

**INDIGENOUS CARBON EMBEDDED IN APOLLO 17 VOLCANIC BLACK GLASS SURFACE DEPOSITS.** K. L. Thomas-Keprta<sup>1</sup> (kathie.thomas-keprta-1@nasa.gov), S. J. Clemett<sup>1</sup>, D.K. Ross<sup>1</sup>, L. Le<sup>1</sup>, D.S. McKay<sup>2</sup>, E.K. Gibson<sup>2</sup>, and C. Gonzalez<sup>1</sup>; ESCG at NASA/JSC, Mail Code JE23, Houston, TX 77058; <sup>2</sup>ARES, NASA/JSC, Mail Code KR, Houston, TX 77058.

**Introduction:** The assessment of indigenous organic matter in returned lunar samples was one of the primary scientific goals of the Apollo program. The levels of such organic material were expected to be and found to be small. Previous work on this topic includes Murphy *et al.* [1] who reported the presence of anthropogenic organics with sub-ppm concentrations in Apollo 11 fines. In Apollo 12 samples, Preti *et al.* [2] detected low levels, < 10 ppb or below, of more complex organic material that may have been synthesized by abrupt heating during analysis. Kvenvolden *et al.* [3] detected porphyrin-like pigments at the ng to pg level in an Apollo 11 bulk sample. Hodgson *et al.* [4] and Ponnampereuma *et al.* [5] suggested that most if not all porphyrins were synthesized from rocket fuel during module landing. Chang *et al.* [6] reported indigenous carbon ranging from 5-20  $\mu\text{g/g}$  in the form of metal carbides in Apollo 11 fines. Hare *et al.* [7] reported amino acids at the 50 ng/g level in Apollo 11 samples but suggested the results may be explained as contamination. More recently, Clemett *et al.* [8] reported simple polycyclic aromatic hydrocarbons at concentrations of < 1ppm in an Apollo 16 soil. Low concentrations of lunar organics may be a consequence not only of its paucity, but also its heterogeneous distribution. If the sample size required for a measurement is large relative to the localization of organics, detection is limited not by ultimate sensitivity but rather by the ability to distinguish an indigenous signature from background level contamination [9].

With the exception of  $\text{CH}_4$  [10, 11] the presence of indigenous lunar organics, however, still remains a subject of considerable debate. Yet several processes should contribute to the lunar organic inventory including: (1) exogenous carbonaceous accretion (three main sources that can deliver organic molecules intact to planetary surfaces are asteroids and fragments thereof, comets and interplanetary dust particles); and, (2) indigenous lunar organic synthesis driven by early planetary volcanism, and cosmic and solar radiation. Because the Moon formed from the crystallization of high temperature (up to  $\sim 1600$  K) silicate melts any organic carbon contained within the precursor material would be converted to simpler organics and gases including  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$ . Possible abiotic synthesis of more complex, saturated and unsaturated hydrocarbons could then have occurred through Fischer-Tropsch type reactions between  $\text{H}_2$  and  $\text{CO}$  catalyzed by metallic Fe [12] in a primordial lunar atmosphere.

We report for the first time the identification of arguably indigenous carbonaceous matter present with-

in pristine surface deposits of a black glass grain collected on the rim of Shorty crater during the Apollo 17 mission by astronauts Eugene Cernan and Harrison Schmitt.

**Procedure and Results:** Being aware of the ease and rapidity of terrestrial contamination, sample 74220, 186 was opened immediately prior to analysis in a nitrogen glove box. Approximately 10 orange and black grains ranging from  $\sim 100$  to several hundred  $\mu\text{m}$  in diameter were randomly selected and mounted on individual aluminum planchets with a single  $\sim 20$   $\mu\text{m}$  diameter pool of crystal bond. Samples were stored collectively in a covered Pyrex petri dish. Overnight and when not being analyzed the petri dish was stored in a dry nitrogen glove box. Analysis sequence was as follows: optical microscopy, UV fluorescence imaging,  $\mu$ -Raman, and FESEM-EDX. Grain surfaces were imaged both optically and under UV illumination (Fig. 1) using an Nikon BX-50 fluorescent microscope equipped with a 330-385 nm excitation filter in combination with a 420 nm long-pass emission filter. A series of optical images was taken over a range of focal distances and the resulting image stack was combined to produce an extended depth-of-field image of a single grain (Fig. 1). Prior to FESEM analysis, a Pt surface coating  $\sim 1$  nm thick was applied to enable imaging and chemical characterization of elements including C.

All grains contained a minimum of five regions of interest (ROI) that fluoresced when exposed to UV (each several  $\mu\text{m}$  in size). One black glass grain contained a ROI,  $\sim 3 \times 5$   $\mu\text{m}$ , that was located on an edge of a rectangular plateau situated on the exposed surface of a black glass droplet (Fig. 1). It was enriched in C up to  $\sim 10$  fold compared to background (Fig. 2). C was heterogeneously distributed and associated with enrichments of Al, Mg, Si, and/or Fe (Fig. 2). Distinct hot spots of Ti, likely rutile, were embedded within the carbonaceous matter (Fig. 2). The ROI was covered on one edge by a curved Si-rich filament (glass?) that appeared to have emanated from the plateau surface (Fig. 2).

**Discussion & Conclusion:** Based on the chemical heterogeneity, the presence of embedded Ti-rich grains, and the spatial association of the ROI with the overlying Si-rich filamentous feature, the C-rich region appears to be indigenous to the sample and therefore is inconsistent with terrestrial contamination. The source of this carbonaceous matter is not constrained. While mostly composed of volcanic pyroclastic droplets, sample 74220 has been slightly reworked by micro-

meteorites and space weathering. Therefore, the source of the C-rich region could either be from the pyroclastic eruption which formed the glass droplets, or have been added during reworking during its residence in the lunar regolith. Future work will include molecular characterization using a novel 118 nm laser two step mass spectrometer [13] and focused ion beam extraction and mineral and chemical characterization using HRTEM. Additional investigations of the double drive tube 74001 and 74002, which have nearly no lunar surface reworking below a few cm, should reveal whether the C-rich material is indigenous to the original volcanic pyroclastic ash deposits or was added during regolith reworking.

**References:** [1] Murphy R.C. *et al.* (1970) *Proc. Apollo 11 Lunar Sci. Conf.* **2**, 1891-1900. [2] Preti G. *et al.* (1971) *Proc. 2<sup>nd</sup> Lunar Sci. Conf.* **2**, 1879-1889. [3] Kvenvolden K. *et al.* (1970) *Proc. Apollo 11 Lunar Sci. Conf.* **2**, 1813-1828. [4] Hodgson G.W. *et al.* (1970) *Science* **167**, 763-75. [5] Ponnemperuma C. *et al.* (1970) *Science* **167**, 760-762. [6] Chang S. *et al.* (1970) *Proc. Apollo 11 Lunar Sci. Conf.* **2**, 1857-1869. [7] Hare P.E. *et al.* (1970) *Proc. Apollo 11 Lunar Sci. Conf.* **2**, 1799-1803. [8] Clemett S.J. *et al.* (2005) *68<sup>th</sup> Annual Meteoritical Soc. Meeting*, Abst. # 5300. [9] Allton J. (1999) *Lunar Planet. Sci. Conf. XXIX*, 1857. [10] Lipsky S.R. *et al.* (1970) *Science* **167**, 778-779 & subsequent papers in issue. [11] Cadogan P.H. *et al.* (1973) *Nature* **241**, 81. [12] Gelpi E. *et al.* (1970) *Geochim. Cosmochim. Acta* **34**, 965-979. [13] Clemett S.J. *et al.* this volume.

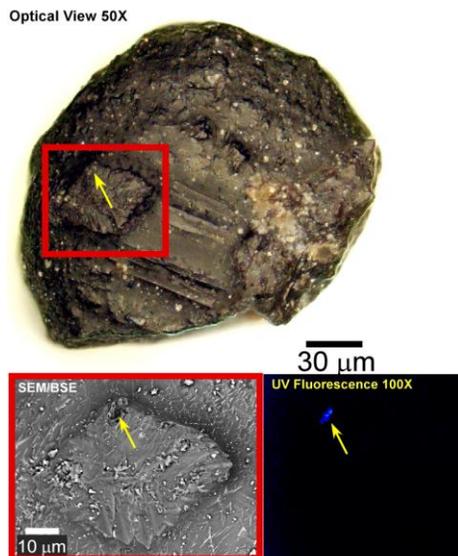


Figure 1. Upper: Optical view (depth-of-field image) of an Apollo 17 black glass grain (74220, 861). C-rich ROI is highlighted by the yellow arrow in all images. Lower left: SEM/BSE views of ROI at intermediate magnification. Lower right: UV fluorescence image (100 X) of the ROI.

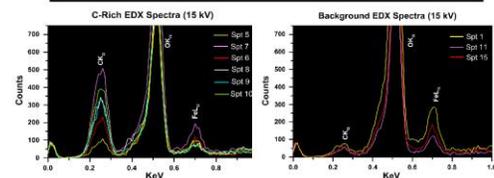
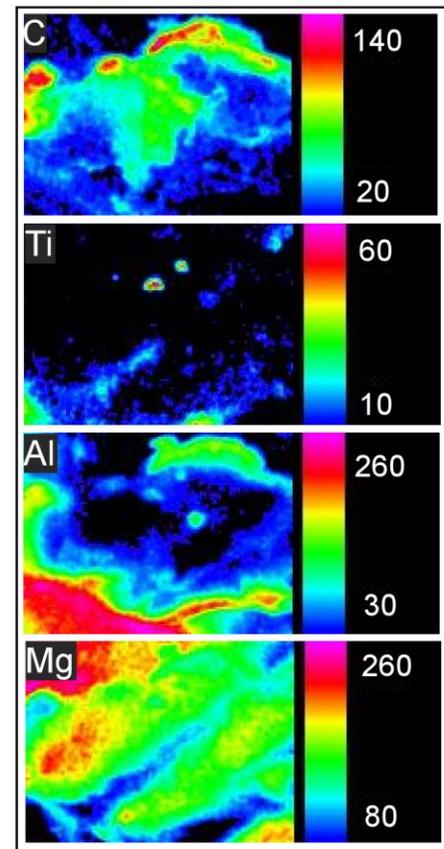
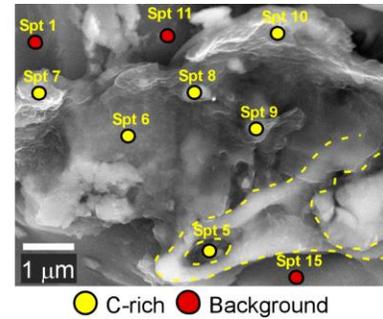


Figure 2. Uppermost view: SEM/BSE view of the C-rich ROI. EDX spt locations are given by the circles. Glassy filament (yellow dashed region) overlies lower corner of the ROI. Middle views: HRSEM/EDX maps of the ROI showing distribution of C, Ti, Al and Mg. Lower views: EDX spt from 0 to 1 keV for C-rich (left) and background (right) regions. ROI is composed of heterogeneously distributed C with counts ranging from ~ 100 to 550. Background C counts range from ~ 50 to 75.