters: x-ray travelling distance through the sample (tilt dependent), sample thickness and density, which are in practice difficult to determine.

Here, we first measured a set of standard materials (fayalite, forsterite, basalt and rhyolite, serpentine, wollastonite and pyrite) in order to determine the O/Si and Fe_L/Si k-factor (the instrument calibration). We then developed a routine using hyperspy (python library for hyperspectral data analysis [5]) to retrieve the [thickness*density]. The principle is that if the theoretical ratio of two x-ray lines is known, one of high energy (not significantly absorbed) and one of low energy (strongly absorbed, such as O-K or Fe-L), then the “thickness*density” value can be determined, based on the constraint that the absorption correction should yield the same results for both the low and high energy x-ray line. With all elements including oxygen being quantified, the water content can then be calculated based on the charge neutrality assumption. The observed lack of positive charges is interpreted as unde-

tected hydrogen present as hydroxyl groups or H₂O molecules.

Using this approach, the water content of the standards are determined as well as related uncertainties. It is then applied to various FIB sections of ALH 77307 and Renazzo, which are weakly altered CO and CR chondrites.

Automated absorption correction and accuracy of the water content determination: Analysis were performed on a Titan Themis, at 300 kV using a four quadrants, windowless, super-X SDD system. k-factors for O, Fe, Mg, Al, S, Ca, and K were measured on standards prepared by ion polishing, which produces samples of various thicknesses. Values of 0.94 is found for O/Si, far from the default value provided by the Bruker software (1.24) and a value of 2.3 is found for the Fe_L/Si (instead of 2.11).

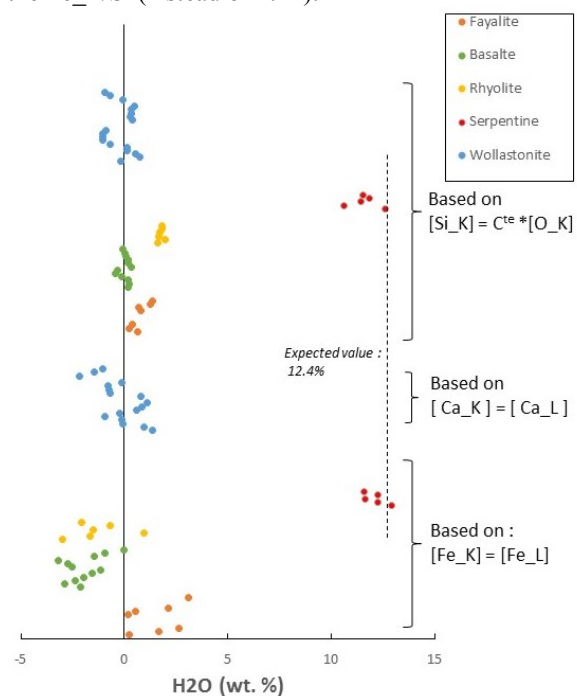


Fig. 1 : calculated H₂O wt.% of standards of various thicknesses using different sets of constraints to correct for absorption.

Hyperspy was used to subtract background, fit Gaussian functions to the spectra and the specific routine was used to automatically find the thickness*density value and thus apply absorption correction. If the Si/O value and the density is known (for a forsterite for instance), then the thickness of the sample

can be retrieved. On the other hand, if the material composition is unknown, one can use the fact that quantification using Fe_K lines should give the same result as using the Fe_L lines.

Figure 1 shows the water content obtained using the Fe_K/Fe_L, Ca_K/Ca_L and the Si/O constraints. The standards have various Fe content (Fe/Si from 1.83 to 0.04) and valence (from 2 to 2.6). We find an internal variability lower than 1 wt.% H₂O and sample to sample accuracy is lower than 2 wt.%. The cations/Si relative accuracy is found to be better than 2 at. % in most cases.

Application to chondrites:

STEM-EDS hyperspectral maps were acquired using four detectors at a beam current of 500 pA. One FIB section was measured at room temperature and the other ones at liquid N₂ temperature. To map the amorphous silicate, we established phase cartographies. Principal component analysis allows to identify the number of different phases present and a "blind source separation" algorithm to obtain a first localization of these phases. The corresponding spectra are extracted and a linear combination fitting of those spectra is then performed to refine the phase cartography. One averaged spectrum per phase was retained for the quantification.

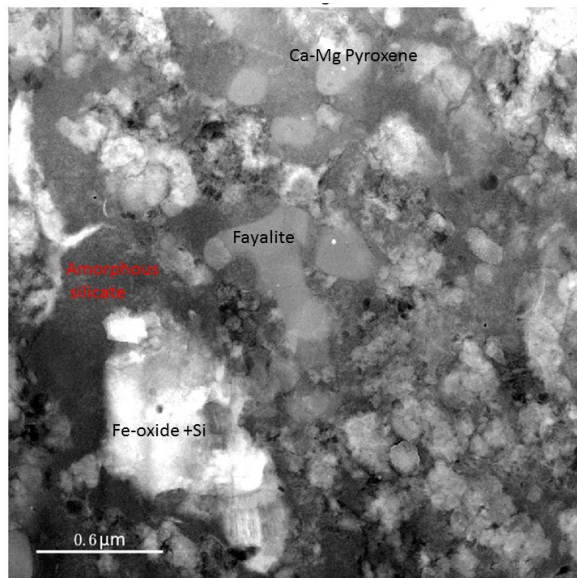


Fig 2 : HAADF STEM image of ALH 77307 showing the various identified phases.

Scanning transmission X-ray microscopy at the Fe_L edge was performed on the same FIB sections to determine the Fe³⁺ content of the amorphous silicate which is required to calculate the water content. Values are always in the range 60 to 70% Fe³⁺/ΣFe.

In ALH 77307, oxide, enstatite, CaMg-pyroxene, Fe-olivine (Fa₄₀ with Ni/Si up to 0.04 at.%), Fe-

sulfides, Fe-Mg sulfate and organics were found in addition to amorphous silicate. The density and Si/O ratio of pyroxene are known which allows to determine the thickness of the FIB section. For amorphous silicate, using this thickness value and an inferred density of 2.9, composition, water content are extracted. Amorphous silicate is Fe-rich (Fe/(Fe+Mg) ~ 0.6), has a stoichiometry close to serpentine ((Fe+Mg)/(Si+Al) ~ 1.3 – 1.7) and shows high Ni and S contents (Ni/Si = 0.1 – 0.3; S/Si = 0.1 – 0.2). Water is present in all analyzed regions and is found to vary between 7 and 12 wt. %.

In the Renazzo FIB section, only Fe-Ni sulfides are found together with the amorphous silicates in the particular analyzed region. It is less Fe-rich (Fe/(Fe+Mg) = 0.44), with a stoichiometry close to serpentine as well ((Fe+Mg)/(Si+Al) ~ 1.4), but the Ni/Si and S/Si ratios are much lower (< 0.01 and 0.05 respectively). It is also significantly hydrated with a H₂O content of 9.5 wt.%.

Discussion: Using the enhanced efficiency of new SDD detectors, appropriate standards measurements and an dedicated data processing routine, we demonstrate that it is possible to determine the water content of any material by TEM-EDS analysis with a precision better than 2 wt. % using Fe_K/Fe_L properties. On the other hand, if the O/Si ratio is known, density and/or thickness can be retrieved.

Applied to chondrites, these analysis confirm the presence of a significant amount of water in the amorphous silicate of CR chondrites [2] and reveal its presence in CO chondrites as well. The enhanced measurement accuracy also enables to show that the water content can be heterogeneous at the micrometer scale, since our three maps in ALH 77307 revealed a H₂O content variation of several % (7, 10 and 12 wt. %). We infer that these hydrated and oxidized amorphous silicate are formed through the interaction with water, which was heterogeneously distributed within the matrix.

ALH 77307 has a more complex mineralogical phase assemblage than CR chondrites, with remains of accreted anhydrous enstatite grain but also with Ni-bearing fayalite and amorphous silicate which might reflect alteration condition at higher temperatures [6].

References:

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