

COUPLED RAMAN / TEM STUDY OF AN UREILITE CARBON PHASES COMPARED TO SHOCKED GRAPHITE ANALOGUES : IMPLICATION FOR SHOCK HISTORY AND NOBLE GAS CARRIERS EVOLUTION. C. Le Guillou¹, J. N. Rouzaud¹, L. Remusat^{2,3}, M. Bourrot-Denise⁴ and A. Jambon⁵. ¹Laboratoire de Géologie de l'ENS, UMR CNRS 8538, 24 rue Lhomond, 75231-PARIS. cleguill@clipper.ens.fr, ²GPS division, Caltech, Pasadena, USA, ³LCBOP, CNRS, Paris, France, ⁴Museum National d'Histoire Naturelle, Paris, France, ⁵Université P. et M. Curie and Institut de Physique du Globe Paris, France

Introduction: Ureilites are enigmatic carbon rich achondrites containing various carbon structures (diamond, lonsdaleite, graphite, disordered carbons)[1]. Since lonsdaleite, the hexagonal diamond polymorph, known from impact craters, was discovered in ureilite 40 years ago [2], the shock origin of diamond was commonly accepted. Nevertheless, more recent isotopic analyses of noble gases in laboratory shocked analogues [3], as well as nitrogen composition in diamond and graphite [4], indicate incompatible genetic relationship and suggest instead 'mild' gaseous hydrocarbons condensation in the protosolar nebula.

In ureilites, graphite is noble gas free whereas diamond and disordered carbons do contain "planetary" noble gases. The nature and origin of this mysterious "disordered" carbon phase remains unknown.

The link between chondrites and ureilites carbon phases has also been questioned as they both have high carbon content (up to ~ 6 wt %) [5]. Is chondritic macromolecular carbon a consistent precursor for ureilite carbon phases? Do genetic crystallographic relationships exist between graphite and diamond, between disordered carbon and diamond? Which informations do they bring on their respective conditions of formation?

In this study, we present the first coupled High Resolution TEM / Raman spectroscopy observations of carbon phases in ureilites to constrain their relationships, origin and further parent body evolution. We have studied an ureilite carbon residue and compared it with laboratory shocked graphite to test the shock hypothesis from a structural point of view.

Experimental: Carbon phases are chemically extracted from a new ureilite (NWA 4742) by HF/HCl treatment. X-ray-Diffraction of the carbon residue shows the presence of disordered carbon, graphite, nanodiamond and lonsdaleite. Laboratory shock loading experiments (~40 GPa), made on graphite precursors yields samples partially transformed into diamond. Details of the experimental setup are given in [3].

Raman spectroscopy is performed with an excitation wavelength of 514 nm on a Renishaw spectrometer. The incoming power is reduced to avoid thermal damaging of the samples as well as peak shifting due to thermal expansion of the materials.

Raman effects on graphitic carbon present two principal modes: at 1580 cm⁻¹ for the E_{2g} graphite mode and at 1350 cm⁻¹ ('defect band' related to structural defects) [6]. Two parameters are defined here to classify the organization degree: the Full Width at Half Maximum of the D band (FWHM-D) and the surface ratio of the D band to the surface of the whole spectra (R).

HRTEM study is performed with a JEOL 2011 operating at 200kV. The different carbon phases are characterized by their inter-reticular distances: 0.206 nm for the diamond 111 planes, 0.3354 nm for the graphite polyaromatic planes, and more than 0.35 nm for the polyaromatic planes of the disordered carbons.

Results and discussion:

Shock experiments:

Matsuda et al. [3] have shown that about 15 weight % of diamonds were present in their samples. Our HRTEM study enables to distinguish four different structural carbon entities: unmodified 'perfect' graphite, graphitic carbon with more or less disrupted planes, and nanodiamonds surrounded by more or less disordered carbon materials. Thus, preservation of crystalline quality graphite is possible whereas partial deconstruction to complete amorphization can also occur [7, 8]. Nanodiamonds of a few tenths of nanometres are formed, always surrounded by strongly disordered graphitic material. These polyaromatic structures are always parallel to the diamond surface, as already observed for graphitized heat treated nanodiamonds [9,10]. They may result from nanodiamond back-transformation due to low cooling rate. It must be noted that, in a such experiment, one single event occurring on one single precursor produces several carbon nanostructures and phase relationships, as met in the ureilite carbon.

Carbon residue observations:

First, Raman spectroscopy was carried out on bulk rock fragments, without any polishing or chemical treatment. Two graphitic carbon families are systematically observed as illustrated in Fig. 1. It shows two typical spectra, one corresponding to strongly disordered carbonaceous materials and the other one to almost perfect graphite. The latter is nevertheless not *stricto sensu* crystalline graphite (presence of a significant D band). Both groups are heterogenous in

terms of organization degree, as illustrated by the scattering of the Raman parameters from the fitted spectra (FWHM vs R , Fig 1).

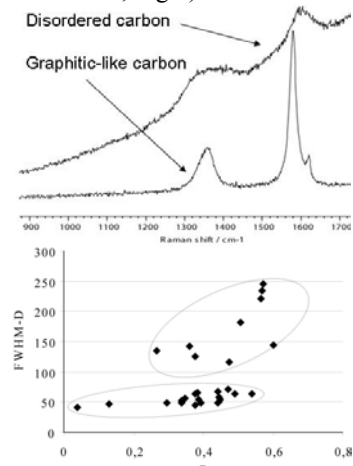


Fig 1: characteristic Raman spectra of non diamond material (up) and fitted parameters of each group (bottom).

HRTEM images of the acid etching residue shows striking similarities with shocked samples analogues. The same crystallographic features are observed, in good agreement with Raman analysis : imperfectly stacked graphite planes and polycrystalline nanodiamonds aggregates made of coherent domains of a few tens of nanometres. The nanodiamonds are frequently surrounded by disordered graphitic material, with their 002 planes parallel to grain surfaces (fig. 2).

However, another type of phase relationship is also observed in this ureilite. Fig. 3 shows the inclusion of nanodiamonds –surrounded in red- in an highly graphitized structure, showing a clear parallelism between both densest planes of each phase (in the electron diffraction pattern, the 002 arcs due to graphitic planes and 111 diamond punctual reflections are aligned). The diamond grains are not completely surrounded by graphitic material, which is present only along diamond 111 planes. Such feature excludes the possibility of a diamond graphitization [9]. Therefore, the formation of diamond from graphite by shock is the best explanation, since only such a quick event enables to preserve precursors morphology [8].

To summarize, it appears that parts of the diamonds are made by shock from graphite. However, this origin alone seems incompatible with the noble gases abundances of each phase. Graphite is noble gas depleted and it is difficult to understand how a depleted precursor could produce gas rich diamonds. One way of understanding this is to invoke a mixture of two diamond populations: an early generation of unknown origin and containing noble gases, and a

second one, formed by shock on graphite. Whatever its origin, diamonds is then back transformed under temperature due to the slow release of the shock heat. It is then easy to understand why disordered carbon contain noble gas, if they result from diamond partial graphitization.

The disorder nature of this phase implies a late shock event. Indeed, significant internal heating would have re-organized its structure into graphite.

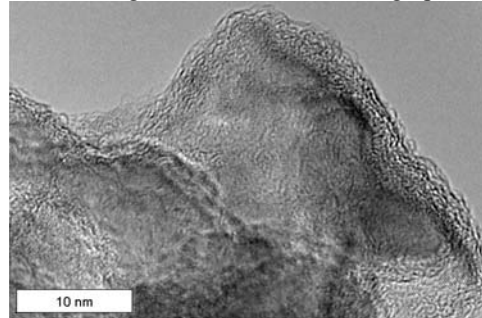


Fig 2: nanodiamonds in NWA4742 surrounded by disordered carbon.

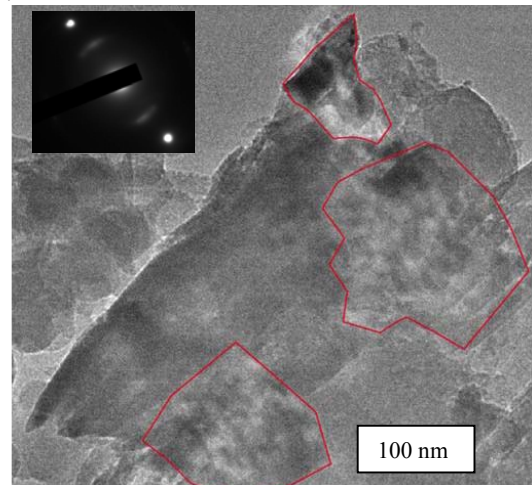


Fig 3: diamond included in a graphite-like particle and the corresponding electron diffraction pattern showing parallel orientation of their dense atomic planes.

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