

In Situ Coordinated Analysis of Carbonaceous Chondrite Organic Matter. N. D. Nevill¹, S. J. Clemett², S. Messenger³, K. L. Thomas-Keprta⁴, P. A. Bland¹, N. E. Timms¹ & L. V. Forman¹, ¹School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, Western Australia, 6845, ²ERC Inc. / ³Robert M Walker Laboratory for Space Science, ARES, NASA Johnson Space Center, Houston, TX, USA, ⁴Barrios, Engineering Science Contract Group (ESCG), 2224 Bay Area Blvd, Houston, Texas 77058, USA.

Introduction: Microanalytical studies of carbonaceous chondrites (CC's) have identified a vast array of isotopically, chemically and texturally distinct organic components. These components were synthesized and processed within a range of physical and chemical environments, including the interstellar medium, the solar nebula and within asteroids. The nature and abundance of these molecules can be used to unravel the geochemical and isotopic record of their origins as well as their subsequent evolutionary journey [1-4].

Traditional geochemical studies of organics in CC's involved bulk analyses via solvent extraction. These studies lead to the characterization of thousands of distinct organic molecules, at the expense of understanding their spatial distribution and contextual information [3, 5]. *In situ* studies have observed rounded, submicron sized organic assemblages (nanoglobules). Nanoglobules are often isotopically distinct, exhibiting signatures of possible interstellar origins as indicated by their tremendous $\delta^{15}\text{N}$ and δD enrichments. These isotopic signatures are consistent with ion-molecule reactions within cold molecular clouds and/or the outer protoplanetary disk [5]. However, owing to their small sizes, little is known about the chemical compositions of the organic nanoglobules and therefore to what extent they have been altered during parent body processing.

We have carried out correlated *in situ* chemical, isotopic and contextual mineralogical analyses of CC matrices to better understand the origins and evolution of organic nanoglobules [6-9]. In this work, our objectives were to identify chemical signatures associated with organic globules that were distinct from surrounding matrix, trends in isotopic-chemical variations among organic nanoglobules, and potential relations of such trends with matrix mineralogy that trace parent body processing.

Approach and Methodology: We conducted μm -scale coordinated and spatially correlated *in situ* studies of meteoritic matrices, focusing chemical, mineralogical and isotopic analyses of major CC classes, spanning various degrees of hydrothermal alteration. Samples include: QUE99177 (CR3), MET00426 (CR3), ALH77307 (CO3.0), Murchison (CM2), Tagish Lake (C2 Ung) and MET01070 (CM1) CC (Fig. 1).

Using an optically flat sapphire window, $\sim 20\text{-}50\ \mu\text{m}$ sized matrix fragments were pressed into Au foil. This provided flat surfaces required for analyses while preserving the local mineralogical context. All sample preparation was carried out in a clean room without chemical treatments or the use of an embedding medium, e.g. epoxy resin, to minimize contamination.

Samples were initially characterized utilizing optical and fluorescence microscopy, the latter providing an overview of the spatial distribution of distinct organic assemblages rich in aromatic and/or conjugated functional groups [9-10]. These analyses were conducted on an Olympus BX60 microscope equipped with both UV and optical imaging light sources.

Mass spectral organic chemical mapping and molecular speciation detection at the $\sim 5\ \mu\text{m}$ scale was conducted utilizing the two-step laser mass spectrometry ($\mu\text{L}^2\text{MS}$) at NASA Johnson Space Center (JSC). The use of vacuum ultraviolet photoionization during analysis allowed for observation across a broad range of organic species.

High spatial resolution ($< 200\ \text{nm}$ pixel dimension) isotopic images were obtained for ^{12}C , ^{13}C , ^{16}O , $^{12}\text{C}^{14}\text{N}$, $^{12}\text{C}^{15}\text{N}$ & ^{28}Si using the NanoSIMS 50 with a focused 16 keV Cs^+ primary ion beam. Terrestrial kerogen was utilized as an isotopic standard for analyses.

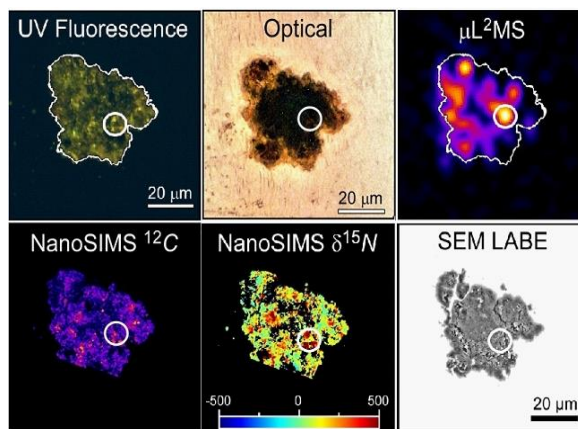


Figure 1: QUE99177 (CR3) analysis maps showing the correlation between optical and UV imaging, a mass integrated $\mu\text{L}^2\text{MS}$ spectral map (17-250 m/z), NanoSIMS ^{12}C and $\delta^{15}\text{N}$ isotopic images and SEM. Correlation can be achieved at the $> 2\ \mu\text{m}$ scale. This comparative analysis was conducted on $\sim 120 < 350\ \mu\text{m}$ of matrix per meteorite, randomly selected from whole rock.

Finally, samples were coated with 2 nm of Pt to reduced surface charging for contextual mineralogical analysis utilizing energy dispersive x-ray spectroscopy (EDX) on a JEOL 7600F field emission SEM at NASA JSC operating at 15 keV accelerating voltage.

Results: Our new findings are consistent with our previous preliminary studies [9]. QUE99177 demonstrated the highest abundance of nanoglobules as determined by UV fluorescence. The emission spectra of the nanoglobules showed a pronounced red-shifted, compared to the diffuse background emission arising from dispersed simple soluble organic species. Organic analysis by $\mu\text{L}^2\text{MS}$ indicated a heterogenous organic distribution that was more enriched in simple carbonyl species such as aldehydes and ketones when in spatial proximate to the nanoglobule concentrations. In several instances organic hot spots identified by $\mu\text{L}^2\text{MS}$ could be directly correlated with $\delta^{15}\text{N}$ -rich inclusions (see Fig. 1). MET00426 also exhibited a significant enrichment in fluorescent nanoglobules and correlating $\delta^{15}\text{N}$ rich inclusions as observed in QUE99177.

In contrast ALH77307 was unique among the CCs studied, fluorescence imaging lacked evidence of nanoglobules within analyzed matrix regions. Subsequent organic mapping by $\mu\text{L}^2\text{MS}$ indicated the abundance of organic species to be an order of magnitude lower than any other CC matrix region studied. Furthermore, the organic species detected were by comparison notably deficient in simple carbonyl species (see Fig. 2). While considered primitive, ALH77307 was dominated by isotopically normal matrix with rare $\delta^{15}\text{N}$ -rich inclusions [10], significantly fewer than observed by Tagish Lake and Murchison [3, 9, 11].

MET01070 represents the most hydrothermally altered CC in our study. Similar to QUE99177, the matrix showed a plethora of fluorescent nanoglobules. However, isotopic studies showed an isotopically normal matrix with rare $\delta^{15}\text{N}$ -rich inclusions. The $\mu\text{L}^2\text{MS}$ analysis indicated a rich abundance of organic species (see Fig. 2).

Discussion: Fluorescence imaging indicates that while the abundance of aromatic nanoglobules varies significantly between different CC matrices, it is not directly correlated with petrographic grade. Nevertheless, the emission spectrum and spatial distribution of nanoglobules does suggest a mutual relationship with parent body hydrothermal alteration. This is further supported by $\mu\text{L}^2\text{MS}$ mapping that indicates a proximate association of simple carbonyl containing species, such as formaldehyde ($\text{H}_2\text{C}=\text{O}$) and acetaldehyde ($\text{CH}_3\text{C}=\text{OH}$), with nanoglobule clusters. Carbonyl polymerization chemistry has been previously proposed as a method for the synthesis of organic solids

from simple interstellar precursors [12-13]. We suggest that at least a subset of nanoglobules are formed through carbonyl condensation polymerization reactions. Since such reaction are reversible, the subsequent interaction of these globules with aqueous fluids, e.g., during hydrothermal parent body alteration, may result in partial depolymerization leading to the observed enrichment of the local matrix by carbonyl monomers.

The relative paucity of organics observed by $\mu\text{L}^2\text{MS}$ in ALH77307 is consistent with its low C abundance (~0.7 wt.% [14]). Nevertheless, the absence of any fluorescent nanoglobules and low abundances of carbonyl species is notable since nanoglobules have been previously reported using different analytical techniques [10]. This suggest that the term nanoglobule encompasses a range of organic solids formed through more than one pathway.

Future research will expand this approach to other CC samples, with the hope to refine models for the origins of geochemical and isotopic trends within nanoglobules, specifically their relationship to nebula and parent body processing.

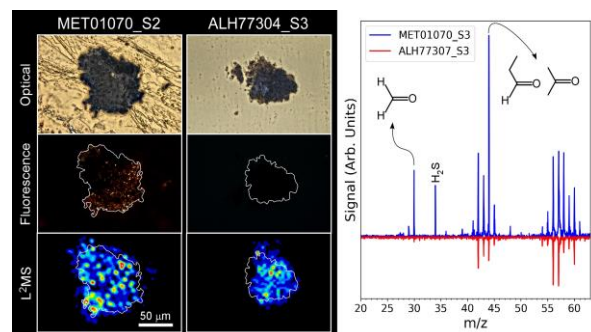


Figure 2: Comparison of MET01070 (CM1) and ALH77307 (CO3) matrix fragments. Fluorescent nanoglobules are abundant in MET01070, but scarce in ALH77307. Correspondingly mass spectra indicate carbonyl moieties are present in much greater abundance in MET01070 than in ALH77304.

References: [1] Abreu N. M. and Brearley A. J. (2010) *GCA*, 74, 1146. [2] Alexander C. M. O'D., et al., (2017) *Chemie der Erde – Geochem.*, 77(2), 227. [3] Sephton M. A. (2002) *Nat. Prod. Rep.*, 19(3), 292. [4] Greenwood et al. (2010) *GCA*, 74(5), 1684. [5] Nakamura-Messenger et al. (2006) *Science*, 314, 1439. [6] Pearson V.K. et al. (2007) *PSS* 55, 1310. [7] Nakamura-Messenger K. et al. (2013) *LPSC* 44, #2795. [8] Clemett S. J. et al. (2014) *LPSC* 45, #2896. [9] Nevill N. et al. (2018) *LPSC* 49, #1007. [10] Floss C. et al. (2014) *GCA*, 139, 1. [11] De Gregorio B. T. et al. (2013) *Met. Planet. Sci.*, 48, 904. [12] Grady M. M. et al. (2002) *Met. Planet. Sci.*, 37, 713. [13] Kebukawa Y. et al. (2013) *ApJ*, 771, 1146. [14] Cody D. G. et al (2011) *PNAS*, 108, 19171. [14] Murae T. et al. (1994) *Proc. NIPR Symp. Anarct. Meteorites*, 4, 384.