

GRAPHITE IN AN APOLLO 17 IMPACT MELT BRECCIA. A. Steele¹, F. M. McCubbin^{1,2}, M. Fries³, M. Glamoclija¹, L. Kater⁴, H. Nekvasil⁵. ¹Carnegie Institution of Washington, Geophysical laboratory, 5251 Broad Branch Rd, Washington DC, 20015. ²Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, ³Planetary Science Institute, Tucson, Arizona. ⁴Witec GmbH, Lise-Meitner-Str 6, D-89081, Ulm, Germany. ⁵Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100.

Introduction: The identification and subsequent characterization of carbon in lunar materials was among the first studies conducted on the returned samples from the successful Apollo program [1-3]. Frustratingly, studies of carbon in lunar rocks could not distinguish between terrestrial contamination and indigenous carbon phases, except for solar wind implanted extralunar carbon [4-6].

We conducted 2 and 3 dimensional Confocal Raman Imaging Spectroscopy (CRIS) analysis on a thin section and on fresh fracture surfaces of Apollo 17 sample 72255,89. This sample was collected from the side of a layered boulder located in land-slide material at Taurus-Littrow [7]. Knoll and Stoffler [8] described 72255 as having a dark, fine grained equigranular crystalline matrix containing larger clasts, and subsequent studies concluded that it is an aphanitic impact-melt breccia [8-10]. The youngest material contained in 72255 coincides with the approximate time of the Serenitatis impact at 3.84 Ga [11].

Results: It has been known for decades that some of the carbon-phases present within the returned lunar samples are associated with terrestrial contamination that originated from sample collection, processing, and storage [12]. Therefore, any study of carbon in lunar samples must take this potential contamination into consideration. The spatially resolved nature and confocal depth profiling abilities of CRIS allow phases of interest to be placed in context with surrounding mineralogy and contamination. This differs from the mainly bulk extraction or pyrolysis techniques used in the Apollo era. Contamination in the form of thin section polymer, diamond and polishing compounds across the surface and within holes and cracks on the thin section, and fluorinated organic compounds on the fresh fracture surfaces are present. No evidence of previous carbon coating of the sample was found; however, standard spectra and extensive mapping of carbon coating shows a D and G band distribution similar to that of amorphous carbon.

Analysis of graphitic carbon in 72255 [13]: Figure 1A and B shows a dark area of aphanitic melt (DAAM) with a clear border to lighter material around it. Fig 1B shows that there is a greater concentration of dark blebs of approximately 2 – 5 μm diameter within the darker area. Fig 1C shows three spectra collected that are representative of the graphite phases analyzed. These show a range of G to D band ratios (~ 1585 and ~ 1345 cm^{-1} respectively) but the G band peak centre positions and FWHM measurements indicate these

phases are highly crystalline graphite. The ratio of the 2D (~ 2690 cm^{-1}) to D band peaks can be seen to increase dramatically between the three phases (from i – iii). This illustrates a trend from graphite to rolled graphene sheets / graphite whiskers (GW). The Raman spectrum of GW is unique among carbon allotropes and is characterized by an unusually intense 2D overtone mode (~ 2690 cm^{-1}) that is diagnostic of this species [14-15]. In all, ~ 0.5 mm^2 area of thin section, 72255,89 has been imaged with over 68 occurrences of subsurface (between 2 and 8 μm within the surface) graphite blebs and 7 occurrences of GW restricted to the 0.1mm^2 area analyzed around the DAAM pocket. The graphite blebs and whiskers occur as discrete black spots in the matrix (see Fig 1B and D) and are between 2 and 5 μm in diameter. These phases are not found in the 0.4 mm^2 area analyzed of lighter material although common carbon contamination phases occur all across the thin section.

Figure 1D shows a transmitted light image of an area mapped by CRIS (Fig 1 E - H). Fig 1E shows the distribution of graphite and GW particles across the target area marked in Fig 1D and at a depth of 4 μm into the sample. These small particles of carbon can be seen as small black blebs in the light microscopy image (Fig 1C as shown by the red arrows). Most of the graphite blebs appear to be within fused grain boundaries in the matrix (Fig 1H). However, some also appear to be within single discrete grains (Fig 1H white and yellow areas). Figure 1I is a 3D depth profile of the D* band from the surface of the section (0 μm) to a GW enclosed 3 μm into the surface of the section. Graphitic carbon was also detected on fresh fracture surfaces of a new allocation (72255,359) that had not been previously prepared for thin section.

Discussion: There are several lines of reasoning that would indicate that the observed graphite and GW are indigenous to the sample; a) both carbon phases are uncommon contaminants and not highly mobile b) they are present through the thickness of the sample with no communication to the outside of the sample, c) while contamination can be chartered across the section, graphite and GW are restricted to the BAAM (Fig 1A), d) polishing does not imbed contamination more than a few nanometers into the sample e) while some graphite and GW sit on grain boundaries there are also occurrences within whole mineral grains (Fig 1H), f) graphite is present on fresh fracture surfaces (72255,359) as well as within the thin section (72255,89). Finally, the most compelling reason to argue the indigeniety of

graphite phases in 72255 is the nature and formation conditions of GW. GWs have been reported in natural settings in two localities on Earth, within CV3 carbonaceous chondrites and several laboratory synthesis methods of GW have been described [14]. All known GW synthesis methods involve deposition from a carbon-containing gas at relatively high temperatures ranging up to 2273 K in a furnace and up to ~3900 K by arc-discharge [15, 16]. While the P-T stability field for synthesized GW is coarsely understood, the formation mechanism for graphite whiskers in natural samples is unknown. Sears [16] showed on the basis of thermodynamic arguments that graphite whisker growth is preferred at higher temperatures than that of crystalline graphite [16]. Therefore, the contamination of the sample by GW to the extent that they are incorporated into the mineral matrix of the sample is extremely unlikely. The graphite and GWs found in this study could not have formed from solar wind implantation, and are either remnants of graphite and GWs from the impactor that formed the breccia or formed from condensation of a carbon rich gas at the time of impact. It is not possible from this study to tell which.

The advent of modern scanning imaging spectroscopy at submicron resolutions can accurately position interesting carbon phases in 3 dimensions even when samples contain terrestrial contamination. This study shows that carbonaceous material is preserved in lunar materials and while the phases we can confidently identify as indigenous are high temperature polymorphs, low temperature organic material may have also survived. This work also expands on the provenance of graphite whiskers in the solar system and indeed may indicate that these high temperature polymorphs of carbon may also form during impact events. Further work on existing Apollo samples using spatially resolvable observations may help resolve the confusion over the presence of other labile organic species such as amino acids. Although this debate may only be resolved with direct observation by remote probes or by the return of sample material that presents less of a challenge for organic analysis than the Apollo and Luna samples.

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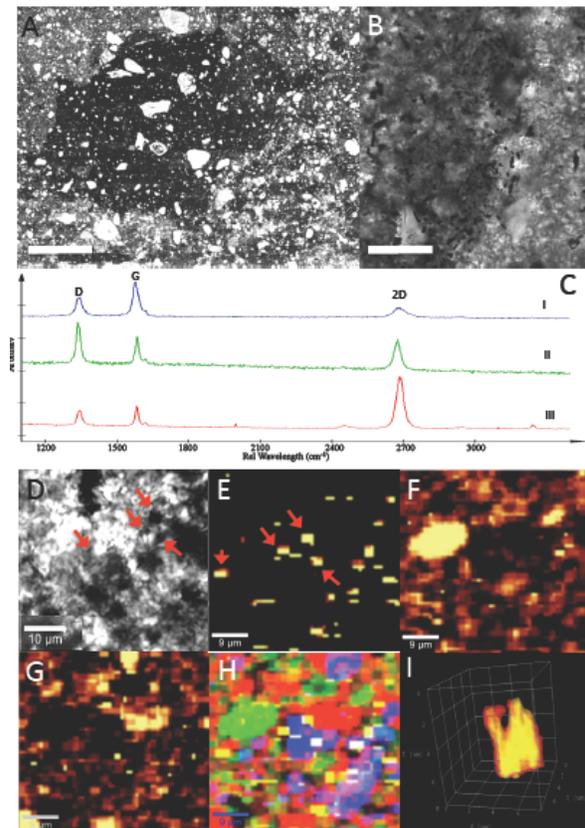


Figure 1. A) Light microscopy image (x 40) showing an area of 72255,89 thin section containing a darker area of aphinitic melt. B) higher magnification image (x1000) of light to dark transition in area shown in Fig 1A. C) Raman spectra of 3 types of graphite analyzed in the sample showing the increase in intensity of the 2D band of graphite (from I – III). D) Light microscope image of an area of the dark aphinitic melt that was subsequently analyzed by CRIS (E - H) CRIS maps of E) graphite 2D (~2650 cm^{-1}) band map (taken 4 μm into the surface of the sample). Red arrows correspond to dark blebs indicated by similar arrows in Fig 1D (Color scale is thermal with yellow areas representative of highest signal intensity). F) Feldspar, G) Pyroxene, H) four color map with G - Feldspar, R - Pyroxene, B - Olivine, Y - graphite. I) 3-D depth profile of the graphite 2D band from the surface to 8 μm beneath the surface of the sample. Reproduced from Steele et al., 2009 [13].