

PREPARATION FOR COMETARY SAMPLE RETURN: NUCLEAR MICROPROBE ANALYSIS OF C AND N IN NaOCN, KOCN, $K_3Fe(CN)_6$, TAGISH LAKE, MURCHISON, AND TWO COSMIC SPHERULES. G. F. Herzog¹, J.-P. Gallien², H. Khodja², G. J. Flynn³, and S. Taylor⁴, ¹Rutgers Univ., Piscataway NJ 08854-8087 <herzog@rutchem.rutgers.edu>, ²Lab. Pierre Süe, CEA-Saclay 91191 Gif sur Yvette FRANCE, ³SUNY-Plattsburgh, Plattsburgh NY 12901-2681, ⁴CRREL, 72 Lime Road, Hanover, NH 03755.

Introduction: With the return of the Stardust Mission from Wild-2, we may have documented samples of a comet. Knowledge of the elemental composition of this material should cast light on the physical conditions in which comets formed. It will also serve as a ground-truth reference against which to check or model data acquired by remote photon spectroscopy or by mass spectroscopy *in situ* [1]. The elemental concentrations of C and N are of interest for several reasons. C and N are principal components of the 'organic' phase(s) found in all comets. Their absolute and/or relative abundances may have taxonomic significance [2]. In the inner part of the early Solar System, at least, carbon played a role in determining the oxygen fugacity and hence the chemical state of many elements [3]. If largely unaltered since formation, the abundance of carbon in cometary grains may be a useful indicator of formation conditions. An early cometary bombardment of Earth [4] may have introduced significant masses of C and N, thereby influencing atmospheric composition, surface temperatures (through the greenhouse effect), and even the evolution of life. Knowledge of C and N concentrations in representative comets could help constrain the size of incoming mass flux.

Most comet Wild-2 particles captured in Stardust aerogel will likely be small, < 10 μm [5]. Accordingly, we sought a method for C and N suitable for the non-destructive characterization of small grains. A technique based on the detection of protons emitted in the nuclear reactions $^{12}\text{C}(d,p)^{13}\text{C}$ and $^{14}\text{N}(d,p)^{15}\text{N}$ and developed at Saclay [6] has the necessary analytical power. We report on experiments aimed at adapting the method for Stardust particles.

Specific goals relevant to the Stardust Preliminary Examination Team were 1) to obtain reliable results for a sample of known composition; 2) to prepare samples in a way that did not compromise proposed subsequent analyses by SEM-EDX and either time of flight SIMS or nano-SIMS; and 3) to compare new with published results obtained with the nuclear microprobe for similar samples. In addition we set out to measure C and N in (melted) cosmic spherules, a type of extraterrestrial sample not previously analyzed for these elements.

Samples and sample preparation: For use as 'known' samples, we sought stoichiometric compounds with high melting points to minimize the risk

of sample decomposition due to heating during analysis. We settled on three such compounds, $K_3Fe(CN)_6$, KOCN, and NaOCN. For extraterrestrial samples, we followed Matrajt et al. [7] by choosing Murchison and Tagish Lake. Our only criterion for selecting grains was size. We took the smallest grains that we could pick up and put down with steel sewing needles. Grain sizes ranged from <10 μm for KOCN and Tagish Lake to ~50 μm in Murchison.

We selected 4 cosmic spherules (CS) with an eye to testing for the effect of heating on C and N concentrations. The external appearance of these CS indicated that they belonged to one of three textural types: barred olivine (more heated), or porphyritic, or scoriaceous (less heated) [see 8].

The nuclear microprobe requires a vertical, conductive target mounted to face the incoming beam. The need for conductivity and the risk of large C and N backgrounds ruled out epoxy as a backing medium. Use of gold [7] would have raised the detection limits of the x-ray microprobe (XRM) analyses planned to follow our work. We therefore decided to support the samples in indium and bought from Goodfellow foils 6 mm in diameter, 0.1 mm thick, and 99.999% pure. Three foils were placed on an aluminum disk 1 inch in diameter, and 5 mm thick. The disk was cleaned with detergent and rinsed with deionized water but otherwise we took no special precautions. The In foils adhered to the Al disk when pressed with a second Al disk. The attachment process decreased the foil thickness to an unknown degree. Once the foils were in place, we pressed the samples into them with the second Al disk. Two CS were lost later, evidently because they were thicker than their embedding foil.

Nuclear reaction analysis: We irradiated samples with 1.9 MeV deuterons focused to a spot size ~2 \times 2 μm . Beam currents, typically ~400 pA, were monitored by connecting the biased sample holder to a current integrator (Ortec 439). Protons were counted with a position-sensitive, annular detector with a depletion depth of 1.5 mm placed at 170° to the beam 35 mm away from the target, and screened by Mylar foil 50 μm thick. Data were reduced by reference to a set of seven in-house laboratory standards: CaCO₃, UO₂, SiO₂, Al₂O₃, Mg, FeS₂, and TiN. The energy spectrum of the emitted protons provided information about the depth distribution of C and N in the grains and also about the local concentrations of Mg, O, Al, and Si.

Table 1. C, N, and O (atom %) in reagents.

| Sample | C | N | O | N/C | O/C |
|---------------------------------------|------|------|------|------|------|
| K ₃ Fe(CN) ₆ _a | 38.2 | 41.8 | | 1.10 | |
| Formula | 37.5 | 37.5 | | 1.00 | |
| NaOCN_b | 24.6 | 26.6 | 33.0 | 1.08 | 1.34 |
| Formula | 25.0 | 25.0 | 25.0 | 1.00 | 1.00 |
| KOCN_a | 24.9 | 25.5 | 32.9 | 1.02 | 1.32 |
| Formula | 25.0 | 25.0 | 25.0 | 1.00 | 1.00 |

X-ray microprobe (XRM) analysis of In: We checked the suitability of indium mounts for XRM analysis at the National Synchrotron Light Source (Brookhaven National Lab) [9]).

Results and discussion: XRM analysis of the In foils showed tolerable counting rates from Pb and Fe but a larger one from Cu. Table 1 gives measured and expected concentrations of C, N, and O (atom %) in K₃Fe(CN)₆, KOCN, and NaOCN. Uncertainties for C and N are on the order of 10%. Agreement is good, ~within 10%, for carbon and nitrogen, but only fair for oxygen. The reason for the higher values of O is unclear. Reduction to D₂O and its loss to the vacuum should have lowered the oxygen concentration, not raised it. Loss of C and N as DCN seems possible, but this hypothesis leaves uncertain the final chemical form of oxygen.

Table 2 summarizes average compositional data for Murchison, Tagish Lake and two cosmic spherules. We calculated concentrations by assuming that the Fe, Mg, Si, and O in the samples occurred with the stoichiometry of olivine, i.e., (Fe,Mg)₂SiO₄. Signals for C and N in Murchison and Tagish Lake were well above blank levels. Calculated concentrations vary widely within grains, over a factor of 10 in C and of 30 in N. Average results are higher than published values (see [7]), probably because of sample heterogeneity. The measured N/C ratios for Murchison, ~0.05, agree well with published values, ~0.044. The observed N/C ratios in Tagish Lake vary from 0.028 to 0.044.

Examination of the proton energy spectra for the cosmic spherules showed that the small C and N concentrations were confined to the surface, and therefore were probably terrestrial in origin. Interior

restrial in origin. Interior concentrations (atom %) are estimated as C<0.1 and N<0.01.

Conclusions: The (d,p) method seems to give reliable N/C atom/atom ratios for grains as small as 15 μm pressed into In backing foils. C and N concentrations found for Murchison and Tagish Lake are heterogeneous on a μm scale and overlap with but are somewhat higher than published values. N/C ratios are similar to published values. Interior concentrations (atom %) of C (<0.1) and N (<0.01) in two cosmic spherules are below detection limits. We infer that deceleration in the atmosphere causes C and N loss from likely precursors grains, namely C-chondrite like materials [10].

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Table 2. Composition (atom %) of extraterrestrial samples.

| Sample | C | N | O | N/C | O/C | Al | Si | Mg |
|---------------------------|------|-------|-----------------|-------|------|------|-------|------|
| Murch_2a | 7.23 | 0.35 | 55.4 | 0.048 | 7.7 | 1.12 | 11.8 | 8.16 |
| Murch_4a | 6.47 | 0.35 | 46.3 | 0.054 | 7.2 | 0.8 | 10.7 | 8.61 |
| Grains [7] | 4.12 | 0.18 | | 0.044 | | | | |
| Bulk ^{1,2} | 2.78 | 0.13 | 48.8 | 0.046 | 17.5 | 0.76 | 8.74 | 8.93 |
| Tagish_2a | 11.8 | 0.52 | -- ⁵ | 0.044 | | 1.81 | 10.5 | 8.6 |
| Tagish_2c | 12.5 | 0.50 | -- ⁵ | 0.040 | | | 12.3 | 8.83 |
| Tagish_3a | 13.4 | 0.37 | 55.7 | 0.028 | 4.2 | | 7.77 | 7.68 |
| Grains [7] | 8.0 | 0.21 | | 0.026 | | | | |
| Bulk ^{1,3} | 7.9 | 0.19 | 44.0 | 0.024 | 5.57 | 0.60 | 6.64 | 7.26 |
| MM300_a | 0.17 | 0.025 | 52.0 | | | 2.57 | 15.1 | 11.2 |
| MM4dark | - | - | 48.5 | | | | 19.4 | 14.5 |
| Barred oliv. ⁴ | | | 58.0 | | | 1.27 | 14.67 | 15.3 |

Notes: 1) C and N from [7]; oxygen by difference. 2) Al, S, Si, Mg from [11]. 3) Al, S, Si, Mg from [12]. 4) [10]. 5) Sample too thin for reliable analysis.