THE DIVERSITY OF CARBON IN COMETARY REFRACTORY DUST PARTICLES

IR spectroscopy of comets, and the Story of the “The Diversity of Primitive Refractory Grains”
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• comet observations team: Mike Kelley (UMD), David Harker (UCSD/CASS), Chick Woodward (UMN)
• review article ‘WIZ2017’: Wooden, Hope Ishii, Mike Zolensky
• discussions with Stardust team members, including Rhonda Stroud

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Cometary Dust: The Diversity of Primitive Refractory Grains
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An Idea to consider

» In the solid state refractory materials …

» More Primitive is related to greater diversity and on smaller scales (nanoscale to submicron scale)
Thomas+92-94 studies showed Carbon content of cometary ‘anhydrous IDPs’ can have 5 wt%–25 wt% C or as high as 45 wt% (90 vol%)

- pyroxene- (Enstatite-) dominated IDPs have systematically higher C abundances
- 2-3x to 13x CI abundances
- up to 90 vol% C
- acts as matrix holding mineral grains

We performed point-count analyses of thin sections of two pyroxene-dominated IDPs: W7027H14 and L2006B23. Results show that W7027H14 contains 40–50 vol% carbonaceous material, which is in good agreement with an estimate of ~40 vol%, assuming a particle diameter of 10 μm, a particle density of 1 g cm⁻³ [9], and ~23 wt% C (bulk). L2006B23 has ~45 wt% C, the highest reported bulk C of any IDP. The volume percent of C is ~90, determined by point counting, and agrees with the theoretical estimate of 90 vol% based on a particle diameter of 15 μm, density of 1 g cm⁻³ [9], 45 wt% C (bulk), and ~50% porosity.

The nature of the carbonaceous material in anhydrous IDPs is poorly known. We have not observed graphitized C (i.e., 0.34 nm spacings) in any particles, nor have we observed C in the form of carbonates. Rather, the carbonaceous material could be poorly graphitized or amorphous. The C-rich phases in L2006B23 have a vesicular texture, indicating the loss of volatiles, probably hydrocarbons. It seems plausible that several C phases could co-exist in anhydrous IDPs.

**Fig. 3.** The modal silicate mineralogy of 11 thin-sectioned IDPs plotted against their carbon abundance. Although the particles are grouped by only three broad mineralogy groups, the correlation of these groups with the C abundance is evident. Olivine-dominated IDPs: (A1) W7013G1, (A2) W7013C16, (A3) U2015E3. Mixed mineralogy IDPs: (B1) W7013G6, (B2) U2015D21, (B3) U2015D22, (B4) W7013E17, (B5) W7013E9. Pyroxene-dominated IDPs: (C1) W7013D12, (C2) W7029*A28, (C3) W7027H14. Points marked with an asterisk have larger uncertainties because the error is the standard deviation of the average of several fragments of the particle.
Stardust & IDPs: Near-IR transmission spectra

Figure 1. Transmission electron micrograph of IDP GS. (A) Carbon map of the particle. The bright areas are C-rich. (B) Bright field image of the particle.

IDP GS = 26P/Grigg-Skjellerup collection (Earth running through stream)
Stardust & IDPs: Near-IR transmission spectra

Figure 2. Micrographs of IDP GS showing the different textures for the carbonaceous materials. (A) Vesicular. The arrow points to the small vesicles. (B) Globular. (C) Dirty. (D) Spongy. (E) Smooth.
Stardust & IDPs: Near-IR transmission spectra

Figure 5. Micrograph of IDP Chocha. (A) Bright field image of the particle. (B) Carbon map of particle.

Figure 6. Micrographs of IDP Chocha showing the different textures of the carbonaceous materials. (A) Spongy. (B) Vesicular. (C) Smooth. (D) Globular (note that this is a filled globule). (E) Dirty.

Figure 7. IR spectrum of particle Chocha.

Chocha aromatic
Stardust & IDPs: Near-IR transmission spectra

Figure 8. Micrograph of Wild 2 particle Febo. (A) Bright field image of the particle. (B) Carbon map of particle. The arrow points toward the fine-grained material.

Febo fine-grained

Figure 11. Micrographs of particle Ada. (A) Bright field of an area of the particle. The arrow points to the C-rich globule. (B) Carbon map of the area shown in (A). The bright areas are C-rich. (C) Bright field image of another C-rich area in this particle. The arrow points to a C-rich globule. (D) Carbon map of the area shown in (C).

Ada 2 regions

Figure 12 shows two FTIR spectra of two different microtomed sections. Peaks are observed at 2954, 2918, 2847, 2160, 1714, 1418, 1216, 1136, and 1106 cm⁻¹. Peak assignments (Table 1) indicate that this particle contains chains of aliphatic hydrocarbons, some of which have C=C groups attached to them. There is also evidence of carbonyl in ketone and carboxylic acids and either olefinic or aromatic C=C bonds.
Stardust & IDPs: Near-IR transmission spectra

Figure 15. Left panel: IR spectrum of asteroid 24 Themis ratioed to the water-ice model of Rivkin & Emery (2010). Right panel: zoom of the spectrum shown in the left panel. Spectrum reproduced from Rivkin & Emery (2010) and Campins et al. (2010).

Figure 14. Comparison of particles Ada and Chocha to acrylic.

Figure 17. IR spectrum of the galactic center source IRS 7, obtained from the Infrared Space Observatory Data Center.

flipped by Diane (R -> ‘absorption’)
### Stardust & IDPs: Near-IR transmission spectra

**Table 1: Peak Assignments**

<table>
<thead>
<tr>
<th>Peak Position (in cm(^{-1}))</th>
<th>Vibration Mode</th>
<th>Interpretation</th>
<th>Sample That Has It</th>
</tr>
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<tbody>
<tr>
<td>3255, 3270</td>
<td>OH</td>
<td>Water</td>
<td>GS, Chocho, Acrylic</td>
</tr>
<tr>
<td>2990</td>
<td>C=O Stretching</td>
<td>Aliphatic hydrocarbons</td>
<td>GS, Chocho, Febo, Ada, Acrylic, DISM</td>
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<tr>
<td>2951, 2954, 2950, 2949, 2958</td>
<td>CH(_3) Asymmetric stretching</td>
<td>Aliphatic hydrocarbons</td>
<td>GS, Chocho, Febo, Ada, DISM</td>
</tr>
<tr>
<td>2920, 2918, 2929, 2925, 2922</td>
<td>CH(_2) Asymmetric stretching</td>
<td>Aliphatic hydrocarbons</td>
<td>GS, Chocho, Febo, Ada, DISM</td>
</tr>
<tr>
<td>2896, 2870, 2860, 2874</td>
<td>CH(_3) Symmetric stretching</td>
<td>Aliphatic hydrocarbons</td>
<td>GS, Chocho, Febo, Ada, DISM</td>
</tr>
<tr>
<td>2845, 2847, 2855</td>
<td>CH(_2) Symmetric stretching</td>
<td>Aliphatic hydrocarbons</td>
<td>GS, Chocho, Febo, Ada, DISM</td>
</tr>
<tr>
<td>2160</td>
<td>C=C Stretching</td>
<td>Esters</td>
<td>Ada</td>
</tr>
<tr>
<td>1740</td>
<td>C=O Carboxyl</td>
<td>Ketone, carboxylic acid</td>
<td>Chocho, Febo, Ada, acrylic</td>
</tr>
<tr>
<td>1730, 1717, 1700, 1714, 1727</td>
<td></td>
<td>Water</td>
<td>Febo</td>
</tr>
<tr>
<td>1685</td>
<td>C=O Carboxyl</td>
<td>Aromatics</td>
<td>Chocho, Febo, Ada, acrylic</td>
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<tr>
<td>1654, 1650</td>
<td>C=C Stretching</td>
<td>Carbonates</td>
<td>GS</td>
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<td>1545-1455</td>
<td>CO(^3)</td>
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<td>Chocho, Febo, Ada, acrylic</td>
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<tr>
<td>1447-1448</td>
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<td>Aliphatic hydrocarbons</td>
<td>Chocho, acrylic</td>
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<tr>
<td>1418, 1435</td>
<td>C=C Stretching</td>
<td>Aromatics</td>
<td>Chocho, acrylic</td>
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<tr>
<td>1350, 1386</td>
<td>CH(_3) Symmetric bending</td>
<td>Aliphatic hydrocarbons</td>
<td>Chocho, Febo, Ada, acrylic</td>
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<tr>
<td>1240, 1270</td>
<td>C=O-C</td>
<td>Esters</td>
<td>Acrylic</td>
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<tr>
<td>1220</td>
<td>CH(_2) Symmetric bending</td>
<td>Aliphatic hydrocarbons</td>
<td>Chocho</td>
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<tr>
<td>1147, 1190</td>
<td>Unknown</td>
<td>Secondary cyclic alcohols</td>
<td>Acrylic</td>
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<tr>
<td>1160</td>
<td>CH(_2) Twisting</td>
<td></td>
<td>Chocho</td>
</tr>
<tr>
<td>1065</td>
<td>C=OH</td>
<td></td>
<td>Acrylic</td>
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<tr>
<td>987, 970, 910</td>
<td>CH=CH Bending</td>
<td></td>
<td>Acrylic</td>
</tr>
<tr>
<td>1070, 1060, 952</td>
<td>Si-O</td>
<td>Pyroxene</td>
<td>GS, Febo</td>
</tr>
<tr>
<td>1216, 1136, 1106, 1010, 930</td>
<td>Si-O</td>
<td>Silicates</td>
<td>Febo, Ada</td>
</tr>
<tr>
<td>880</td>
<td>Si-O</td>
<td>Olivine</td>
<td>Febo</td>
</tr>
</tbody>
</table>

**Note.** The assignments are based on what was previously reported in the literature (Matrajt et al. 2004, 2005; Muñoz Caro et al. 2006 and references therein).
Stardust & IDPs: Near-IR transmission spectra

<table>
<thead>
<tr>
<th>Object/Sample</th>
<th>CH$_2$/CH$_3$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DISM (GC IRS7)</td>
<td>0.96–1.25</td>
<td>Sandford et al. (1991)</td>
</tr>
<tr>
<td>DISM (GC IRS7)</td>
<td>0.92–1.2 average 1.06</td>
<td>Pendleton et al. (1994)</td>
</tr>
<tr>
<td>Extragalactic ISM (Seyfert 2)</td>
<td>2.0</td>
<td>Dartois et al. (2004)</td>
</tr>
<tr>
<td>Tagish Lake</td>
<td>4.36</td>
<td>Matrajt et al. (2004)</td>
</tr>
<tr>
<td>IDPs</td>
<td>1.0–5.6 average 2.4</td>
<td>Flynn et al. (2003)</td>
</tr>
<tr>
<td>IDPs</td>
<td>1.88–3.69 average 2.47</td>
<td>Matrajt et al. (2005)</td>
</tr>
<tr>
<td>Wild 2 samples</td>
<td>1.7–2.8 average 2.15</td>
<td>Muñoz Caro et al. (2008)</td>
</tr>
<tr>
<td>Wild 2 samples</td>
<td>2.5</td>
<td>Keller et al. (2006); Sandford et al. (2006)</td>
</tr>
<tr>
<td>IOM Murchison</td>
<td>1.5</td>
<td>Ehrenfreund et al. (1991)</td>
</tr>
<tr>
<td>IOM Murchison</td>
<td>1.09</td>
<td>Flynn et al. (2003)</td>
</tr>
<tr>
<td>IOM Orgueil</td>
<td>1–1.51</td>
<td>Ehrenfreund et al. (1991)</td>
</tr>
<tr>
<td>Ultracarbonaceous IDP Chocha</td>
<td>4.6</td>
<td>This study</td>
</tr>
<tr>
<td>Ultracarbonaceous IDP GS</td>
<td>1.01</td>
<td>This study</td>
</tr>
<tr>
<td>Wild 2 Febo</td>
<td>1.96</td>
<td>This study</td>
</tr>
<tr>
<td>Wild 2 Ada</td>
<td>4.3</td>
<td>This study</td>
</tr>
<tr>
<td>Comet 103P/Hartley 2 (coma)</td>
<td>No CH$_3$ or CH$_2$ bands so no ratio calculated</td>
<td>A’Hearn et al. (2011); Wooden et al. (2011)</td>
</tr>
<tr>
<td>Asteroid 24 Themis</td>
<td>Not calculated</td>
<td>Campins et al. (2010); Rivkin &amp; Emery (2010)</td>
</tr>
</tbody>
</table>
103P/Hartley 2 (prelim Wooden+11, paper in prep.)
aliphatics and aromatics revealed when molecules subtracted

Keck molecules (Dello Russo)
GNIRS molecules+organics (Wooden)
GNIRS molecules = Keck deresolved

weak aromatic, ~30 cm$^{-1}$ wide
Stardust & IDPs: Other studies

Diverse forms of primordial organic matter identified in interplanetary dust particles

Graciela MATRAJ1, Scott MESSENGER2, Don BROWNLEE3, and Dave JOSWIAK1

Organic matter from comet 81P/Wild 2, IDPs, and carbonaceous meteorites; similarities and differences

S. WIRICK1*, G. J. FLYNN2, L. P. KELLER3, K. NAKAMURA-MESSENGER3, C. PELTZER1, C. JACOBSN1, S. SANDFORD4, and M. ZOLENSKY3

FTIR analysis of the organics in IDPs: Comparison with the IR spectra of the diffuse interstellar medium

G. Matrajt1, G. M. Muñoz Caro1, E. Dartois1, L. d’Hendecourt1, D. Deboffe1, and J. Borg1
CP IDPs: Other studies —— aliphatic carbon in 26P/G-S IDPs

amorphous carbon

Figure 1. Carbon map of L2009 (a) and Comet Wild 2 particle C2044,0.36,1 (b).

Comet Wild 2’s iron sulfide’s carbon map shows more carbon associated with this sulfide than carbon with the IDP iron sulfide. Only one of the 5 sections has carbon XANES spectra similar to the carbon XANES spectra of L2009 shown in Figure 1 where the carbon species is amorphous with a carbonyl attached (fig.2).

Figure 2. Carbon XANES spectra from iron sulfide in Comet Wild 2 (solid black) and the iron sulfide from IDP L2009 cluster 10.
cometary IDPs

_left: IR spectra show aliphatic carbon in IDPs, normalized to 10µm Si-O feature
_below: C-XANES probes kinds of bonds

standards
cometary IDPs

*left: IR spectra - must crush or thin slice the IDP to see feature

When we perform FTIR spectroscopy on whole IDPs (~10 μm in size), which are too thick for good transmission of infrared light through the thickest portion of the particle, we detect the 10 μm silicate absorption features but generally do not see the ~3.4 μm C-H stretching features. When we crush the IDP, exposing the interior, we detect the 10 μm and the 3.4 μm features, suggesting that organic matter is not present near the surface of the IDP but is present in the interior. The loss of near-surface organic matter would be expected for IDPs exposed to damaging ultraviolet light and particle radiation in space, and this provides some evidence that the aliphatic hydrocarbon is indigenous to the IDPs. However, the absence of aliphatic hydrocarbons near the surface of the IDPs might also result from the hexane washing, used to remove the surface coating of silicone oil from the IDPs, or from surface heating during atmospheric entry.
Organic grain coatings in primitive interplanetary dust particles: Implications for grain sticking in the Solar Nebula

George J. Flynn¹, Sue Wirick², and Lindsay P. Keller²

the time or mechanism of its production. The individual grains in these CP IDPs are coated by layers of carbonaceous material [3], typically ~100 nm thick, which holds the grains together. We have analyzed these

G. J. FLYNN et al.: ORGANIC RIMS ON PRIMITIVE GRAINS

Fig. 1. Scanning electron microscope image of an ~11 μm chondritic IDP collected from the Earth’s stratosphere by a NASA aircraft. The individual surface features are micron or submicron grains that have aggregated to form this dust particle. (NASA photo)

Fig. 2. High-resolution (~25 nm per pixel) x-ray absorption image of part of an ultramicrotome slice of a CP IDP, L2001+B6, showing the individual micron- and submicron-size mineral grains (dark gray). An image of the organic matter selected by cluster analysis (red) is superimposed, showing that the ~100 nm thick rims of organic matter form the contact surfaces between the individual mineral grains. (Field of view ~2.5 μm wide.)

Werbos, S. J.; Wirick, S.; Keller, L. P.; Sandford, S.

Fig. 2. (A, B) Transmission electron microscopy (TEM) images of two adjacent ultramicrotomed sections from FC9,0,13,1,5 containing dense, lobate, organic matter. (C) A different section of the same particle (FC9,0,13,1,4) only consisted of a single amorphous grain (Fig. 4) with no detectable carbonaceous matter contaminants. Only two types of cometary organic matter appear to be relatively unaltered during particle capture. These are (1) polycarboxyl-containing organic matter, similar to that observed in insoluble organic matter (IOM) from primitive meteorites, interplanetary dust particles (IDPs), and in other carbonaceous Stardust samples, and (2) highly aromatic refractory organic matter, which primarily constitutes nanoglobule-like features. Anomalous isotopic compositions in some of these samples also confirm their cometary heritage. There also appears to be a significant labile aliphatic component of Wild 2 organic matter, but this material could not be clearly distinguished from carbonaceous contaminants known to be present in the Stardust aerogel collector.

Fig. 3. Electron energy loss spectroscopy (EELS) spectra of organic matter from the Stardust Preliminary Examination. (A) Organic matter in compressed aerogel from sample C2054,0,35,32,10 (Fig. 1A). (B, C, D) Solitary organic matter in sample FC9,0,13,1,5. Spectrum B was acquired from the organic matter shown in Fig. 2A, while Spectra C and D were acquired from the organic matter shown in Fig. 2B. (E) Epoxy and organic mixture from sample FC12,0,16,1,10. (F) Pure epoxy in sample FC12,0,16,1,10. (G) Laboratory-produced amorphous carbon film.
Stardust C-XANES spectra

Diversity - wide variation in functional groups and texture

The XANES spectrum of this section (Fig. 7A) contain photoabsorptions due to aromatic carbon-carbon bonding, aromatic ketones, and carboxyl functional groups (Table 2), similar to XANES spectra from the organic matter from Track 13 (Fig. 7B, and Spectra 7 and 8 from Fig. 1 of Cody et al. 2008a). These spectra imply that the cometary organic matter in this particle consists of complex polyanromatic domains modified by oxygentic functional groups and interconnected by short aliphatic chains (Cody et al. 2008a; De Gregorio et al. 2010).
UCAMMs: chocked full of organics, GEMS and olivine (crystals) with ranges of Mg-Fe contents from Fo100–Fo60 (mineral compositions similar to Stardust and some Giant IDPs)

Transmission Electron Microscopy of CONCORDIA UltraCarbonaceous Antarctic MicroMeteorites (UCAMMs):
Mineralogical properties

E. Dobrica, C. Engrand, H. Leroux, J.-N. Rouzaud, J. Duprat

UCAMMs are dominated by disordered carbonaceous matter that extends over surfaces of up to ~90% of the particle. Embedded in this carbonaceous matter, we observed small and complex assemblages of fine-grained mineral phases, isolated minerals, glassy phases that resemble Glass with Embedded Metal and Sulfides (GEMS) that were first found in Interplanetary Dust Particles (IDPs), and rounded objects containing both glass and crystalline materials. The mineral assemblages are chondritic in composition, within a factor of 2. Crystalline materials represent at least 25% of mineral phases. This value
UCAMMs: chance to highlight FeS, which is present in most cometary samples and chondrites. FeS can be primary condensate or alteration product.

Pollack+94 FeS complex index of refraction: missing data highly absorptive!
We believe that we have seen materials that are strong candidates for being the first (or fundamental) accretionary particles. Some primitive IDPs are made almost entirely of submicron components that are likely to be FAPs. They are generally equant and range from 0.1 to 1 μm across. They average about a quarter of a micron and very few are smaller than 100nm. They are solid materials composed of amorphous silicates, organic material, GEMS, and crystalline materials including Fo, En and Fe sulfides. Some are single mineral phases but most are made of several components. They are solid (non-porous) rocks and we refer to them as “femtorocks” because of their mass and multi-component nature. The femtorocks often contain organic materials and silicates and we believe that they are functionally equivalent to Mayo Greenberg’s core-mantle interstellar grain model even though they consist of multiple cores and not a single core surrounded by a single organic mantle. The elemental composition variation among femtorocks is remarkable. As seen in Figure 1, their Fe, Mg and Si compositions vary widely with little modulation due to mineralogical control. They contain minerals but the amorphous components dominate their compositional spread. In the Fe-Mg-Fe ternary, the only first order effect is the scarcity of compositions with Mg/Si appreciably greater than unity (enstatite). IDPs made of femtorocks (FAPs?) similar to those seen in figure 1 match CI relative abundances for aggregates larger than 3 microns but at the submicron, fundamental component, level they vary all over the map.

Figure 1 Atom fraction ternary of submicron grains (femtorocks) from U2-20 GCA - a cluster IDP. The large heterogeneity at the submicron scale is remarkable and relatively unconstrained by mineralogical stoichiometry. The large dispersion is similar to data on particle compositions obtained at comet Halley.
Halley & IDPs: Mineralogies show olivine contains Mg and Fe
WIZ2017 Fig.1 - see caption for full citations and for full discussion of mineralogy (comets, compared to carbonaceous chondrites)
remarking remarkably similar XANES (especially compared to diversity in comets): functional groups similar
variations on nano to micron size scales
40% of C is ‘lost’ in isolation of IOM. What was lost?

The IOM shows tremendous variation in its elemental and isotopic compositions both within and between chondrite groups (Fig. 1). These variations are due, at least in part, to parent body processes, but may also reflect variations in the materials accreted by the different chondrite groups (Section 6). In the chondrites that appear to have experienced the most benign parent body conditions (CIs, CMs and CRs), the bulk compositions of their IOM, normalized to 100 Cs, are in the range \( \sim C_{100}H_{70-80}O_{15-20}N_{3-4}S_{1-4} \). For comparison, the SOM in the Murchison (CM2) meteorite has an estimated bulk composition of \( \sim C_{100}H_{155}O_{20}N_{3}S_{3} \) (Schmitt-Kopplin et al., 2010) that, except for its H/C, resembles the bulk composition of IOM. However, the abundances of the different compounds in the SOM vary considerably within and between chondrite groups (Table 1). The compositional variations in SOM, at least within a group, appear to be largely determined by parent body processes (e.g., Martins et al., 2007; Aponte et al., 2011; Glavin et al., 2011; Hilts et al., 2014), with some fraction of the SOM possibly being the product of alteration of IOM by parent body processes (e.g., Sephton et al., 2003; Huang et al., 2007).

Fig. 9. Average bulk XANES spectra of IOM from several primitive carbonaceous chondrites: Murchison (CM2), Orgueil (CI1), QUE 99177 (CR2), Tagish Lake (C2, lithology 5b) and ALH 77307 (CO3.0). The C XANES spectra show the greatest variation in functional chemistries between different meteorite groups and petrologic types, but are still very similar. As shown in the representative spectrum from Tagish Lake, the N XANES spectra from primitive IOM are relatively featureless, only containing minor spectral “shoulders” on the main N absorption edge. In addition, IOM C XANES spectra rarely show spectral features other than the main \( \pi^* \) and \( \sigma^* \) peaks for \( \equiv C=O \) and \( C-O \) bonds, respectively. The C XANES data are taken from De Gregorio et al. (2013), while the data for Tagish Lake are unpublished.
Meteoritic IOM (Alexander+17)

- different textures, ‘fluffy’, ‘globules’
- greater diversity on smaller scales
- differences between chondrite classes
- aggregate of nanoglobules - texture dominated by fine-grained structure

Fig. 1. The variations in bulk IOM H and N elemental and isotopic compositions within and between chondrite groups (updated from Alexander et al., 2007b, 2010). The OC WSG 95300 is not shown in (a) because its δD value is almost 12,000‰ and H/C = 0.103. TL is Tagish Lake, Sem is Semarkona (L3.00), DOM is DOM 08006 (C3.00), Kaba is a CV 3.1 and Bells is an anomalous CM2. CM(H) are heated CMs, probably as a result of impacts.
Meteoritic IOM

- remarkably similar (compared to diversity in comets)
- variations on nano to micron size scales

Nevertheless, the degradative chemical and pyrolysis techniques both indicate that at least the chemically accessible and thermally labile components of IOM are composed of small aromatic units (typically 1–3 rings, although some larger units are present) that have a high degree of substitution by aliphatic subgroups. The high degree of substitution and the macromolecular nature of IOM indicate that there must be considerable cross-linking by the aliphatic material between the aromatic units that has generated a 3D network. This is consistent with the bulk IOM properties inferred by NMR and FTIR, which also indicate that the aliphatic material must be composed of short chains that are highly branched. Both the chemical degradation and Raman studies suggest that a significant fraction of the cross-linking moieties involve O-bearing functional groups. Relatively little is known about S and N speciation in IOM. XANES shows that S occurs in a number of different functional groups with a range of oxidation states, but at present it is not possible to say anything more quantitative. The N XANES spectra are almost featureless, providing few clues to its speciation, and the difficulty of obtaining $^{15}$N NMR spectra from IOM is a puzzle.
Meteoritic IOM in IR

- large chemical and structural variations between chondrites
- but note 3.4µm band is less diverse than in comet samples

Raw absorbance is about same as Tholin; not ‘dark’ enough to be cometary highly absorbing grains seen in cometary IR spectra.

Ternary diagram: one way to see -CH2, -CH3, C=C bond ratios

also see Derenne & Robert 2010 MAPS, on model for IOM
67P/C-G IOM-like organic matter

- most similar to high molecular weight macromolecular carbon (meteoritic IOM) (Fray+16)
- higher H/C ratio (Fray+16)
- higher N/C ratio (Fray+17), but less than in UCAMMs
- (Bardyn+17)(Fray+17)
- missing lower molecular weight -COOH (carboxylic)
- IOM-like material constitutes 50% of C in 67P
- much more organics than in Stardust

chondrites and IDPs. Thus, the 67P particles and the nucleus are rich in organic matter, as already suggested from indirect observations (Fulle et al. 2016; Herique et al. 2016), and this indicates that comets have been aggregated in an organic-rich region of the protoplanetary disc.
Comet IR spectra have 5 components, which includes warm featureless grains that produce near-IR ‘continuum’ emission at >3μm:

- **Amorphous Mg:Fe silicates**; porous – GEMS-like
- Amorphous-like olivine (glassy, disordered)
- Amorphous-like pyroxene (glassy, disordered)
- **Abundant amorphous carbon-like (n,k)**
- **Crystalline silicates** (when detected) are:
  - Mg-rich \([\text{Mg}/(\text{Mg}+\text{Fe})>0.9]\)
  - NO layer-lattice silicates (e.g., Montmorillonite, smectite)
  - no spectral detection of \(\text{Al}_2\text{O}_3\)

9P/Tempel 1 (Harker, Woodward, Wooden 2005, Science, 310, 278)
Intro to Cometary Spectral Energy Distributions: Hale-Bopp & changes with time (rh)

scattered sunlight

ubiquitous warm featureless continuum

\( \Rightarrow \) fitted with amorphous carbon
Spitzer spectra of comets show a wide range of amorphous carbon-to-silicate ratios and grain size distributions that peak at grain radii varying from ~0.2 µm to ~1 µm.

Highest contrast features are lowest carbon to silicate ratio and small ~0.2 µm grains. Lowest contrast features are a combination of higher amorphous carbon and larger peak grain radii.

~0.2 µm and larger and porous grains, ‘low’ amorphous carbon relative to silicates (high sil-to-Acar)

~0.5–1µm low porosity or solid grains, ‘high’ amorphous carbon relative to silicates
Comet 9P/Tempel 1 had a changing silicate-to-amorphous carbon ratio in the inner coma during +3 hr after Deep-Impact:
(Gemini-N: Harker+05, Harker+07 (ternary diagram below)
Subaru: Sugita+05)

103P/Hartley 2 has high amorphous carbon relative to silicates

103P/Hartley 2, Harker+18 AJ in press

“Take home message”: Amorphous carbon versus silicates, and silicate crystalline fraction are not simply dependent on dynamical history of the comet (inner solar system evolution) or dynamical family (origin), i.e., not dependent on whether comet is a short-period ‘Jupiter Family’ or Ecliptic comet vs. long-period ‘Oort cloud’ comet or Isotropic comet.
Comet 67P had 2 **outbursts** of dust on 2015-09-13, 14 UT: Reflected light increased at 2-2.5\(\mu\)m and became bluer. Dust temperatures jumped from \(~300\text{K}\) to \(~600\text{K}\). Emission modeled with porous \((D=2.5)\) 100nm-radii grains, mix of 66% amorphous carbon and 34 vol% amorphous Mg-Fe olivine or separate components (VIRTIS, Bockelee-Morvan+17)

“Both the colour and colour temperature measured at the peak of brightness of the September 14 outburst are satisfactorily reproduced with a population of carbon/olivine grains, constituted almost uniquely of small grains with a mean radius of \(a_{\text{mean}} \sim 0.1\ \mu\text{m}\). However, the high bolometric albedo \(\sim 0.6\) is not explained.”

Olivine-only grains could explain the peak albedo but not the highest temperatures. Perhaps there are 2 grain components separately governing the scattered light and thermal emission, both \(\sim 100\ \text{nm}\). Changes with time could be progressively larger grains crossing field-of-view.
Deep Impact 9P/Tempel 1 had polarized light at leading edge of ejecta: dark particles!

- One possibility is that the carbonaceous grains are smaller than the silicate grains so that such carbonaceous grains got faster speeds due to acceleration by gas drag.
- Alternatively, suppose that the grains with the faster ejection velocity belonged to the surface layer.

(Furusho+07)
1P/Halley: ‘CHON’ grains dominated flyby when VEGA, GIOTTO closer to nucleus and 19% of CHON are elemental C-only grains.

Carbonaceous components in the comet Halley dust

M. N. Fomenkova, S. Chang, and L. M. Mukhin


![Graph showing distribution of dust grain types](image)

**Fig. 1.** Spatial variability of dust grain distribution in the coma (PUMA-1 data). For 100 second intervals along the trajectory, we considered $\alpha_{org}(100)$, the proportion of particles containing organic material (CHON and Mixed), and $\alpha_{org}(100)$, the proportion of particles lacking organic material (Rock):

$$\alpha_{org}(100) = \frac{N_{CHON} + N_{Mixed}}{N_{CHON} + N_{Mixed} + N_{Rock}} \quad \alpha_{org}(100) = \frac{N_{Rock}}{N_{CHON} + N_{Mixed} + N_{Rock}},$$

1) CHON particles dominated by carbon and/or organics represent ~22% of measured comet Halley dust grains (by number) and reveal a wide variety of compositional types. Decomposition of these particles in the coma may provide extended sources of some gaseous species.

3) Elemental carbon grains, various kinds of hydrocarbons, and probably polymers of cyanopolyynes and multichain monoxides appear to be distinct contributors to the particle population. They represent, correspondingly, 19, 10, 2, and 1% of all CHON grains.
Mg-rich crystalline silicates produce strong 10µm features when coma is dominated by submicron silicate grains.
Oort cloud comets C/2001 Q4 (NEAT) & Hale-Bopp have similar silicate mineralogy; both have strong jet activity and abundant Forsterite crystals.

\[ f_{\text{crystal}} = \frac{\text{crystal}}{\text{amorphous} + \text{crystalline}} \approx 0.7 \]

C/2001 Q4 has variable silicate-to-amorphous carbon ratio, which lowers the contrast (height) of the silicate feature (next slide).

Hale-Bopp at 2.8 AU

Q4

Silicate Feature Flux/Continuum Ratio
C/2001 Q4 (NEAT) HIFOGS 11May04.30UT compared with 0.3*Hale-Bopp 15Feb97UT

Flux/BB

Hale-Bopp*0.3 = Q4 NEAT
C/2001 Q4’s silicate feature drops in contrast (height) over 1.5 hours, as jets move grains through beam and dust composition changes: there are fewer silicate grains relative to amorphous C grains (right).

Is this true? Assertion: Amorphous Carbon is a separate grain component from the silicates in this comet.
Outer icy bodies require darkening materials on their surfaces, and amorphous carbon is used in models.

Can cometary dark materials provide clues to the abundance of this material and to its composition?

Comet samples can contain up to 45 wt% C (90 vol%).

Challenge: Tholins and IOM are relatively transparent!

Amorphous carbon darkens and then organics are added to get absorption bands (Cristina Dalle Ore, private communication)

Table that Diane assembled in 2008.

<table>
<thead>
<tr>
<th>Object Class</th>
<th>Object Name</th>
<th>Amorphous Carbon</th>
<th>Titan Tholin</th>
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<th>Ice Tholin</th>
<th>Kerogen Type II</th>
<th>Water Ice</th>
<th>Olivine</th>
<th>A</th>
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<td>0.7, 0.10 µm</td>
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</table>

Notes: [a] Titan Tholin N2:CH4=0.9:0.1 [15]; [b] Tritan Tholan: N2:CH4=0.999:0.001 [17]; [c] Ice Tholin H2O:C2H6 [15]; [d] Kerogen Type II [ ]; [e] A means Albedo at 0.55µm; [f] Jarosite KFe3(SO4)2(OH)6


Notes: [a] Titan Tholin N2:CH4=0.9:0.1 [15]; [b] Tritan Tholan: N2:CH4=0.999:0.001 [17]; [c] Ice Tholin H2O:C2H6 [15]; [d] Kerogen Type II [ ]; [e] A means Albedo at 0.55µm; [f] Jarosite KFe3(SO4)2(OH)6

Cometary carbonaceous ‘domains’ are diverse in abundance and forms

- Carbonaceous matter in comets is highly variable in abundance, and has different forms of carbon with organic and possibly inorganic C
- Not all organics are like insoluble organic matter (IOM)
- Some organic matter is highly labile (soluble organic matter)
- Some elemental carbon is seen (with names highly disordered carbon, poorly graphitized carbon, or amorphous carbon)
- Different cometary IDPs have different characteristics:
  - Chondritic porous IDPs can have high C as amorphous carbon or IOM-like (high molecular weight organic matter), Forsterite and Enstatite crystals
  - Giant IDPs have Olivine with range of Fe contents and IOM-like
  - IDPs with higher concentrations of Mg-rich crystals (Enstatite in particular) have higher C abundances (Thomas+93 GCA)
- Ultra Carbonaceous Antarctic Micrometeorites (UCAMMs, likely cometary) have high contents of carbonaceous matter (90% by volume).
- Thermal modeling of IR spectra of comets show a large variation in the ratio of dark absorbing grains [near-IR continuum] to silicates, i.e., ‘amorphous carbon’-to-‘silicate’ ratios
- Cometary organics are more diverse than meteoritic organics (IR spectra and XANES), in functional groups and ratio of -CH2 to -CH3 in aliphatics
- Is there link between organics in samples and dark particles spectrally seen in cometary coma?
- What role may FeS play in darkening surfaces compare to organics? We need better FeS optical constants.
Details on minerals follow, for those who are interested
Organics and refractories in comets and meteorites?

What are primitive materials?
What are possible source regions?
Can we define primitive materials and consider different bodies that contain them?
Many details are discussed in:

"There is more than one street lamp." To bridge the conversation, we discuss the sources & ideas in WIZ2017. (Open Access to main and suppl.)
Regime of Crystalline Silicate Condensation
When & Where
Transport outward (comets & Trojans & ?)
LIME Low iron Mn-Enriched
OLIVINE
100% ≤ Mg ≤ 98% FeO%
160°-rich ↔ "early"

Models Fedkin & Grossman
Can be condensates
of dust-enriched 10°
aquously-altered (AT)

100% e (Frank et al. 14)
8% (Stardust, Brownlee 16)

CR type II
Cometary

CR type I
Bigger sample

Enstatite-rich IDPs have more carbon
GEMS-rich IDPs have more Mg-rich crystals and little Fe-rich crystals
Do GEMS-rich IDPs have more carbon? Is survival of amorphous silicates and carbonaceous matter correlated?

Regime of Fine-Grained Chondrule Formation
"Iris" in Stardust is an igneous system "mini" 
Z1270 Fe-o chondrule fragments of type II

100% Dobson UCAMMS

Early 16O-rich reservoir

Association of Carbon with Mg-mineral crystals
Abundance Range

Some -
CPIDPs = UCAMMS
Stardust
Halley
50% by volume

very high carbon

Thomas et al. 1994-95 studies
retention or destruction of carbon

50% by volume

Do GEMS-rich IDPs have more carbon? Is survival of amorphous silicates and carbonaceous matter correlated?
a story that emerges from Defouilloy+16LPSC, Defouilloy+17: high Mg-content olivines are early **condensates** because Fo100-Fo98 have 16O-enrichments (like AOAs and CAIs)
Stardust’s olivines with Fe>10% are μ chondrules like ‘Iris’

Iris (Fo60, X_{Fe}≈0.4) formed from a melt (droplet) in high oxygen fugacity gas. Iris is an ‘igneous’ particle, not a condensate.

Iris: log(fO2)=−13.3 (IW−0.25 at 1000 °C), at a pressure of 1 bar or less
Stardust’s olivines can be compared to CR chondrules (Schrader)
Stardust’s olivines can be compared to CR chondrules (Schrader)

Range of increasing Mn-Fe lines could be ‘zoning’ or Schrader suggests ‘discrete igneous systems’ (like Iris)
minor element Mn contents show ‘genetic’ relationship between olivines in Stardust and in Giant IDPs (‘C’) and carbonaceous chondrites (‘A’) and CR (‘B’)

Cometary Wild 2 (Stardust = dots, triangles = Brownlee; Frank) and a Giant IDP (red squares) show comet olivines sample more conditions than any single primitive carbonaceous chondrite. Don Brownlee calls this a “decline in diversity” but I think it is more diversity. Words?
olivines Fo90 – ~Fo50 are not condensates, they are μ chondrules.
• Condensation of Fe-bearing silicates requires high oxygen fugacity in the solar nebula:
  – drive in silicate dust (silicates donate oxygen)
  – drive in ice grains ($\text{H}_2\text{O}$ donates oxygen)

Cuzzi and Zahnle 2004

• Inward migration of cometesimals
• Outward transport of Fe-bearing silicates
• While comet grains are aggregating & before or during nuclei accretion
Other wild possibilities?

» Could some of the dust ‘bunnies/rhinos’ that were heat-zapped to form chondrules have GEMS-like precursors?

Brownlee et al. 2005 LPSC COOKED GEMS — INSIGHTS INTO THE HOT ORIGIN OF CRYSTALLINE SILICATES IN CIRCUMSTELLAR DISKS AND THE COLD ORIGIN GEMS.

At just about 700 ºC the typical GEMS texture of silicate glass with fine embedded metal and sulfides transforms to an igneous-like texture of silica rich glass and prominent subhedral to euhedral grains of moderately iron rich olivine and pyroxene. At such a temperature, this remarkable transformation occurs by sub-solidus processes.
## Summary

Comets and cometary samples show a range of compositions!

- **Comets are the least processed small bodies but they contain a diversity of materials that have different degrees of ‘primitiveness’.**
- **Comets contain condensates and µ chondrules, or Fundamental Accretionary Particles and highly processed particles, as well as inherited ISM materials that rarely reveal presolar signatures.**
- **How chondrules form is still a mystery.**
- **Maybe consider comet particles as inputs to chondrule-forming zones?**

### Table

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<tr>
<th>Cometary Collection Processes</th>
<th>L</th>
<th>C</th>
<th>O</th>
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Table notes:
- ✓ = strongly debated tentative or putative identification
- + = tentative or putative identification
- • = not discernible by measurement technique(s)
- ° = rare
- □ = abundant
- XX = dominant
- § = semirefractory organic has a limited lifetime in the coma, and is a probable parent of gas-phase ‘distributed sources’ (CO, formaldehyde, CN)
- g+chem = grain surface chemistry, via gas-grain reactions on cold grain surfaces
- vp = vapor phase
- ‡ = Remote-sensing not in the mid-IR to far-IR, including visible light scattering and near-IR molecular spectroscopy, radio spectroscopy
- δ = process plays a role; (δ) process may play a role

GCP-JDP = Giant CP JDP
SONSETA = Stone GEMS TIE-SIMS analysis
[^1]: the origins of cometary amorphous silicates are debated so the evidence is delineated into 4 distinct rows: isotopically anomalous presolar GEMS, amorphous silicates (no isotopic information), isotopically-solar GEMS (hypothesized to be ISM amorphous silicates), and isotopically-solar GEMS (hypothesized to be solar-system amorphous silicates)
Mg-rich crystalline silicates dominate 10µm spectra of comet Hale-Bopp and are seen at some level in most all comets.

- Mid-IR wavelength positions of crystalline resonance peaks show high Mg-contents:
  - crystalline pyroxene: \((\text{Mg}_x\text{Fe}_{1-x})\text{SiO}_3\) \(0.7 \leq x \leq 0.9\)
  - crystalline olivine: \((\text{Mg}_y\text{Fe}_{1-y})_2\text{SiO}_4\) \(0.9 \leq y \leq 1.0\)

Olivine: Koike et al. 2003, A&A 399, 1101