

## THE OXIDATION STATE OF IRON IN SILICATE MINERALS FROM THE MATRICES OF CO CARBONACEOUS CHONDRITES.

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**Introduction:** Carbonaceous chondrite meteorites are amongst the most primitive extra-terrestrial materials available for study. They consist of chondrules and calcium-aluminium-rich inclusions (CAIs) set within a matrix of fine-grained (<1  $\mu\text{m}$ ) materials including amorphous and crystalline silicates, metal, Fe-sulphides and Fe-oxides. In many “type 3” carbonaceous chondrites the matrix has remained largely unaltered since it was accreted into their parent bodies. The matrix therefore preserves the original building blocks of the solar system and is an important tracer of the formation and evolution of asteroids.

Amorphous silicates can comprise up to 50 vol% of the matrix in the most pristine carbonaceous chondrites [e.g. 1]. However, the origin of the amorphous silicates remains enigmatic; analyses are challenging due to small domain sizes and the heterogeneous nature of the matrix. The amorphous silicates could be a presolar phase [2], a product of nebula condensation [3, 4], or result from later parent body alteration [5, 6].

Hopp and Vollmer [7] recently used transmission electron microscopy (TEM) combined with energy-dispersive X-ray (EDX) analysis and electron energy loss spectroscopy (EELS) to investigate amorphous silicates in the pristine ungrouped carbonaceous chondrite Acfer 094. They interpreted mobilization of Fe and high (>0.6)  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios to show that the amorphous silicates had reacted with fluids in the parent body. Similarly, using TEM and scanning transmission X-ray microscopy (STXM), [8] analysed  $\text{Fe}^{3+}$ -rich hydrated amorphous silicates in pristine CR chondrites, and showed that their mineralogy and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios varied as a function of hydration.

We are investigating the effects of thermal metamorphism on crystalline and amorphous silicates in the matrices of CO carbonaceous chondrites, which range in petrologic type from 3.0 to 3.8. Our aim is to better understand the initial formation conditions of the silicates, and to quantify how the degree of asteroidal heating has influenced their abundance, structure, chemistry and transformation behaviour. Here we present results from the CO chondrites DOM 08006 (CO 3.0), Kainsaz (CO 3.2) and Moss (CO 3.6).

**Methodology:** Suitable areas of matrix were identified in each meteorite by scanning electron microscope (SEM)-EDX mapping and analysed by electron

microprobe. Electron transparent foils ( $\sim 10 \times 5 \times 0.09 \mu\text{m}$ ) were cut and extracted from each area using the focused ion beam (FIB) technique and attached to a Cu TEM grid.

The  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of matrix materials in the FIB sections were measured using STXM on beamline I08 at Diamond Light Source, UK. Energy-dependent image stacks ( $\sim 2 \times 2 \mu\text{m}$ ) were collected over the Fe  $L_3$ -edge (705 – 715 eV) with an energy resolution of 0.1 eV, a spatial resolution of  $\sim 50 \text{ nm}$  and a dwell time per pixel of 5 ms. Fe  $L_3$ -edge spectra were then extracted from specific grains/regions within the energy stacks ranging in size from  $\sim 50$  to 500 nm in size. In addition, we also analysed several standards including San Carlos olivine, magnetite and an Fe-(oxy)hydroxide.

The FIB sections were subsequently imaged by TEM using an FEI T20 instrument at the University of Glasgow operated at 200 kV.

**Results:** Electron microprobe results clearly show chemical variations in relation to the degree of metamorphism. Plotting data on a Fe-Si-Mg ternary diagram reveals a decrease in Fe within the matrix, of about 10 wt%, in the more highly metamorphosed samples and an enrichment in Mg in the matrix (Fig. 1).

Bright-field TEM images of DOM 08006 and Moss show how the matrix texture changes with increasing thermal metamorphism (Fig. 2). The matrix in DOM 08006 has an amorphous groundmass embedded with  $\sim 0.1 \mu\text{m}$  silicate, sulphide, metal and phyllosilicate grains. The matrix of Moss by comparison consists mainly of micron to sub-micron euhedral crystals that are interpreted to have formed by recrystallisation of the amorphous groundmass, metal grains and other matrix silicates.

At the Fe  $L_3$ -edge there are two absorption peaks, the relative intensities of which are related to the abundance of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  [e.g. 8, 9]. Fig. 3 shows typical Fe  $L_3$ -edge spectra extracted from silicates in DOM 08006, Kainsaz and Moss. Also included in Fig. 3 are spectra for San Carlos olivine ( $\text{Fe}^{2+}$ ) and an Fe-(oxy)hydroxide ( $\text{Fe}^{3+}$ ). Based on our mineral standards we can qualitatively infer that silicates in the matrix of DOM 08006 are rich in  $\text{Fe}^{3+}$ , Kainsaz contains about 10%  $\text{Fe}^{3+}$ , and Moss is dominated by  $\text{Fe}^{2+}$ . The spatial variation in the spectra was much greater for DOM

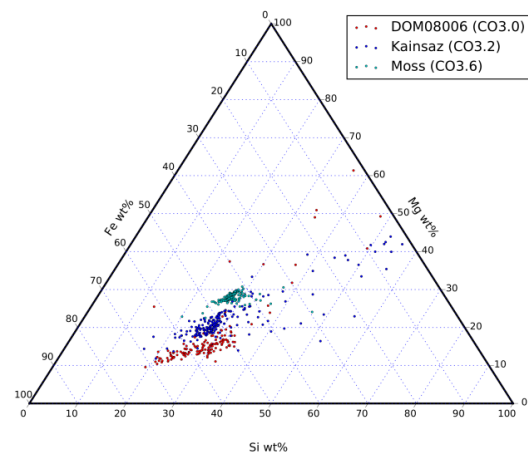
08006, with some regions found to be less  $\text{Fe}^{3+}$ -rich than other areas.

**Discussion:** Matrix is one of the first components of primitive carbonaceous chondrites to be affected by parent body alteration. Highly reactive amorphous silicates can therefore be used as an indicator of the progression of metamorphism. We find that amorphous silicates are abundant in the matrix of DOM 08006 and are typically  $\text{Fe}^{3+}$ -rich, although there is some variation in the Fe oxidation state within the sample. If the amorphous silicates condensed in the solar nebula, we would predict that they should be rich in  $\text{Fe}^{2+}$  due to the reducing environment. However, while DOM 08006 is believed to be one of the most primitive carbonaceous chondrites, there is recent evidence that it is a breccia and has experienced minor aqueous alteration [10, 11]. Even low levels of parent body processing would have oxidized the amorphous silicates. This finding is in agreement with the model proposed by [7] for  $\text{Fe}^{3+}$ -rich amorphous silicates in Acfer 094, and in aqueously altered CR chondrites [8]. In addition, we note that DOM 08006 is an Antarctic find of weathering grade A/B [10, 12]. Terrestrial alteration may explain why the silicates in DOM 08006 show greater variation in the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios compared to the relatively minor differences observed between grains in Acfer 094 [7].

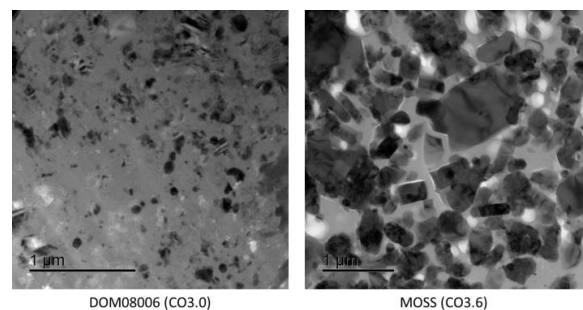
In Kainsaz and Moss very few amorphous silicates are present because they were readily destroyed by parent body thermal metamorphism. The crystalline silicates are all  $\text{Fe}^{2+}$ -rich, which might be because the environmental conditions became increasingly reduced with thermal metamorphism due to the removal of oxidizing  $\text{H}_2\text{O}$  and the initial presence of reducing agents such as H and C [14].

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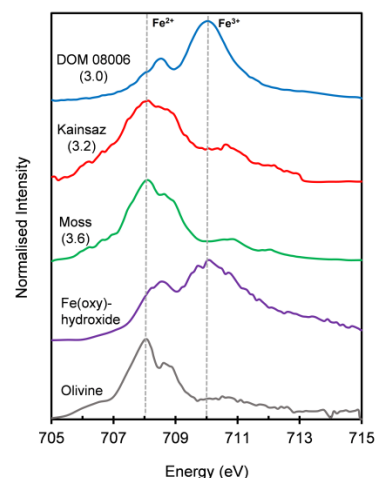
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**Figure 1.** Fe-Si-Mg ternary diagram from the matrix of DOM 08006 (CO3.0), Kainsaz (CO3.2) and Moss (CO3.6).



**Figure 2.** Bright-field TEM images of DOM 08006 (CO3.0) matrix on the left, and of Moss (CO3.6) matrix on the right. (Scale bar 1  $\mu\text{m}$ ).



**Figure 3.** Fe  $L_3$  edges of CO chondrites that underwent different degrees of thermal metamorphism. The dashed lines respectively indicates the peak corresponding to the  $\text{Fe}^{2+}$  at  $\sim 708$  eV and the peak of the  $\text{Fe}^{3+}$  at  $\sim 710$  eV.