

CHARACTERIZATION OF THREE CARBON- AND NITROGEN-RICH PARTICLES FROM COMET 81P/WILD 2. J.-P. Gallien¹, H. Khodja¹, G. F. Herzog², S. Taylor³, E. Koepsell⁴, C. P. Daghljan⁴, G. J. Flynn⁵, I. Sitnitsky⁵, A. Lanzirotti⁶, S. R. Sutton⁶, and L. P. Keller⁷, ¹ CNRS, CEA Saclay, Gif-Sur-Yvette, France, ² Rutgers U., Piscataway, NJ 08854-8087 (herzog@rutchem.rutgers.edu), ³ CRREL, 72 Lyme Road, Hanover, NH 03755, ⁴ Dartmouth College, Hanover, NH 03755, ⁵ SUNY-Plattsburgh, Plattsburgh NY 12901-2681, ⁶ U. Chicago Chicago, IL 60637, ⁷ NASA Johnson Space Center, Houston, TX 77058.

Introduction: Comets may sample the early solar system's complement of volatile-forming elements - including C and N - more fully and reliably than do the terrestrial planets or asteroids. Until recently, all elemental analyses of unambiguously cometary material were carried out remotely. The return of the Stardust mission makes it possible to analyze documented material from P81/Wild 2 in the laboratory [1]

Wild 2 particles fragmented when they stopped in the aerogel collectors [2]. We have studied three fragments thought to be rich in C and N by using several techniques: FTIR to characterize organic matter; synchrotron-induced x-ray fluorescence (SXRF) to determine Fe and certain element/Fe ratios; SEM to image sample morphology and to detect semiquantitatively Mg, Al, Si, Ca, and Fe; and nuclear reaction analysis (NRA) to measure C, N, O, and Si.

Experimental methods: L. Keller and K. Messenger extracted two dark particles C2054,0,35,21 or C21 and C2054,0,35,23 or C23 from the wall of Track 35. A. Westphal and C. Snead selected a third dark particle, C41, from the wall of track C2044,0,41.

Transmission FTIR spectra for C21 and C23 were collected as in [3]. Background spectra were acquired from the substrate immediately adjacent to the sample. Detection limits are typically in the percent range.

We measured C, N, O, and Si in C21, C23, and C41 by using a nuclear reaction analysis (NRA) method (d, p) [4] with samples mounted in indium [5]. The spatial resolution of NRA for C and N was ~2 μm . A separate x-ray detector in the NRA chamber provided information about iron concentrations.

The 3 particles were carbon-coated for SEM study. We obtained semi- rather than fully quantitative elemental concentrations from the SEM spectra because the particles were not flat and polished.

X-ray fluorescence analyses of selected elements were made with the x-ray microprobe of Brookhaven National Laboratory [6]. The x-ray beam excited about one third of the area of the particles. Background L x-ray fluorescence from In was typically small for Ti, Cr, Mn, Fe, Ni, and Zn, but problematic for Ca, K, and Sc [5].

Results: The FTIR spectra from C21 and C23 show a strong Si-O stretching feature from 1100-900 cm^{-1} as do spectra for amorphous

silicates and silica aerogel. Several absorption features in the C-H stretching region are consistent with long chain aliphatic hydrocarbons, namely, a strong CH_2 asymmetric stretch at $\sim 2925 \text{ cm}^{-1}$, a weaker CH_3 asymmetric stretch at $\sim 2960 \text{ cm}^{-1}$, and an aliphatic CH stretching band near 2855 cm^{-1} . In addition, a weak carbonyl C=O absorption appears in the spectrum of grain C23. The IR spectrum of unflown aerogel is known and differs from that of 81P/Wild 2 organic matter [3].

Carbon- and nitrogen-rich C21 ($\sim 30 \mu\text{m} \times 10 \mu\text{m}$) comprises subunits $1 \mu\text{m}$ to $5 \mu\text{m}$ in size. C, O, Si, Al, Ca, Na, Mg, S, and Fe appear in the SEM x-ray spectrum. Spot data, as well as element maps, show the presence of small ($1 \mu\text{m} \times 1 \mu\text{m}$) bright grains rich in O and Ca. They may be contaminants although, if so, it is odd that they are extremely rare in surrounding indium. By and large, both O and Si are uniformly distributed.

Particle C23 ($20 \mu\text{m} \times 15 \mu\text{m}$) contains mainly Si, O, S, Mg, Fe, and, tellingly, Ni. At high magnification ($\times 20,000$) blebs of FeSiNi are seen in the vesicular silicon-rich substrate. C23 consists mainly of compressed and heated aerogel.

The portion of C41 analyzed ($5 \mu\text{m} \times 5 \mu\text{m}$) contains Si, O, Mg, and lesser amounts of S and Fe. Like C23, it consists mainly of aerogel. Some contaminants - blocky crystals composed mainly of Ca and O, and rounded particles rich chlorine and Na-rich needles - were found embedded in the indium foils.

NRA results (Table 1) show that C21 contains more atoms of C than of any other element with O ranking second and the O/Si ratio of ~ 10 , greatly exceeding the ratio of 2 for SiO_2 . Consistent with the SEM results, Si and O predominate in C23 and C41.

Table 1. Areas (μm^2) and numbers of atoms (10^{12}) of C21, C23 and C41 without and with blank (bl) corrections.

	C21	C21-bl	C23	C23-bl	C41*	C41-bl
Area	234		304		252	
C	4.0	4.0	0.66	0.65	0.04	0.04
N	0.078	0.078	0.038	0.038	0.004	0.004
O	2.9	2.3	8.0	0.3	1.4	0.31
Mg	<0.07		<0.13		<0.02	
Si	0.30	--	3.8	--	0.53	--
X	1.45	1.45	1.15	1.15	0.14	0.14

*Central area of $24 \mu\text{m}^2$ only. X = Fe and other elements. .

Within the uncertainties, the Si/O atom/atom ratios of C23 (0.5) and C41 (0.4) are the same as in silica. Nitrogen contents were readily measurable in all 3 particles. Although C21 contains 6-7 times more C than C23, IR absorbances are comparable for the two fragments. We infer that C21 contains more graphitic C, which is infrared inactive. The nature of the preserved organic matter in the Wild 2 fragments varies considerably.

As configured experimentally, our SXRF analyses were most reliable for elemental ratios but also give the numbers of atoms present with larger uncertainties. We corrected both NRA and SXRF data for blanks estimated from the measured (NRA) Si contents and an aerogel analysis [7], assuming that all of the Si in the fragments came from (unfractionated) aerogel. The calculated blanks were negligible for all elements other than oxygen and silicon. We assume that heating or compression of aerogel did not alter its composition.

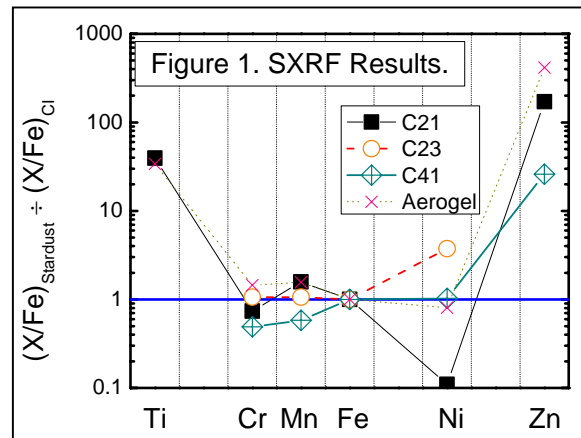
The CI- and iron-normalized ratios Cr/Fe, Mn/Fe, and Ni/Fe ratios mostly lie within a factor of 10 of CI values (Figure 1). Relative to CI, Ti is enriched in C21 and Zn in aerogel-rich C23 and C41. By all indications, the enrichments reflect the composition of extra-terrestrial matter. Still, it is curious that aerogel also has high Ti/Fe and Zn/Fe ratios.

After corrections for excitation volumes, the numbers of Fe atoms determined by SXRF are smaller than those inferred from DXRF, perhaps in part because of non-uniform mass distributions in the particles

Discussion: Several observations indicate that the fragments come from Wild 2. 1) C23 and C41 are embedded in compressed or partially melted aerogel. 2) SEM results for C23 and C41 show the presence of finely dispersed sub-micron beads of nickel-bearing sulfide. 3) SXRF data show that all 3 particles contain Ni and have Cr/Fe, Mn/Fe, and Ni/Fe ratios at or near-CI values. C21 is morphologically and compositionally unusual and needs more study.

Mn/Fe, Cr/Fe, and Ni/Fe ratios averaged for all three fragments agree with CI values to within a factor of two. Averaged Ti/Fe and Zn/Fe ratios are higher than CI values. Flynn et al. [6] suggested that comets may provide the best estimate of the solar Zn abundance.

All three particles contain relatively large concentrations of C and N. The C/N atom-atom ratios are 51 for C21, 17 for C23, and 9.5 for C41, values within the range set by carbonaceous chondrites [8] and comparable to XANES measurements of other Stardust fragments [9]. We suspect that the measured values may not represent faithfully the C/N ratios of the original impactors because 1) sections of aerogel surrounding



tracks lack visible fragments but contain organic material [9]; and 2) C/N ratios increase from low values measured remotely at Wild 2, to 4 in the Sun, to ~10 in CI chondrites, IDPs, and Halley dust and ice; to 50 in the more processed CO and CV chondrites [8-11]. The trend in C/N ratios presumably reflects in part the higher volatility of N-rich organic compounds of low molecular weight (see [9]). By extension, loss of organic matter from C21, C23, and C41 due to heating during deceleration may have raised C/N ratios. Analyses of larger fractions of the particle tracks for C and N would be desirable to check for evidence of nitrogen not retained by particles.

After correction for oxygen from aerogel, the O/C ratio of C21 is ~0.6, comparable to results for samples with higher N/C ratios from [9]. The IR spectrum excludes OH and the low Mg and Fe contents exclude abundant silicates as O's partner in C21. Aerogel-corrected O/C ratios of C23 and C41 are lower, but have larger uncertainties. The variation in O/C ratios indicates variability in the character of the carbon that the fragments retain.

References: [1] Brownlee D.E. et al. (2006) *Science*, 314, 1711-1716. [2] Hörz et al. (2006) *Science*, 314, 1716-1719. [3] Keller L.P. et al. (2006) *Science*, 314, 1728-1731. [4] Mosbah M. et al. (1995) *NIM*, B77, 450-456; Gallien J.-P. et al. (2004) *NIM*, B217, 113-122. [5] Herzog G.F. et al. (2006) *LPSC, XXXVII*, Abstract 1694. [6] Flynn G.J. et al. (2006) *Science*, 314, 1731-1735. [7] Tsou P. et al. (2003) *JGR*, doi:10.1029/2003JE002109. [8] Lodders K. and Feigley Jr., B. (1998) *Planetary Scientist's Companion*, Oxford U. Press. [9] Sandford S.A. et al. (2006) *Science*, 314, 1720-1724. [10] Farnham T.L. and Schleicher D.G. (2005) *Icarus*, 173, 533-558; ; Jessberger E. K. and Kissel J. (1991) *Comets in the Post-Halley Era*, Kluwer, 1075-1092. [11] Kissel J. et al. (2004) *Science*, 304, 1774-1776.