REFRACTORY ORGANICS IN COMET 67P/CHURYUMOV-GERASIMENKO: ADDITIONAL EVIDENCE FOR LARGE-SCALE MIXING IN THE PRIMITIVE SOLAR NEBULA? J. A. Nuth,[1] N. M. Johnson,[2] F. T. Ferguson,[2,3] M. Hilchenbach,[4] S. Merouane,[4] J.A. Paquette,[4] O. Stenzel,[4] H. Cottin,[5] N. Fray,[5] A. Bardyn,[5] D. Baklouti,[6] and L. Le Roy,[7] [1]NASA Goddard Space Flight Center, Code 690, Greenbelt MD 20771 (joseph.a.nuth@nasa.gov), [2] NASA Goddard Space Flight Center, Code 691, Greenbelt MD 20771, [3]The Catholic University of America, Chemistry Department, Washingtom D.C. 20064, [4]Max-Planck-Institut für Sonnensystemforschung, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany, [5]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 94000 Créteil, France, [6]Institut d'Astrophysique Spatiale (IAS), CNRS/Université Paris Sud, Bâtiment 121, 91405 Orsay, France, [7]Center for Space and Habitability (CSH), University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland

Introduction: The COSIMA instrument [1] on board the Rosetta spacecraft [2] collected and analyzed samples of individual particles from the coma of Comet 67P/ Churyumov-Gerasimenko. Initial results of the analysis of several particles have been presented elsewhere [3–6] while analyses of the organic component of the dust particles has been shown to compare favorably to laboratory spectra of IOM extracted from the Orguil and Murchison meteorites [7]. Here we will compare the spectra of the same two particles to laboratory spectra of organic grain coatings produced via Surface Mediated Reactions of CO, H_2 and N_2 on amorphous iron silicate grains [8].

The Stardust mission [9] unambiguously established that small refractory dust particles were transported from the innermost regions of the primitive solar nebula to the regions where Kuiper-belt comets formed [10] as had been previously predicted [11-13]. Unfortunately it is much more difficult to pinpoint the origin of the organics detected in Stardust grains [14] due to the high encounter velocity of the Stardust mission with Comet 81P/Wild-2. Dust grains from Comet 67P/Churyumov-Gerasimenko were collected much more gently and so provide more representative samples of the refractory organic components of comets. We do note however that the most volatile carbon-containing molecules, such as CO, CO_2, CH_4, etc. were lost to some ill-defined extent prior to analyses.

COSIMA Analyses: COSIMA detected more than 35,000 particles and fragments of particles collected in the vicinity of comet 67P/Churyumov–Gerasimenko and 424 analyzed by SIMS in positive mode and 365 in negative mode. These particles show various morphologies and mineral compositions, inferred from time-of-flight secondary ion mass spectrometry (TOF-SIMS). Figure 1 presents findings on the organic content of two representative particles, named Kenneth and Juliette [7]. Kenneth was collected between 11 and 12 May 2015, while Juliette was collected between 23 and 29 October 2015. Both were analysed a few weeks after their collection and both are larger than 100 microns in diameter. Figure 1 shows a comparison of the mass spectra measured on the Kenneth and Juliette particles (in red) and those measured nearby on the porous gold substrates (the 'targets') on which the particles were collected (in black). We note that the COSIMA instrument continuously rasters across the target during analyses. The absolute intensity of secondary ions decreases as the beam moves from the target onto a particle and the composition of the secondary ions changes to reflect the composition of the grain.

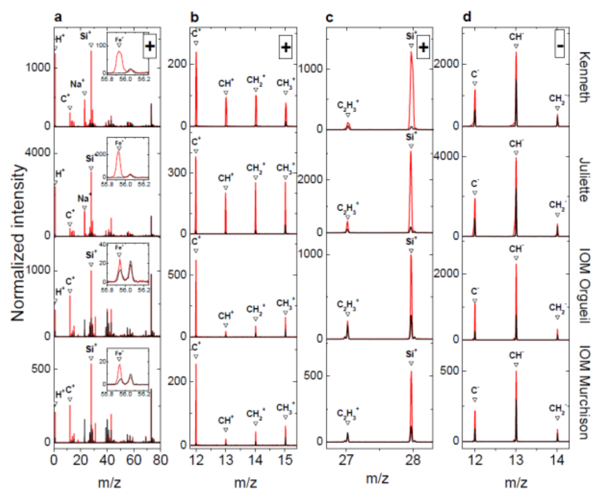

Figure 1 | Comparison of cometary and meteoritic TOF-SIMS data. The spectra in red were acquired on two cometary particles, Kenneth and Juliette, and on two IOM samples, extracted from the Orgueil and the Murchison meteorites. The spectra in black have been acquired on the porous gold substrates on which the cometary particles were collected and IOM samples prepared. The spectra are normalized to the intensity of characteristic mass fragments of polydimethylsiloxane (PDMS) **a**, Positive-ion spectra. **b**, **c**, Enlargements from **a**. **d**, Negative-ion spectra. A full discussion of Figure 1 can be found in [7].

Analyses of COSIMA Spectra: In an attempt to match the spectra of carbonaceous grains collected from Comet 67P/ Churyumov-Gerasimenko, the COSIMA Team obtained spectra from a wide range of plausible analog materials using the COSIMA instrument reference model (COSIMA RM) in the laboratory at the Max Planck Institute in Gottingen. Spectra of IOM from the Murchison and Orguil meteorites are shown in Figure 1. Spectra of representative aliphatic and aromatic molecules and a spectrum of carbon formed via surface mediated reactions [8] on amorphous iron silicate smokes are shown in Figure 2. All spectra are dominated by surface carbons and the terminal hydrogen atoms for each sample.

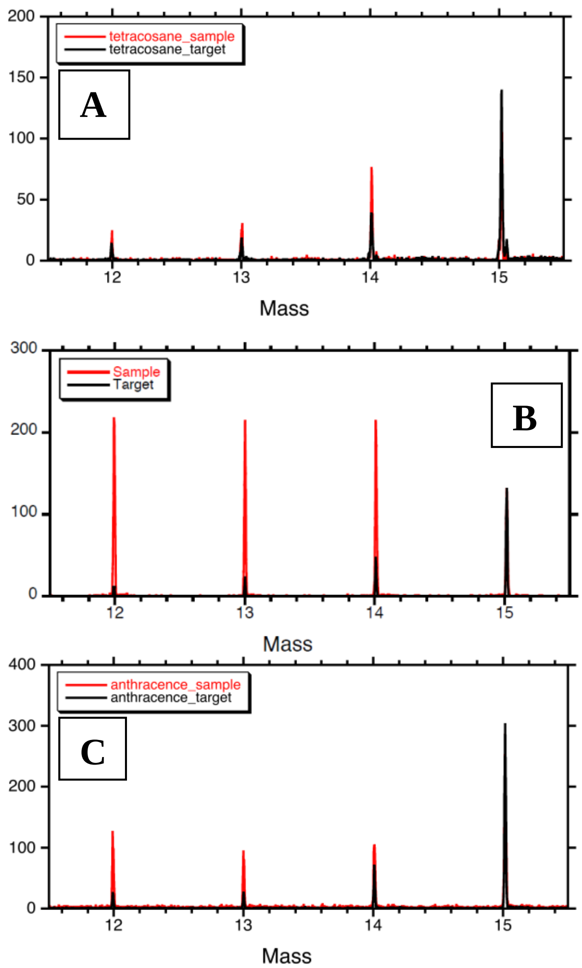

Figure 2. Carbon mass spectra for (A) the long-chain aliphatic molecule tetracosane (6) (B) carbon-coated grains on amorphous iron silicate smokes produced via surface mediated reactions of $CO+N_2+H_2$ at 723K and (C) the aromatic molecule anthracene (6). Each spectrum is normalized to mass 15. Red denotes sample spectra; black is background.

Inspection of Figure 1 shows that the peak heights for mass 12 in Kenneth and Juliette are higher than for masses 13, 14 and 15 which are all about the same intensity. Figure 2 demonstrates that sp^2 (aromatic) carbon comes closer to matching this pattern whereas sp^3 (aliphatic hydrocarbons) shows a minimum at mass 12 followed by monotonically rising peaks at mass 13 and 14. The IOM spectra show massive peaks at mass 12, with a small, but monotonically rising progression of peaks at mass 13, 14 and 15. The mass spectrum of the carbonaceous matter produced via surface mediated reactions is fairly flat; a mix of sp^2 and sp^3 carbon.

Origin of non-volatile carbonaceous grains: Non-volatile carbon on grains collected from Comet 67P/ Churyumov-Gerasimenko analyzed by COSIMA is consistent with materials produced at high temperatures. Such organics may have formed in the innermost regions of the primitive solar nebula by surface mediated reactions of CO, N_2 and H_2.. The organics analyzed by COSIMA do not resemble the wide range of organic molecules originally expected based upon the assumption that such organics would be produced under low temperature conditions in the outer nebula or in the interstellar medium [6]. Low temperatures produce more aliphatic carbon. These grains show a mix of sp^2 and sp^3 carbon and implies that they may have seen temperatures sufficiently high to either drive off hydrogen or to prevent hydrogenation. An alternative may be that they have seen extremely high doses of radiation [15].

In summary, the most volatile (and most aliphatic) organic molecules were likely lost soon after the grains were captured on the COSIMA collector leaving the more refractory carbon of intermediate and low volatility for analysis. Similarly, the IOM represents organic material from which the most labile (and again, the more aliphatic) molecules have been removed, leaving the more complex species behind. Analog carbon produced via surface mediated reactions was formed at 725K, but has not been further processed. It contains a balance of intermediate and low volatility organics that is a mixture of both aromatic and aliphatic components.

References: [1] Kissel, J. et al. Space Sci. Rev.128, 823–867 (2007). [2] http://sci.esa.int/rosetta [3] Schulz, R. *et al*. *Nature* **518,** 216–218 (2015). [4] Langevin, Y. *et al. Icarus* **271,** 76–97 (2016). [5] Hilchenbach, M. *et al. Astrophys. J.* **816,** L32 (2016). [6] Le Roy, L. *et al. Planet. Space Sci.* **105,** 1–25 (2015). [7] Fray, N., Bardyn A., Cottin, H., et al., *Nature* ***538***,72–74 (2016). [8] J.A. Nuth, N.M. Johnson F.T. Ferguson and A. Carayon, *MAPS* 51, 1310–1322. [9] http://stardust.jpl.nasa.gov/home/index. [10] M. E. Zolensky, T. J. Zega, H. Yano et al., *Science* 314, 1735-1739 (2006) [11] J.A. Nuth, 1999. Lunar Planet. Sci. 30 (# 1726, CD-ROM). [12] J.A. Nuth, 2001. *Am. Sci.* 89, 228–235. [13] J.A. Nuth and N.M. Johnson, 2006. *Icarus* 180, 243–250. [14] S.A. Sandford, J. Aléon, C.M. O'D. Alexander, et al., 2006, *Science* 314, 1720-1724. [15] Jenniskens, P., Baratta, G.A., Kouchi, A., Groot, M.S.D., Greenberg, J.M. and Strazzulla, G. (1993) A&A 273, 583-600.