Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

MNRAS **462,** S323–S330 (2016)
Advance Access publication 2016 November 5

doi:10.1093/mnras/stw2844

Variations in cometary dust composition from *Giotto* to *Rosetta*, clues to their formation mechanisms

Cécile Engrand,[1★] Jean Duprat,[1★] Emmanuel Dartois,[2★] Karim Benzerara,[3] Hugues Leroux,[4] Donia Baklouti,[2] Anaïs Bardyn,[5,6] Christelle Briois,[6] Hervé Cottin,[5] Henning Fischer,[7] Nicolas Fray,[5] Marie Godard,[1] Martin Hilchenbach,[7] Yves Langevin,[2] John Paquette,[7] Jouni Rynö,[8] Rita Schulz,[9] Johan Silén,[8] Oliver Stenzel,[7] Laurent Thirkell[6] and the COSIMA team

[1]*Centre de Sciences Nucléaires et de Sciences de la Matière (CSNSM) CNRS-IN2P3/Univ. Paris Sud, Université Paris-Saclay, Bât. 104, F-91405 Orsay Campus, France*
[2]*Institut d'Astrophysique Spatiale (IAS) CNRS/INSU-Univ. Paris-Sud, Université Paris-Saclay, Bât. 121, F-91405 Orsay Campus, France*
[3]*Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, CNRS UMR 7590, Sorbonne Universités, MNHN et UPMC, Case postale 115, 4 place Jussieu, F-75252 Paris Cedex 05, France*
[4]*Unité Matériaux et Transformations (UMET), CNRS/Univ. Lille1, F-59655 Villeneuve d'Ascq, France*
[5]*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, F-94000 Créteil, France*
[6]*Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS/Université d'Orléans, F-45071 Orléans, France*
[7]*Max-Planck-Institut für Sonnensystemforschung (MPS), Justus-von-Liebig-Weg 3, D-37077 Göttingen, Germany*
[8]*Finnish Meteorological Institute, Erik Palménin aukio 1, FI-00560 Helsinki, Finland*
[9]*European Space Agency (ESA), Scientific Support Office, Keplerlaan 1, Postbus 299, NL-2200 AG Noordwijk, The Netherlands*

Accepted 2016 November 2. Received 2016 November 2; in original form 2016 July 8

ABSTRACT

This paper reviews the current knowledge on the composition of cometary dust (ice, minerals and organics) in order to constrain their origin and formation mechanisms. Comets have been investigated by astronomical observations, space missions (*Giotto* to *Rosetta*), and by the analysis of cometary dust particles collected on Earth, chondritic porous interplanetary dust particles (CP-IDPs) and ultracarbonaceous Antarctic micrometeorites (UCAMMs). Most ices detected in the dense phases of the interstellar medium (ISM) have been identified in cometary volatiles. However, differences also suggest that cometary ices cannot be completely inherited from the ISM. Cometary minerals are dominated by crystalline Mg-rich silicates, Fe sulphides and glassy phases including GEMS (glass with embedded metals and sulphides). The crystalline nature and refractory composition of a significant fraction of the minerals in comets imply a high temperature formation/processing close to the proto-Sun, resetting a possible presolar signature of these phases. These minerals were further transported up to the external regions of the disc and incorporated in comet nuclei. Cometary matter contains a low abundance of isotopically anomalous minerals directly inherited from the presolar cloud. At least two different kinds of organic matter are found in dust of cometary origin, with low or high nitrogen content. N-poor organic matter is also observed in primitive interplanetary materials (like carbonaceous chondrites) and its origin is debated. The N-rich organic matter is only observed in CP-IDPs and UCAMMs and can be formed by Galactic cosmic ray irradiation of N_2- and CH_4-rich icy surface at large heliocentric distance beyond a 'nitrogen snow line'.

Key words: comets: general – interplanetary medium – meteorites, meteors, meteoroids – minor planets, asteroids: general – ISM: abundances – dust, extinction.

★ E-mail: cecile.engrand@csnsm.in2p3.fr (CE); jean.duprat@csnsm.in2p3.fr (JD); emmanuel.dartois@ias.u-psud.fr (ED)

Published by Oxford University Press on behalf of the Royal Astronomical Society

1 INTRODUCTION

One of the major challenges in planetary science is to understand the context and the mechanisms of the formation of the Solar system, 4.5 billion years ago. Small bodies such as asteroids and comets have escaped planetary formation and therefore still hold crucial information on the formation and early evolution of the Solar system. Primitive meteorites like carbonaceous chondrites have retained the composition of the protosolar cloud for most elements (with concentrations ranging over more than three orders of magnitude), except for volatile elements (e.g. H, He, C, N, O) that are depleted in meteorites with respect to the Solar photosphere (Lodders 2010). Among these small bodies, comets have remained at low temperature since the time of their formation and have retained a higher proportion of volatile elements. Remote sensing studies show that they contain a wealth of volatile species that are (for many of them) detected as ices in the interstellar medium (ISM), although C- and N-bearing compounds are on average depleted in comets with regard to the ISM values (e.g. Bockelée-Morvan et al. 2005; Mumma & Charnley 2011; Boogert et al. 2015). The key question is whether comets were mainly formed by aggregation of a large proportion of ices and dust from the initial presolar cloud, or whether a large proportion of these original constituents of cometary matter was further processed in the nascent Solar system and subsequent dynamical processing in the protoplanetary disc. Because they hold a large concentration of carbonaceous materials (i.e. organic matter), comets could also have played a role in the origin of life on Earth (e.g. Oró et al. 2006; Cottin et al. 2015).

This paper reviews the current knowledge on cometary dust compositions and the associated implications in terms of their formation mechanisms. Cometary dust compositions have been measured by *in situ* and remote sensing instruments in the last decades, each analysis adding pieces to the puzzle of how and where comets formed. *Giotto* analyses of comet 1P/Halley dust have shown the presence of organic particles (showing only C, H, O, N signatures), silicate particles and mixed particles (e.g. Kissel et al. 1986a). Astronomical observations showed that crystalline silicates are present in comets (Crovisier et al. 1997; Malfait et al. 1998; Wooden et al. 2004). Laboratory analyses of comet 81P/Wild 2 samples brought back by the Stardust mission suggested the existence of a continuum between asteroids and comets (e.g. Brownlee et al. 2006; Gounelle 2011). A significant proportion of interplanetary dust particles (IDPs) collected in the stratosphere by NASA, and of micrometeorites collected at the Earth surface most probably have a cometary origin (Ishii et al. 2008; Duprat et al. 2010) and constitute large and well-preserved cometary samples available for laboratory analysis.

2 THE COMPOSITION OF COMETARY DUST FROM REMOTE AND SPACE EXPERIMENTS

Remote sensing analyses of comets have shown the presence of a wide variety of volatile and more refractory compounds (Wooden et al. 2000; Bockelée-Morvan et al. 2005; Mumma & Charnley 2011). The *Giotto* and *Vega* space missions to comet 1P/Halley have shown the comet dust to be composed of silicates (crystalline and amorphous, in various proportions) and organics mixed in various proportions at a small spatial scale; the estimated size of 1P/Halley particles detected by these missions was at or below the micrometre scale (Kissel et al. 1986a,b; Kissel & Krueger 1987) (Fig. 1).

One striking result of the 1P/Halley data was the observation that the C/Mg and N/Mg elemental ratios are enriched by a factor of ∼10 and ∼8, respectively, compared to CI-type carbonaceous chondrite composition (Jessberger et al. 1988), whereas the rock-forming elements are chondritic within a factor of 2 (Fig. 2). This led to the introduction of so-called 'CHON' particles that were identified as mostly made of carbonaceous components, usually mixed with a minor abundance of rock-forming elements (Fomenkova et al. 1994).

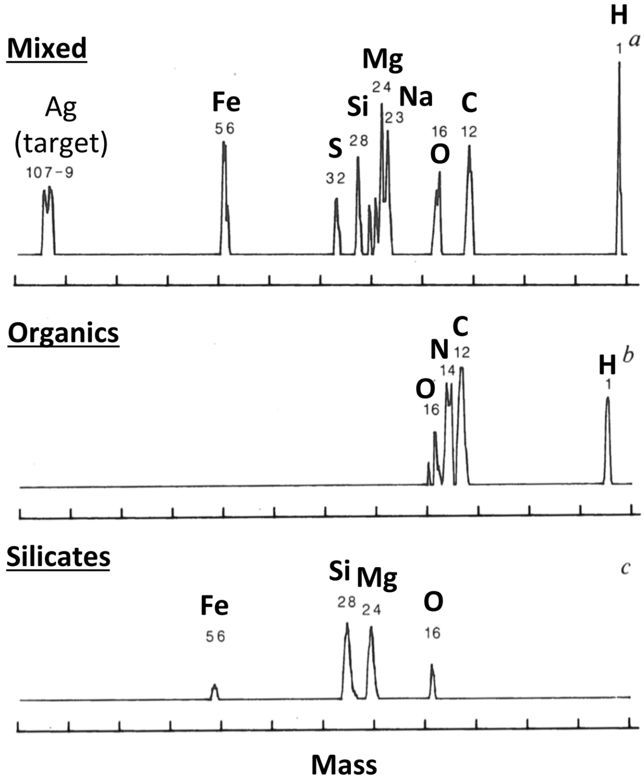

Figure 1. Typical mass spectra obtained by the PIA instrument (particle impact analyser), a mass spectrometer on the *Giotto* spacecraft (vertical log scale) (adapted from Kissel et al. 1986a). Proposed element identification has been added to the mass peaks for clarity. The mixed (a) and organics (b) types represent 80 per cent of the total number of spectra (see original article for details). Reprinted by permission from Macmillan Publishers Ltd: Nature, copyright (1986).

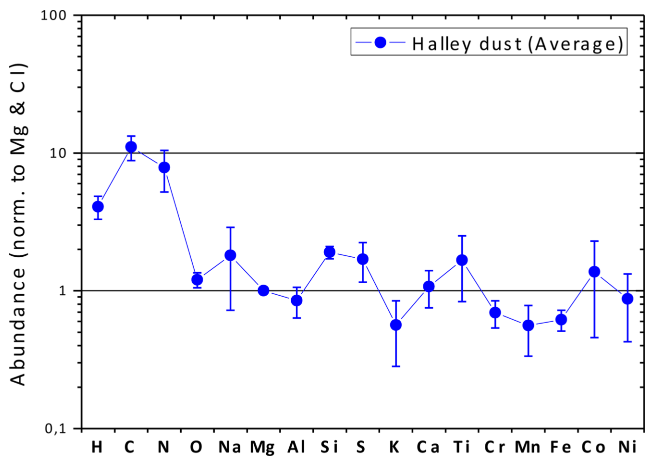

Figure 2. Average abundance of elements normalized to Mg and to CI chondrite abundances measured in comet 1P/Halley dust by the dust impact mass analyser (PUMA) on the Vega mission (Kissel et al. 1986b; Jessberger et al. 1988). CI abundances from Lodders (2010).

The Deep Impact mission excavated material from the surface of comet 9P/Tempel 1. The mid-infrared spectra of the dust ejected by the impact into the coma were interpreted as resulting from a mix of grains with compositions of amorphous carbon, amorphous pyroxene, amorphous olivine, crystalline Mg-rich olivine and crystalline pyroxenes (Harker et al. 2005; Sugita et al. 2005). The mass ratio of crystalline over amorphous silicates for submicron-sized grains is on the order of 0.3, which is a high value compared to the low abundance of crystalline silicates in the ISM (a few per cent, Kemper et al. 2005), although smaller than the values observed for Oort cloud comets C/1995 O1 (Hale-Bopp) and C/2001Q4 (NEAT), 2.1 and 2.4, respectively (Harker et al. 2004; Wooden et al. 2004).

Samples of dust particles from comet 81P/Wild 2 were returned to Earth by the Stardust mission in 2006. They were collected in aerogel with entrance velocity of 6 km s^{-1} and some of them made craters in the aluminium foils separating the aerogel tiles. Analyses of 81P/Wild 2 samples trapped in aerogel and of residues in the craters in the Al foils have shown that this comet contains mineral components similar to those found in primitive meteorites, including fragments of refractory minerals found in Ca–Al-rich inclusions (CAIs) (Zolensky et al. 2006; Simon et al. 2008; Schmitz et al. 2009), and chondrule fragments (Leroux et al. 2008a; Nakamura et al. 2008). However, during the capture process, the impacting 81P/Wild 2 dust particles were dispersed along the impact tracks and mixed with the aerogel (Leroux et al. 2008b; Stodolna et al. 2012). The mineralogy of terminal particles (at the end of the tracks) is dominated by olivine and pyroxene minerals, the number of pyroxene grains compared to that of olivine being higher ($\sim$1) than that currently observed in carbonaceous chondrites, where olivine grains dominate the silicate mineralogy (number of pyroxenes/olivines $<$0.1) (Zolensky et al. 2006; Tomeoka et al. 2008). Apart from these single minerals present at the end of the impact tracks, fine-grained particles mixed with melted aerogel have partially survived the impact and are present along the tracks, together with significant amounts of crystalline silica (Leroux 2012; Roskosz & Leroux 2015). The oxygen isotopic composition of the minerals exhibits $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios within the range observed in carbonaceous chondrites (Nakashima et al. 2012; Ogliore et al. 2015). No evidence for ^{26}Mg excess was found in the 81P/Wild 2 minerals, suggesting that short-lived ^{26}Al radionuclide was not incorporated at the time of their formation, implying a formation a few million years after the formation of the meteoritic CAIs (Ogliore et al. 2012; Nakashima et al. 2015). The abundance of isotopically anomalous presolar grains in 81P/Wild 2 is estimated to be less than 1000 ppm (Floss et al. 2013).

Only low amounts of labile and refractory organic matter have been identified in 81P/Wild 2 samples, probably as a consequence of the hypervelocity impact (De Gregorio et al. 2011; Matrajt et al. 2013). The identification of genuine cometary organic matter was also hampered by the contamination of the collecting aerogel medium by residual organic groups from the production process, and partly volatilized during Stardust particles impact (Muñoz Caro et al. 2008; Sandford et al. 2010). Glycine however was identified as indigenous to 81/Wild 2 samples, based on its non-terrestrial carbon isotopic composition (Elsila et al. 2009).

Dust particles of comet 67P/Churyumov–Gerasimenko (67P/C–G) were collected by three dust analysers onboard the *Rosetta* mission. The grain impact analyser and dust accumulator (GIADA) instrument provided both the flux and velocity measurement for particles larger than about 150 µm. The micro-imaging dust analysis system (MIDAS) instrument characterized the morphology of dust particles at the sub-micrometre level. The cometary secondary ion

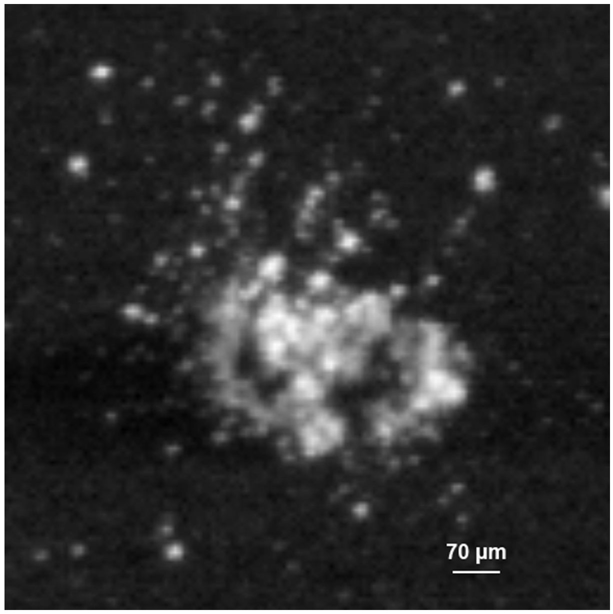

Figure 3. Optical image of dust particle Günter Jerisjarvi.1 from comet 67P/Churyumov–Gerasimenko collected by COSIMA and imaged by COSISCOPE (target 2D1). See Langevin et al. (2016) for more examples of dust particles.

mass analyser (COSIMA) instrument provided the morphology of dust particles larger than $\sim$10 µm, and measured their compositions by time of flight mass spectrometry (TOF-SIMS). Before perihelion, GIADA measured an average velocity of the particles reaching the spacecraft of 3.5 m s^{-1} (Della Corte et al. 2015; Rotundi et al. 2015). The average density of the particle measured by GIADA around the nucleus of 67P/C–G is estimated at 1.9 $\pm$ 1.1 g cm^{-3} (Rotundi et al. 2015). COSIMA was equipped with COSISCOPE, an optical microscope, to observe the morphology of the collected particles (Langevin et al. 2016). The images show that the particles were disaggregated during collection, revealing for about half of them a fluffy porous texture and low cohesive strength (Fig. 3) (Hornung et al. 2016). The MIDAS instrument has also revealed the fine-grained nature of the 67P/C–G particles at the sub-micrometre scale (Bentley et al. 2016). The flux and size distribution of the particles surrounding *Rosetta* was measured using the COSIMA images, with particles collected from 10 µm to hundreds of micrometres (and up to a millimetre for porous aggregates) (Merouane et al. 2016). The elementary composition of 67P/C–G dust particles was measured by COSIMA (Kissel et al. 2007; Krüger et al. 2015). In the early phase of the mission, the analysis of the elementary data showed that their average Na/Mg ratio is significantly higher than the CI composition (Schulz et al. 2015), and this characteristic was consistently observed until the end of the *Rosetta* mission. The bulk composition of the cometary dust particles is broadly compatible with that of micrometeorites and IDPs, although displaced towards the Fe-rich end-member in the Mg–Al–Fe ternary diagram (Fig. 4; Hilchenbach et al. 2016). This apparent Fe enrichment could be related to a high abundance of Fe sulphides. Some analyses performed on the particles are consistent with the presence of a CAI in the particles analysed by COSIMA (Paquette et al. 2016). Finally, the carbonaceous matter of 67P/C–G bears close similarity with the insoluble organic matter present in meteorites (Fray et al. 2016). Altogether, the morphology of the 67P/C–G particles as well as their compositions point towards a close relationship between the

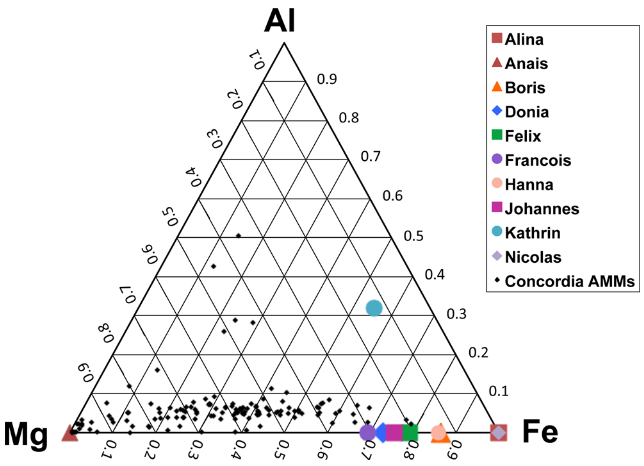

Figure 4. Mg-Al-Fe ternary diagram of the composition of 10 cometary dust particles from comet 67P/Churyumov–Gerasimenko analysed by COSIMA compared to that of 130 micrometeorites from the Concordia micrometeorite collection (data from Hilchenbach et al. 2016, Duprat et al. 2007 and unpublished data).

cometary dust and both IDPs collected in the stratosphere by NASA (IDPs) and micrometeorites recovered from polar ice caps (Hilchenbach et al. 2016; Langevin et al. 2016).

The low albedo of the surface of comet 67P/C–G measured by the *Rosetta*/visible and infrared thermal imaging spectrometer (VIRTIS) instrument can be explained by a dark refractory polyaromatic carbonaceous component mixed with opaque minerals, possibly very fine-grained Fe sulphides (Capaccioni et al. 2015; Quirico et al. 2016).

There are no direct measurement of icy dust particles ejected from a comet, and the *Deep Impact* mission (NASA) has shown that the surface of 9P/Tempel 1 was depleted in ice and enriched in carbonaceous matter over at least tens of centimetres (Kadono et al. 2007). Water ice is also rare at the surface of 67P/C–G (De Sanctis et al. 2015). The composition of the cometary volatiles provides however an indirect measurement of the composition of the ices buried in the subsurface of comets. Remote sensing observations of tens of comets have shown the richness of organic molecules in cometary comae. The composition of cometary ices deduced from cometary volatiles resembles that of interstellar ices, although second order differences also exist (e.g. Bockelée-Morvan et al. 2000; Bockelée-Morvan et al. 2005; Mumma & Charnley 2011; Boogert et al. 2015). The ROSINA gas mass spectrometer onboard *Rosetta* detected in 67P/C–G almost all the volatiles that had been previously found in comets by remote sensing (Le Roy et al. 2015). The D/H ratio of the water vapour in 67P/C–G is $(5.3 \pm 0.7) \times 10^{-4}$ (Altwegg et al. 2015), a value that expands the range of D/H values measured in cometary water vapour, now ranging from the terrestrial value ($\sim 1.5 \times 10^{-4}$) to about three times this value (i.e. ∼25 times the protosolar value) (Altwegg et al. 2015; Bockelée-Morvan et al. 2015). ROSINA data also showed that the comet ices in the nucleus of 67P/C–G are heterogeneous in composition (at least for the CO_2/H_2O ratio) (Hässig et al. 2015). The low N_2/CO ratio measured in 67P/C–G by ROSINA is interpreted as a low formation temperature of the nucleus (<30 K) (Rubin et al. 2015a). Molecular oxygen is present in 67P/C–G at an average level of $O_2/H_2O \sim 3.8$ per cent (Bieler et al. 2015). Whether this constitutes primordial molecular oxygen incorporated in the cometary ices during comet formation is debated (Dulieu, Minissale & Bockelée-Morvan 2016; Mousis et al. 2016; Taquet et al. 2016). A reanalysis of 1P/Halley data acquired by the neutral mass spectrometer during the *Giotto* mission has shown the presence of O_2 at a similar level, indicating that O_2 is probably a common and relatively abundant molecule in comets (Rubin et al. 2015b). Glycine and its precursor molecules (methylamine and ethylamine) have been detected in the gas phase of 67P/C–G (Altwegg et al. 2016). The detection of phosphorus is also reported in this paper. Although its parent molecule has not been identified, P detected in the gaseous phase likely originates from PH_3, with a tentative inferred P abundance of 1.8×10^{-4} relative to water that is close to the Solar system value of 5×10^{-4}.

3 COMPOSITION OF DUST PARTICLES OF POTENTIAL COMETARY ORIGIN COLLECTED ON EARTH

3.1 Stratospheric chondritic porous IDPs

Cosmic dust particles collected by NASA in the Earth's stratosphere (at 17–19 km altitudes) since 1981 are referred to as 'IDPs' (Brownlee 1985). IDPs are usually smaller than 50 µm, most of them being in the ∼2–15 µm size range. About 40 per cent of IDPs are chondritic porous anhydrous particles (CP-IDPs) (Fig. 5) and possibly originate from comets (e.g. Ishii et al. 2008). This class of particles was also recently found in Antarctic snow and ice collections (Duprat et al. 2007; Noguchi et al. 2015). In 2003, IDPs were also collected during a specific time period predicted to show an increase in dust flux due to particles originating from Jupiter family comet 26P/Grigg–Skjellerup (Busemann et al. 2009).

The mineralogy of CP-IDPs mostly consists of anhydrous crystalline phases such as Mg-rich olivines and pyroxenes, low-Ni Fe sulphides and sub-micrometre glassy phases called GEMS (glass with embedded metals and sulphides) (Bradley 2005). GEMS may be inherited from the presolar cloud, although this origin is still debated (Keller & Messenger 2011; Bradley 2013 and references

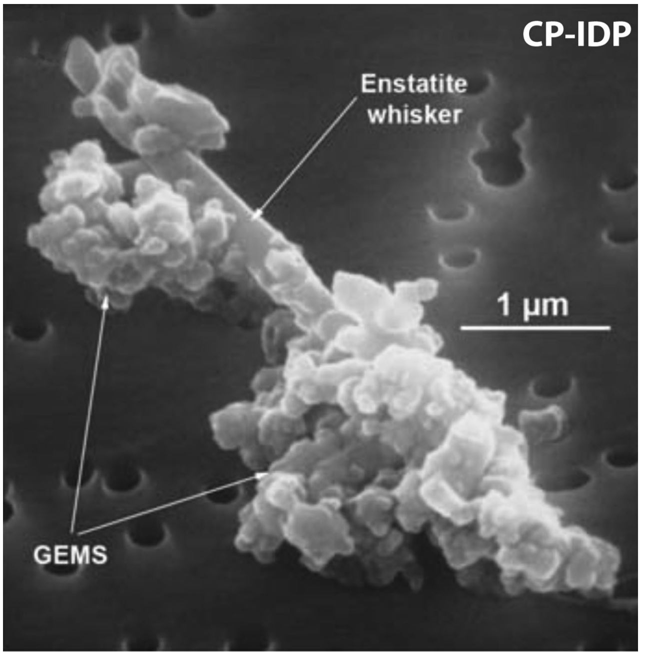

Figure 5. Secondary electron micrograph of a chondritic porous IDP of proposed cometary origin. From (Ishii et al. 2008). Reprinted with permission from AAAS.

therein). The mineralogy of CP-IDPs is usually richer in pyroxenes than that of carbonaceous chondrites. CP-IDPs show elevated carbon contents (from ∼5 to ∼45 wt%) in form of organic matter, usually exhibiting large isotopic anomalies in both their hydrogen and nitrogen isotopic compositions as compared to the terrestrial value (e.g. Keller et al. 1994; Bockelée-Morvan et al. 2015). CP-IDPs also contain large abundances of presolar silicates (from 400 to 15 000 ppm) identified by their anomalous isotopic compositions (e.g. Busemann et al. 2009 and references therein). The infrared spectroscopic signatures of minerals in CP-IDPs are broadly compatible for instance with that of comets 1P/Halley and C/1995 O1 (Hale-Bopp) (Hanner & Zolensky 2010; Brunetto et al. 2011).

3.2 Ultracarbonaceous Antarctic micrometeorites

Micrometeorites represent the dominant input of extraterrestrial matter on Earth on short time scale, with a main contribution in the 100–200 μm size range (Taylor et al. 1998). They have been collected in many places on Earth where the accretion rate of terrestrial dust is low. Since 2000, micrometeorites are recovered from snow of the central regions of Antarctica at Dome C close to the Concordia French–Italian station (Duprat et al. 2007) and the Dome Fuji station (Noguchi et al. 2006). In both Concordia and Dome Fuji micrometeorite collections, rare particles dominated by organic material and containing a minor stony component have been identified, the ultracarbonaceous Antarctic micrometeorites (UCAMMs) (Nakamura et al. 2005; Duprat et al. 2010) (Fig. 6). The high carbon contents of UCAMMs associated with minor mineral components have no counterpart in meteorite collections but are compatible with that reported for the CHON particles detected in the dust of comet 1P/Halley by the *Giotto and Vega* missions in 1986 (Lawler & Brownlee 1992). The hydrogen isotopic composition of UCAMM organic matter shows extreme deuterium enrichments (up to 30 times the terrestrial value – i.e. 300 times the protosolar value) that trace cold chemistry ($T < 50$ K), possibly in the outer regions of the protoplanetary disc, or in the presolar cloud (Duprat et al. 2010). The organic matter of UCAMMs shows the characteristics of a bulk disordered polyaromatic carbonaceous phase that is nitrogen-rich on average (with atomic N/C ratios up to 0.20) (Dobrică et al. 2011; Dartois et al. 2013). This organic matter contains (at least) two different carbonaceous phases, a smooth N-rich phase with an atomic N/C ratio up to 0.20, an N-poor 'granular' phase with a larger amount of minerals and a lower atomic N/C ratio (∼0.05) that is compatible with that of carbonaceous chondrites (Yabuta et al. 2012; Engrand et al. 2015). The UCAMM minerals range from 50 nm to several hundreds of nanometres in size (Dobrică et al. 2012). Some of them are embedded in the N-poor organic matter as small pockets of mineral aggregates or less often as isolated single mineral. Their mineralogy is mostly dominated by Mg-rich olivines and pyroxenes, Fe–Ni sulphides and GEMS. GEMS in UCAMMs have a composition similar to that of CP-IDPs, some of them however containing more Fe-sulphides and less Fe–Ni metal grains than GEMS in IDPs (Dobrică et al. 2012). Two equilibrated hypocrystalline-like objects possibly formed from a heating event of GEMS were found in UCAMMs (Dobrică et al. 2012). The pyroxene to olivine abundance ratio in UCAMMs is on average larger than 1, similar to CP-IDPs and 81P/Wild 2 samples. UCAMMs contain significant abundance of silica-rich glass. Accessory mineral phases such as Mg-Al spinel, sphalerite, niningerite, perryite and Cr-rich pyroxenes are also observed (see Dobrică et al. 2012). So far, no carbonate or phyllosilicate minerals have been found in UCAMMs. The analysis of the hydrogen and nitrogen isotopic composition of organic matter in UCAMMs from the Concordia collection does not show clear spatial correlation between the D-rich and ^{15}N-rich phases (Duprat et al. 2014; Bardin et al. 2015).

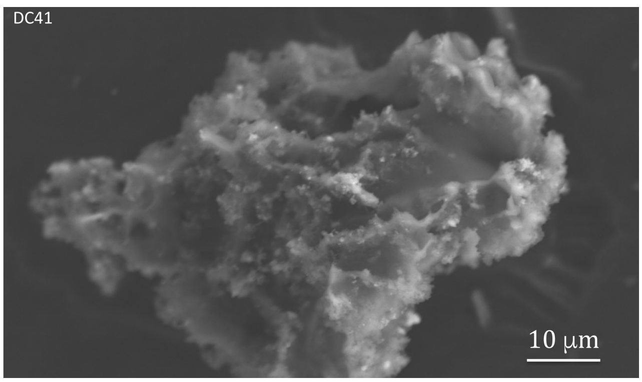

Figure 6. Secondary electron micrograph of a UCAMM of proposed cometary origin.

The precursor of the smooth N-rich organic matter can be formed by Galactic cosmic ray irradiation of N_2- and CH_4-rich ices. Such a process could have occurred at the surface of a Kuiper belt or Oort cloud icy object, beyond the nitrogen snow line (Dartois et al. 2013). Experiments at the GANIL heavy ion accelerator facility in France, simulating the effects of the Galactic cosmic ray ions, have shown the efficient production of a poly-HCN like residue showing mid-infrared signature after annealing similar to that of the UCAMM organic matter (Augé et al. 2016).

4 DISCUSSION: FORMATION OF COMETARY DUST, CONNECTION TO THE INTERSTELLAR MEDIUM (PRESOLAR DENSE CLOUD)?

Comets are among the best remnants of the matter present at the formation of the Solar system. Cometary dust was initially thought to have formed from the aggregation of dust particles directly inherited from the presolar cloud and originating from previous generations of stars (Greenberg 1998). Significant insight has been gained from the analyses of cometary dust by the *Giotto, Vega, Stardust, Deep Impact* and *Rosetta* space missions and thanks to laboratory investigation of specific classes of micrometeorites and IDPs. A substantial part of these particles, i.e. CP-IDPs and UCAMMs most probably originates from the outer regions of the protoplanetary disc, where comets formed. Cometary dust appears to be made up of ices mixed with minerals and carbonaceous phases of different origins.

4.1 Ices

The inheritance of cometary ices from the dense ISM is called into question by the comparison of the composition of volatiles from cometary ices with that of ices observed remotely in the dense phases of the ISM. Almost all the species detected in the interstellar dense phase ices are identified in cometary volatiles (Bockelée-Morvan et al. 2000; Bockelée-Morvan et al. 2005; Mumma & Charnley 2011; Boogert et al. 2015). The comparison however deserves to be made into the details of their compositions and measurement limitations. The measurement sensitivities of volatile abundances in comets often outperform the limits of remote ISM observations, and some species still cannot be compared. ISM dense phases can be separated in massive young stellar objects, low mass young stellar objects (LYSO) and background stars that are able to probe starless portions of dense clouds. The phase that should be the closest to the young Sun is the LYSO phase. The abundances relative to H_2O of all C- and N-bearing species reported in comets are generally below those of LYSOs, with some overlaps (Boogert et al. 2015). Methanol abundances are highly variable and ammonia ices appear more abundant in LYSOs than in comets. Upper limits on LYSOs abundances are on the verge to provide further constraints for the comparison (e.g. H_2S). The detection of molecular oxygen in 67P/C–G and its confirmation in 1P/Halley at the level of a few per cent relative to water ice was not expected as a component of a cometary nucleus, and its presence is interpreted as incorporation as a primordial component from the presolar cloud (Bieler et al. 2015; Rubin et al. 2015b; Taquet et al. 2016), although this is debated (Dulieu et al. 2016; Mousis et al. 2016). Unfortunately, O_2 cannot be directly probed in infrared and it can be observed remotely in ISM ices only via interactions inducing low infrared activity in the ice matrix. The derived upper limits for the abundance of O_2 ices in the ISM are then at least one order of magnitude higher than the cometary detection, making it difficult to conclude on the presence of O_2 ices in the ISM (Vandenbussche et al. 1999; Ehrenfreund & Schutte 2000).

As similar temperature ranges and physical conditions can exist in the dense phases of the ISM and in the external regions of the protoplanetary disc, it is difficult to draw a definitive conclusion that all cometary ices are directly inherited from the presolar dense cloud, although a significant proportion of them could be.

4.2 Minerals

Whether (and how much of) the mineral grains in comets have preserved their presolar compositions is still an open question. In extraterrestrial matter, presolar grains can only be unambiguously identified through large anomalies in their isotopic compositions compared with Solar system (chondritic) values. Their abundance provides a lower limit of the actual abundance of presolar grains, as isotopically normal grains might also originate from the presolar cloud, due to destruction–recondensation processes that can erase the isotopic signatures (Zhukovska et al. 2008; Frisch & Slavin 2013). Grains nowadays observed by remote sensing in the diffuse ISM are mostly amorphous with olivine- and pyroxene-like compositions (as iron-rich phases have no clear infrared signatures, their presence or absence in the ISM is debated). Their crystallinity is at most a few per cents (Kemper et al. 2005), although recent observations suggest that the degree of crystallinity of the silicates in the ISM and embedded sources could be slightly higher (Wright et al. 2016). Micron- to sub-micrometre-sized grains are efficiently amorphized by cosmic rays at ISM timescales, before the dense cloud condensation (Demyk et al. 2004; Bringa et al. 2007; Davoisne et al. 2008). The composition of dust particles originating from the contemporary local ISM can also be assessed from the Stardust and Cassini space missions (Westphal et al. 2014; Altobelli et al. 2016). At least seven interstellar dust (ISD) candidates have been identified in the Stardust interstellar dust collector (Westphal et al. 2014), and 36 particles of interstellar origin were measured *in situ* by the cosmic dust analyser (CDA) on board Cassini (Altobelli et al. 2016). The analyses of the seven Stardust ISD show compositions compatible with the presence of amorphous and crystalline silicates, and sometimes the presence of iron in reduced form [as Fe(0) in metal or Fe^{2+} in sulphides] and other minor or unidentified phases (Westphal et al. 2014). The high crystallinity of two particles in this set was unexpected, but their total mass (a few picograms) only represents a very minor fraction of what is observed by remote sensing, so it is not statistically significant and cannot be used to contradict the astronomical observations of mostly amorphous dust in the ISM. The 36 ISD analysed by CDA show the presence of magnesium-rich grains of silicate and oxide compositions, some of them with iron inclusions. The composition of these grains is compatible with CI abundances for the major rock-forming elements (Mg, Si, Fe and Ca), whereas S and C are depleted with regard to CI (Altobelli et al. 2016).

Laboratory analysis of cometary dust (81P/Wild 2 samples, CP-IDPs) shows that the isotopically anomalous mineral grains represent at most about 1 per cent in mass. In CP-IDPs, some GEMS phases show this isotopically anomalous signature, whereas others do not (Messenger 2000).

The presence of a large fraction of refractory and crystalline minerals in comets, CP-IDPs and UCAMMs demonstrate that at least a part of the minerals in cometary dust underwent high-temperature events in the inner regions of the protoplanetary disc. There is also evidence for reprocessing of olivine and pyroxene assemblages that acquired equilibrated composition by subsolidus processes in 81P/Wild 2, CP-IDPs and UCAMMs samples. Such a process most probably occurred in the inner regions of the protoplanetary disc. An efficient transport mechanism from the inner to the outer regions of the protoplanetary disc is thus required to explain the mineral composition of cometary dust. Crystalline silicates have been observed in external regions of discs around T-Tauri stars, outlining the fact that these transport mechanisms are not unique to the early Solar system (Olofsson et al. 2009). Several dynamical processes can provide such a transport to the outer regions of the disc, achieving an efficient mixing of the minerals throughout the disc (e.g. Shu et al. 1997; Bockelée-Morvan et al. 2002; Ciesla 2009; Vinković 2009). The fact that the size of the minerals in the cometary dust appears to be smaller than that in meteorites is in agreement with the transport of such small solids towards the external regions of the protoplanetary disc. A debated mineralogical gradient is observed in protoplanetary discs (e.g. van Boekel et al. 2004; Bouwman et al. 2008; Sargent et al. 2009), which has to be reconciled with the large pyroxene to olivine abundance ratio in cometary samples.

The direct presolar heritage of minerals in comets could therefore remain limited.

4.3 Organic matter

Comets are rich in organic matter, as shown by the large range of organic volatile species present in the coma. The D/H ratios of cometary molecules in the gas phase involving C- and N-bearing molecules have been measured in several comets. These D/H ratios are about one order of magnitude higher than that of cometary water, suggesting a high D/H ratio of cometary organics (Bockelée-Morvan et al. 2015). Organic matter in dust of cometary origin (CP-IDPs, UCAMMs) exhibits large D enrichments (Messenger 2000; Aleon et al. 2001; Duprat et al. 2010). Such large deuterium enrichments may be inherited from fractionation through ion–molecule reactions at low temperature (T < 50 K). In such a process, the D/H ratio of a restricted reservoir of molecules in the gas phase increases because exothermic reactions between ${H_3}^+$ and HD (the main D reservoir) form H_2D^+, ${HD_2}^+$ and ${D_3}^+$, in the absence of scavengers for the reaction such as CO (Millar et al. 1989; Roberts et al. 2004). The H_2D^+ (and ${HD_2}^+$, ${D_3}^+$) reservoir is limited in size by the cosmic D/H abundance, but may carry extreme D/H ratios for this coldest phase. Its subsequent reaction with other molecular species frozen at grain surfaces will eventually form highly deuterated molecular organic species that may subsequently get frozen on grain's surfaces (Aikawa et al. 2012; Ceccarelli et al. 2014). Deuterated species (DCO^+, DCN) have been observed in the cold mid-plane of protoplanetary discs, where the temperature is low enough (T < 30 K) and the density is high enough for CO to be frozen on grains so that deuteration exchanges can efficiently occur (e.g. van Dishoeck et al. 2003; Guilloteau et al. 2006; Öberg et al. 2012).

At least two carbonaceous phases are found in cometary matter: an N-poor and an N-rich organic matter such as that observed in UCAMMs. There is currently no consensus on the formation process of N-poor organic matter observed in extraterrestrial matter. It could either contain a component inherited from the presolar dense cloud phase (often misquoted as originating from the ISM) (Hagen et al. 1979; Pendleton & Allamandola 2002; Muñoz Caro & Schutte 2003; Sandford et al. 2016), or else being formed later in the inner protoplanetary disc and transported to the external regions to acquire its deuteration through reaction with H_2D^+ (or $HD_2{}^+$ or $D_3{}^+$) (Gourier et al. 2008; Remusat et al. 2009). The N-rich organic matter can be formed *in situ* by Galactic cosmic ray irradiation of N_2–CH_4-rich ices in the outer regions of the Solar system in a region located beyond a volatile ice (N_2, CH_4, CO) snow line (Dartois et al. 2013; Augé et al. 2016). A restricted fraction of the organic matter seen in comets may thus have been formed at the surface of icy bodies orbiting at large heliocentric distances.

ACKNOWLEDGEMENTS

This work was supported by CNES, CNRS/IN2P3, DIM-ACAV and ANR project OGRESSE (11-BS56-026-01) in France. The micrometeorite collection at the French–Italian Concordia station at Dome C in Antarctica is supported by the French Polar Institute (IPEV) and benefits from logistical support of PNRA (Italy) at Dome C. AB acknowledges support from the CNES and the Labex ESEP (N°2011-LABX-030) for its support and funding through the Idex PSL (N°ANR-10-IDEX-0001-02). COSIMA was built by a consortium led by the Max-Planck-Institut für Extraterrestrische Physik, Garching, Germany in collaboration with Laboratoire de Physique et Chimie de l'Environnement et de l'Espace, Orléans, France, Institut d'Astrophysique Spatiale, CNRS/Université Paris Sud, Orsay, France, Finnish Meteorological Institute, Helsinki, Finland, Universität Wuppertal, Wuppertal, Germany, von Hoerner und Sulger GmbH, Schwetzingen, Germany, Universität der Bundeswehr, Neubiberg, Germany, Institut für Physik, Forschungszentrum Seibersdorf, Seibersdorf, Austria, Space Research Institute, Austrian Academy of Sciences, Graz, Austria and is led by the Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany. The support of the national funding agencies of Germany (DLR, grant 50 QP 1302), France (CNES), Austria, Finland and the ESA Technical Directorate is gratefully acknowledged. We thank the *Rosetta* Science Ground Segment at ESAC, the *Rosetta* Mission Operations Centre at ESOC and the *Rosetta* Project at ESTEC for their outstanding work enabling the Science return of the *Rosetta* Mission. *Rosetta* is an ESA mission with contributions from its Member States and NASA.

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