

TESTING THE RETENTION OF SOLUBLE ORGANIC SPECIES IN A COMETARY NUCLEUS SIMULANT: PREPARING FOR COMET SAMPLE RETURN.

N. H. Spring^{*1}, C. D. K. Herd¹, D. N. Simkus¹, R. W. Hiltz², A. W. Skelthorne², R. M. Whittall³, J. Zheng³. ¹Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2E3, Canada., ²Department of Physical Sciences, MacEwan University, Edmonton, AB, T5J 4S2, Canada. ³Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada. *Corresponding author email: nspring@ualberta.ca.

Introduction: A cometary nucleus sample return mission is one of the top priorities for NASA's New Frontiers program. If selected, several grams of cometary material will be returned in the coming decades. Such a sample would be the largest of its kind ever to be processed, relative to the individual dust particles already returned by the NASA Cosmic Dust Program and the NASA Stardust Mission [1]. A cometary nucleus sample will present new challenges for curation teams intent on preventing loss of volatiles from a delicate and unprecedentedly pristine sample.

The potential lability of the organics in a returned comet sample is currently unknown. Compounds observed in interplanetary dust particles (IDPs), and/or on comets, such as primary amines, alcohols, aldehydes and carboxylic acids [e.g. 2-5] may be lost over time at ambient T (25 °C) on Earth, or even at sub-zero temperatures. Our goal is to experimentally determine the optimal temperature range for large-scale curation and handling of cometary material. In addition to preservation of sample pristinity, working comfort of curatorial staff and function of laboratory equipment are important factors to be considered.

The Subzero Facility for Curation of Astromaterials at the University of Alberta [6] provides a unique opportunity to test how volatile organics, contained within a simulant sample, behave under different curation conditions. Samples can be handled without exposure to air, in a purified Ar glove box, housed within a controlled environment chamber, which maintains any set temperatures between -30 °C and -10 °C.

Simulant Design: Detailed insights into the chemical and physical properties of comet surface material have recently been provided by Rosetta. It is generally thought, through observations [e.g. 7-11], modelling [e.g. 12] and laboratory experiments [e.g. 13], that comet 67P/C-G is composed of aggregate pebbles, ranging from the mm to m scale; with the aggregates composed of silicates, Fe-metal, organics (and ices) at the nm to μm scale; a good match with the laboratory observations of IDPs and dust returned from comet Wild 2 [14]. For these experiments, we designed an ice-free, organic-rich, dusty simulant.

The three key factors in development of the simulant were identified: 1) grain size; 2) grain sorting – both of which affect porosity and permeability, and therefore the distribution, exposure and volatile escape pathways

of any compounds added; and 3) inclusion of a bulk carbonaceous 'glue', to which volatile compounds may potentially be adsorbed (relative to mineral surfaces).

Methods:

Simulant. Our simulant is a simplified carbon-rich, chondritic-porous IDP analogue, consisting of silica nano-powder (fumed grains, 80-300 nm, Sigma Aldrich #S5505) for the mineral component, and humic acid (Sigma Aldrich #53680) for the bulk carbonaceous component. Additional components found in IDPs such as sulfides and Fe-Ni metal grains would only change the overall density, which is not an essential part of this experiment; these components were thus excluded. Humic acid was chosen for the bulk carbonaceous component as it shares a similar disordered, macromolecular, kerogen-like structure to that found in carbonaceous chondrites and IDPs [15].

The humic acid was milled down to the nanoscale (<50 nm) using a SPEX 8000D ball mill, and added to the silica powder in a flask which was filled with ethanol. The mixture was then placed in an ultrasonic bath for 2 hours to aid dispersion and mixing. The ethanol was allowed to evaporate and the simulant analyzed by scanning electron microscopy to compare to the texture and composition of IDPs. Figure 1 shows SEM images of the final simulant mixture, which has a C content of 15-30 wt.%. The texture is generally finely powdered (μm scale), but some mm-scale clumping occurs.

Organic Species. Two aldehydes, formaldehyde and acetaldehyde, were selected for an initial suite of experiments as they can both be extracted via the same derivatisation procedure and they have contrasting boiling points (formaldehyde at -19 °C and acetaldehyde at 20.2 °C); this difference is useful to explore variation in loss with temperature. Concentrations of 350 nmol/g of acetaldehyde and 100 nmol/g formaldehyde were selected based on literature values for these compounds in the CR2 meteorite GRA 95229 [16], the highest concentrations measured across several carbonaceous chondrites. These compounds may be present on comets, as indicated by spectral interpretation of data from 67P [2-5]. The compounds were both added to the same solution in ethanol and thoroughly mixed before being added to the simulant.

Incorporation and Extraction of Organics. The experimental design seeks to simulate the extraction of soluble organic compounds from cometary material,

based upon the method used by [17] to extract aldehydes from powdered Tagish Lake carbonaceous chondrite.

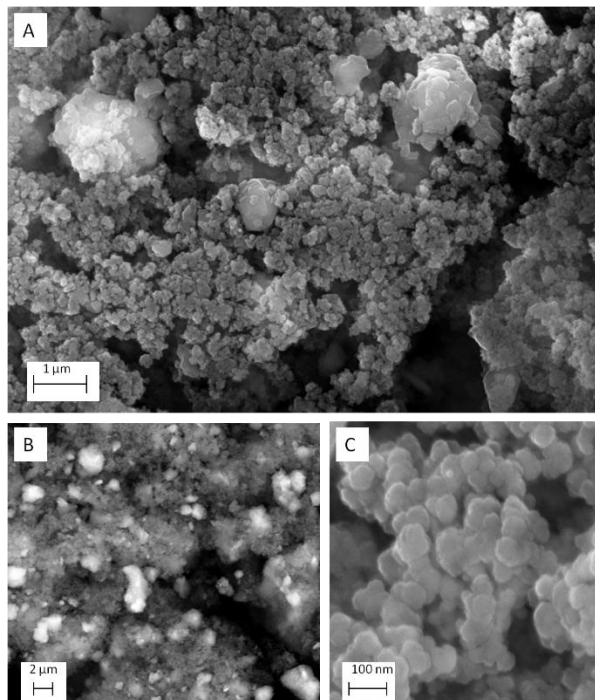


Figure 1 - Back-scattered electron images (15 kV) of the bulk simulant at different magnifications: A: 10 K, B: 2 K and C: 100 K. The simulant is a highly porous, fine aggregate of silica particles coated in humic acid organic matter. Some larger clusters of material remain due to incomplete mixing, but this creates a more realistic simulant; as IDPs contain a significant portion of 1 μm - 5 μm -sized grains.

For each experiment, seven vials containing 0.3 g of bulk simulant were prepared. This amount (based on volume) was chosen to simulate realistic curation conditions – it is not likely that a larger amount of comet sample would be prepared in one session and exposed for much longer than an hour. Two to three vials were prepared for each of the three environmental conditions: left with lids on and off in a clean room, and with the lid off in an Ar-circulated glove box at -15C. Each was exposed for 1 hour. A control simulant was also created, which was taken through every step of the procedure without the addition of the compounds.

To disperse the compounds throughout the simulant, 500 μL of the aldehyde-ethanol solution was added to each simulant and control, enough to nearly saturate the simulant. Most of the solution was left to evaporate (although not completely) by leaving the lids off the vials for 1.5 hrs in a fume hood. After one hour under experimental conditions, millipore water was added to extract the aldehydes. The mixtures were then centrifuged to remove any solid simulant, and the derivatizing agent 2,3,4,5,6-Pentafluorobenzyl Hydroxylamine (PFBHA - 0.2 mg/mL solution in millipore water) was added and

left to derivatize the aldehydes for 6-18 hours. The reaction was quenched by sulfuric acid, then dichloromethane (DCM) was used to extract the aldehyde derivatives from the solution. The DCM layer containing the derivatised compounds was extracted and added to 0.2 N sulfuric acid as a second cleaning step. Finally, the DCM layer was drawn off and evaporated down to 100 μL to concentrate the solution for GC-MS. A standard solution was prepared following the same procedure (except initial evaporation and centrifuging). An internal standard (dodecane) was added to each sample and standard to correct for instrumental variation.

GC-MS. Gas chromatography separation was performed at The University of Alberta or MacEwan University on an Agilent 7890 A, using a Zebron ZB-5MS column (26 m length, 250 μm diam., and 0.25 μm film thickness). Detection was performed in selected ion monitoring mode at masses 181 Da, 195 Da and 209 Da.

Results and Discussion: Initial results indicate that the samples subjected to sub-zero temperatures are lost (or preserved) at the same rate as those kept at room temperature without exposure to atmosphere. When exposed at room temperature (lid off), there are significant losses relative to the other samples, but only acetaldehyde is lost (30-60% loss). It is currently unclear why this is the case – whether it is differing adsorption mechanisms between the two compounds, or if there is greater loss of formaldehyde at the initial ethanol evaporation stage, rendering any further loss during the experimental condition stage negligible.

Adaptation of the experimental approach is ongoing, in order to increase reliability of the data and reduce any factors during the lengthy preparation that may interfere with the accuracy of the results. Further experiments will be carried out at varying sub-zero temperatures, as well as using other relevant compounds such as amines and carboxylic acids. Physical and chemical variations in the composition of the simulant will also be tested.

References: [1] Allen C. et al. (2011) *Chemie der Erde-Geochem.* 71:1–20. [2] Goesmann F. et al. (2015) *Science*, 349. [3] Quirico E. et al. (2015) *Icarus* 272, 32–47. [4] Le Roy L. et al. (2015) *A&A*, 583. [5] Wright I. P. et al. (2015) *Science* 349. [6] Herd C. D. K., et al. (2016) *Met. & Planet. Sci.* 51, 499–519. [7] Bentley M. S. et al. (2016) *Nature* 537, 73–75. [8] Schultz R. et al. (2015) *Nature*. 518, 216–218. [9] Rotundi A. et al., (2015) *Science* 347. [10] Fulle M. et al. (2016) *MNRAS* 462, S132–S137. [11] Merouane S. et al. (2016) *A&A* 596, A87. [12] Fulle M. et al. (2016) *A&A* 583, A14. [13] Blum J. et al. (2014) *Icarus* 235, 156–169. [14] Brownlee D. (2014) *Annu. Rev. Earth Planet. Sci.* 42:179–205. [15] Pizzarello S. et al. (2006) *MESSII*, 625–651. [16] Pizzarello S. and Holmes W. (2009) *Geochim. et Cosmochim. Acta* 73, 2150–2162. [17] Simkus D. N., et al. (2016) *47th LPS*. Abstract #2370.