

Revisiting The Origin Of Macromolecular Carbon (MMC) In Lunar Basalts 15556 & 10044. B.A. Konecke, J.W. Boyce, R.S. Jakubek, M.D. Fries, K. Righter, F.M. McCubbin, and R.A. Zeigler. ARES, NASA Johnson Space Center, Houston, TX 77058, USA

Introduction: Volatile elements influence the geochemical evolution of planetary bodies and they are in magmas at every stage, from melting within planetary interiors to eruption at the surface. Analyses of lunar mare basalts supported the hypothesis that lunar magmas were depleted in volatiles (H-C-F-Cl-S), relative to their terrestrial analogs [1]. Nevertheless, several early studies of samples returned during the Apollo program proposed that the mare basalt eruptions, including the “fire fountain” eruptions, were propelled by the oxidation of magmatic graphite to CO (and/or CO₂) gas [2, 3]. Seminal studies during the 1970’s measured the bulk concentration and isotopic compositions of C from Apollo 11 samples, and identified several carbonaceous compounds, including: (a) gaseous (CO, CO₂, and traces of CH₄), (b) metallic carbide, and (c) potentially elemental carbon [4-6]. These studies reported a relatively broad range of C contents (~100-400 µg/g) and isotopic values ($\delta C^{13} = -30$ to $+20$), and suggested that these heterogeneities can be explained by contribution from multiple factors, including: (a) indigenous carbon, (b) solar wind implantation, (c) bombardment and/or meteorite impact, and (d) terrestrial contamination [5, 6]. However, unequivocal observations of magmatic graphite in lunar basalts have never been made.

Macromolecular carbon (MMC)—graphitic carbon varying from nearly amorphous to highly crystalline varieties—was identified as inclusions hosted by igneous pyroxenes from Martian meteorites and were attributed to being indigenous to Mars [8]. The authors carefully considered the textural and mineralogical relationship of the MMC phases, and concluded that the subset of MMC located within and/or adjacent to cracks, or at a disrupted surface (e.g., cut) were most consistent with terrestrial contamination. The near absence of confirmed instances of lunar magmatic MMC within the literature [9], combined with the wide range of isotopic values and bulk carbon contents measured in lunar basalts begs the question as to whether previously measured carbon is of an indigenous origin, or the result of terrestrial contamination. Using Raman spectroscopy, we have observed MMC in lunar basalts subjected to different forms of anthropogenic modification related to sample preparation including polished sections, sawn surfaces, and fractured surfaces adjacent to sawn surfaces. We have observed MMC of unknown origin in all of these settings. Here we report the preliminary textural and spectroscopic characteristics of MMC hosted within the groundmass of Apollo 15 (15556) and Apollo 11 basalts (10044) as part of our ongoing investigation of the origin of these carbonaceous materials.

Analytical Methods: Raman spectra and visible light images were collected on: (a) a used diamond impregnated band saw blade used by the Lunar Curation lab, (b) carbon-coated glass slide, (c) polished thin section of 15556,272; (d) both sawn, and fractured surfaces of sample 15556,111, and (e) previously carbon-coated and polished thin section of sample 10044,55. All of the Raman data were collected using a WITec $\alpha 300R$ confocal Raman microscope, equipped with a WITec diode laser generating 488 nm light. A 20x objective was used to collect all Raman spectra, and resulted in a beam spot of ~8 µm in diameter on the sample. Raman images were collected using a motorized x-y-sample scanning stage with an auto-focus feature. Each spectrum was collected with a 1 s accumulation time. The reflected light images of the samples are presented in Figure 1. Individual Raman spectra collected on carbonaceous features in lunar samples were collected with a laser power of 2 mW (measured at the laser) and accumulation times of ~30 s to ~2 min. The Raman spectra collected on the samples investigated in this study are presented in Figure 2.

Results: Raman spectroscopy analyses of the samples investigated in this study yielded three distinct phases of carbon, including: (a) diamond, (b) amorphous carbon induced by thermal sputtering of a graphite rod during carbon coating, and (c) MMC. The Raman spectra of a diamond grain from the diamond band saw is characterized by a single sharp peak at ~1332 cm⁻¹, and represents the only carbon phase observed on the blade. The spectra collected on the carbon coated glass slide contains two broad peak features at ~1100 cm⁻¹ and ~1500 cm⁻¹ that are characteristic of amorphous carbon. The carbonaceous features analyzed in 15556,111, 15556,272 and 10044,55 are characterized by a broad peak feature at ~1355 cm⁻¹ and a sharp peak feature at ~1600 cm⁻¹, and is consistent with the peak features of MMC [8, 9]. The MMC observed on the sawn surface of 15556,111 is ~30 µm² (Figure 2) and located within the groundmass, and below the sawn surface (see Figure 1); whereas the MMC located on the fractured edge was < ~15 µm², and also located within the groundmass. Alternatively, the MMC grain observed in 10044,55 is ~10 µm² and is located within a >100 µm² vesicle and/or hole. Raman maps and spectra were collected on both the sawn and a fractured surface of 15556,111 to evaluate possible contribution from the diamond saw blade during processing to the carbon phases observed. Here, we note that we did not observe diamond grains or evidence of amorphous carbon and/or carbon coating in 15556,111, 15556,272 or 10044,55 samples.

Discussion and implications: We report the presence of MMC in: (1) previously unpolished, non-carbon coated sample 15556,111; (2) a polished section of 15556,272 (never C-coated); and (3) a polished section of sample 10044,55 (previously C-coated). The relative intensities of the D and G bands are qualitatively similar to the data from [9]. Neither textural nor spectroscopic evidence for diamond or discrete amorphous carbon (i.e. from carbon coating) were observed on any of the measured areas of 15556,111 or 10044,55. This observation, however, does not necessarily preclude currently unknown contamination mechanisms. For example, high temperature annealing (>1000°C for several hours in vacuum) and large shear forces that develop during polishing of diamond with diamond, have been shown to initiate the transition of diamond to graphite-amorphous carbon [10, 11]. Additionally, insufficient quenching during diamond sintering and/or back catalyst reactions can facilitate the back transformation of diamond to graphite on diamond saws [12]. However, the textural, morphological and spectroscopic observations of the diamond grains on the band saw blade are not consistent with the onset of diamond-graphite transformation.

An alternative scenario evokes friction heating of the diamond band saw during processing, which does not use cooling fluid(s) in order to prevent contamination. The presence of diamond (and metallic Fe-Ni) fragments embedded in the black-amorphous/glassy streak material observed on the sawn surface of meteorites have been determined to most likely introduced during dry-cutting with the diamond band saw blade [13]. An internal study performed at NASA-JSC determined that the thin layers of glassy and/or amorphous material was consistent with localized melting (e.g., estimated $T = \sim 1200\text{--}1500^\circ\text{C}$) via frictional heating [14]. However, if these processes are responsible for the addition of MMC to the sample, we would expect residual material to be present on the diamond band saw blade and the sawn surface of the sample, including materials used for the electroplating (e.g., Fe-Ni-Cr alloy) process.

Regardless of the source of the MMC observed in 15556, its existence has fundamental implications for past, present, and future research and curation activities including: (1) A reassessment of sample handling and processing techniques in order to limit the magnitude of terrestrial contamination for current and future sample return missions, and/or (2) A reevaluation of the indigenous lunar carbon budget, including the redox buffering potential of graphite saturated lunar magmas, and broad implications for the volatile evolution of planetary bodies.

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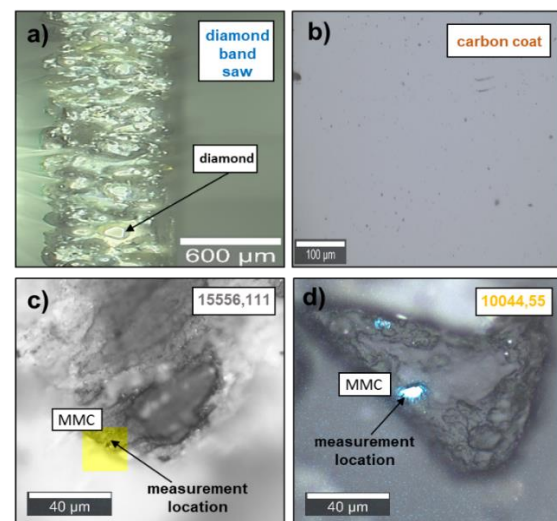


Figure 1: Reflected light images of samples: (a) cutting edge of the diamond band saw blade; (b) carbon coated glass slide; (c) MMC phase from sample 15556,111; (d) MMC phase from sample 10044,55.

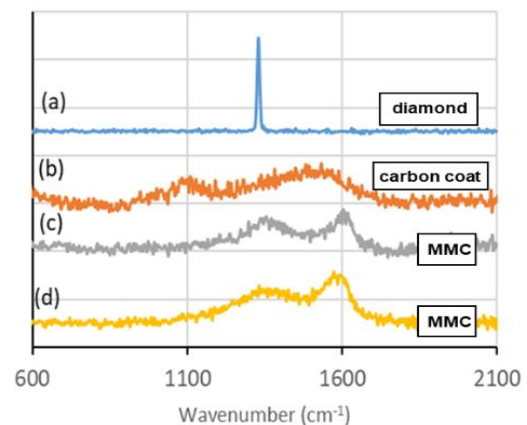


Figure 2: Raman spectra of carbonaceous species. (a) diamond from sawblade; (b) carbon coated glass slide; (c) MMC grains from sample 15556,111 and 272 (unpolished and polished); (d) MMC grain from sample 10044,55.