GRAPHISATION IN PRESENCE OF IRON – ASTRONOMICAL IMPLICATIONS

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Introduction

Extraterrestrial carbons can be directly studied by sampling meteorites, i.e. objects coming from the young solar system. Primitive chondrites are representative of the matter synthesized in the protosolar nebula and preserved without significant aqueous alteration or thermal metamorphism. They contain an insoluble organic matter (IOM), which is structurally very disordered graphitic carbon in carbonaceous chondrites [1]. These carbons are chemically and structurally similar to a saccharose-based semi-coke, which is well known to be not graphitisable, even after a heat-treatment up to 3000°C. Primitive achondrites, such as acapulcoites and lodranites, are meteorites coming from partially differentiated planetesimals. They have textures and mineralogy indicative of partial melting, but preserve numerous primitive geochemical characteristics. They contain noble gases similar to those trapped in the organic matter of chondrites as well as various forms of carbon (disordered carbon, graphite…). The least differentiated acapulcoites present textures similar to those observed in the most metamorphosed chondrites, which suggest that acapulcoites-lodranites register the progressive evolution of a chondritic body by metamorphism and partial melting. In these meteorites the carbon component is frequently closely associated with metal (iron-nickel alloys, with Fe=90-95 wt%) which shows evidences of at least partial melting (**Fig. 1**).

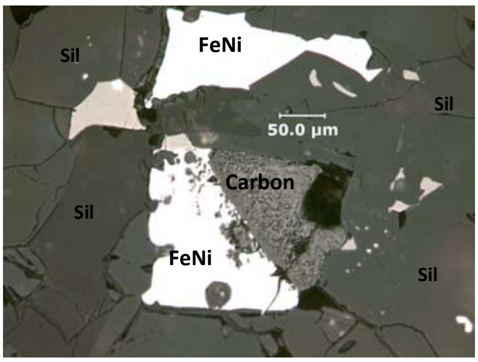

Fig. 1. Polished section of the Acapulcoite meteorite as seen by optical microscopy (reflexion mode) and showing the assemblage of silicates, iron-nickel alloys and carbon.

As characterized by Raman microspectrometry, these carbons are usually more or less highly graphitised, despite the relatively low temperature at which they were subjected (<1200°C). This suggests that the graphitisation could be catalysed by iron. Such catalytic graphitisation was frequently recognised during heat-treatment below 2000°C of various carbonaceous precursors [2]. A better understanding of the structural evolution of these extraterrestrial carbons should allow us to reconstruct the chronology of possible thermal events occurring during the metamorphism on the parent-planetesimal. To reach this aim, our strategy is to synthesize credible laboratory analogues. For that, we used blends of iron with carbonaceous precursors similar to the disordered organic matter found in the primitive meteorites. Then, we compare graphitised carbons found in the natural samples (acapulcoites achondrite meteorites) with these experimental analogues. The structural study was carried out at the µm-nm scales, by combining Raman microspectrometry and High Resolution Transmission Electron Microscopy (HRTEM).

Experimental

The present study is focused on the carbon components of an acapulcoite (achondrite meteorite) and some laboratory analogues. We used the classical saccharose-based chars obtained by heat-treatment of pure saccharose up to 400°C and 1000°C. Blends of 75 weight % of pure iron (micrometre-sized powder) with saccharose chars were performed in an agate mortar. Then, these blends were pyrolysed under argon flow at 700, 1250 and 1600°C (heating rate–: 300°C.h^{-1}, 20 min at the highest temperature followed by a quenching).

The structural organisation of meteoritic carbons was first studied on polished sections by Raman microspectrometry (InVia Renishaw, operating with an Ar^+ laser at 514,5 nm)–: besides punctual analysis on about 1 μm^2 areas, a Raman mapping was performed (resolution up to 1 µm) in order to visualize and quantify the heterogeneity of the graphitisation degree (see **Fig. 2** below). This parameter was determined from the width of the E_{2g} band (at about 1580 cm^{-1}) to avoid the artefact on the D/G ratios recognised when polished sections are used [3].

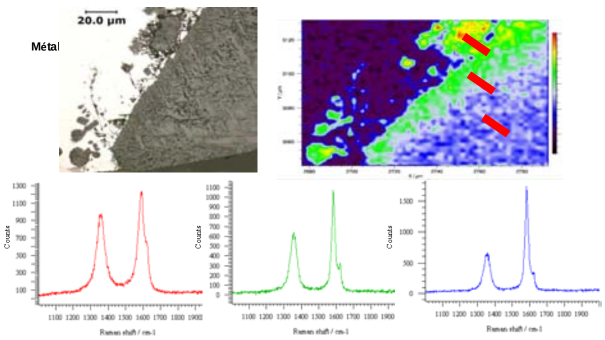

Fig. 2. Raman mapping of a carbon inclusion in contact with molten iron; a: optical microscopy image; b: Raman map (the red, green and blue colours correspond to the spectra with increasing the graphitisation degree, and the position of different FIB sections are shown by the red bars.

Ultrathin (< 100 nm) sections of areas of interest (coexistence of carbon and metal components) were prepared by Focused Ion Beam (FIB). With the help of a Raman map, it becomes possible to accurately choose the positions of the sections. In the example given in the **Fig. 2**, FIB sections were performed at the interface between carbon and metal, and at two places within the carbon phase corresponding to different degrees of graphitisation ; the position of these 3 FIB sections are indicated by red bars in **Fig. 2**. Transmission Electron Microscopy, and especially its high resolution mode (HRTEM), allows an accurate structural characterisation at the nanometre scale of different carbons present on the periphery or inside the metal, in the case of natural carbons from meteorites as those used as laboratory analogues.

Results

Our work is still in progress. In this part, we will present only significant preliminary results, illustrating our approach. In the Fig. 3, we show the Raman-TEM crossed results obtained on a representative area of the Acapulco meteorite (see **Fig. 2** and **3**).

The carbon component is always located close to the previously molten iron-rich metallic phase. It appears structurally heterogeneous (see the Raman map of the **Fig. 2**); however all these carbons appear highly graphitised. This is confirmed by the TEM study of FIB sections and is illustrated by the **Fig. 3** images below. 'True' graphite (perfect planar layers (image a), graphite hkl reflections in the electron diffraction patterns, negligible D band in the Raman spectrum) coexists with less graphitized carbon b: the layers are shorter, more distorted, less perfectly stacked (image b) and a noticeable D band is present in the Raman spectra.

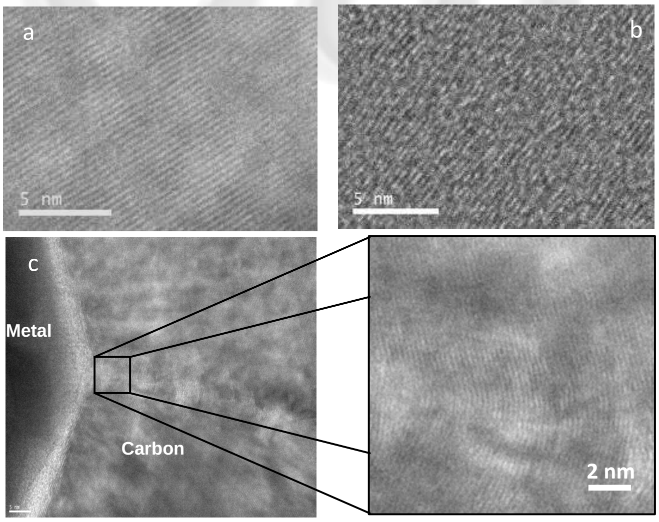

Fig 3. Carbon components of the Acapulco meteorite. HRTEM images corresponding to the FIB sections of the figure 2; a: 'perfect' graphite, b: 'imperfect' graphite, c: preferential orientation of the graphene layers around the iron grain .

Moreover, we found obvious crystallographic relationships between the metallic phase and the graphitized carbon, since the graphene layers are parallel to the surface of the metallic grain (see image c). This strongly suggests a catalytic effect of the iron on the carbon growth, as for a dissolution-reject mechanism.

In order to specify such possible mechanism, blends 25 wt% saccharose-based chars – 75 wt % heated at 1600°C were characterised by Raman and TEM. Both techniques show a quasi-complete transformation into graphite of the saccharose char : the D band has disappeared from the Raman spectra (**Fig. 4a**) whereas the sample is made of graphite lamellae (**Fig. 4b**). Only catalytically formed mesoporous turbostratic carbon particles can be rarely found, whereas no microporous non transformed saccharose-based particle was imaged. This demonstrates the occurrence of a graphitisation at 'low temperature' (1600°C) becomes possible in presence of iron.

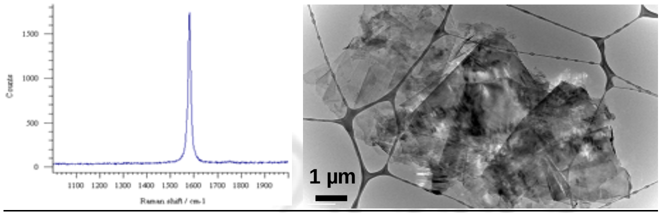

Fig 4. Laboratory analogues : carbons obtained by heat-treatment at 1600°C of saccharose-based char and iron; a : Raman spectrum ; b : bright field TEM image.

SEM study shows that the molten iron is able to react with the crucibles made of glassy carbons or graphite. To avoid possible minor artefacts, new pyrolysis are now performed with BN crucible. Further SIMS (Secondary Ion Mass Spectroscopy) characterization is planned to follow if the carbon isotopic composition ($\delta^{13}C$) is sensitive to such natural or laboratory graphitisation in presence of iron.

Conclusion

The graphite formation from disordered carbon seems to follow the same way in the meteorites under the effect of metamorphism and in laboratory analogues. In both cases, it is possible thank to a paramount catalytic effect due to the presence of iron. These preliminary results, and the corresponding mechanisms, have to be specified by the study of additional blends heated at lower temperature (750°C, 1250°C).

References

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