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Rapporteur Paper on the Composition of Comets

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Abstract The ISSI workshop on "Origin and evolution of comet nuclei" had the goal to put together recent scientific findings concerning the "life" of a comet from the formation of the material in a dark molecular cloud to the accretion in the early solar system, from cometesimals to comet nuclei which were shaped and altered by cosmic rays, by radioisotopic heating, to their sublimation in the inner solar system. Astronomers, space researchers, modelers and laboratory experimentalists tried to draw the coherent picture. However, it became clear that there are still a lot of open questions, findings which seem to contradict each other, missing laboratory data, and experimental biases not taken into account. The Rosetta mission will make a big step forward in cometary science, but it will almost certainly not be able to resolve all questions. The main outcome of this workshop was the fact that comets are much more diverse than commonly thought and they are not only different from comet to comet but may consist of morphologically and chemically inhomogeneous cometesimals which may even have different places of origin.

Keywords Comets · Comet composition · Cometary evolution

1 Introduction

Comets are commonly believed to be the most pristine bodies of our solar system. Although this may well be true this doesn't mean that comets consist solely of original, unaltered material from the dark molecular cloud from which our solar system emerged. Comets and their material have been changed by the accretion shock, shaped by the solar nebula, mixed with material from the inner solar system which has experienced strong heating, and undergone processing while travelling through the inner solar system. When Oort postulated the existence of a cloud of comets surrounding the solar system (Oort 1950) it was understood for quite some time that this is where comets come from. Later, this picture was disturbed by the detection of the Kuiper belt, followed by the scattered disk (see e.g. Morbidelli and

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Valsecchi 1997). By then it was acknowledged that Jupiter family comets have their origin in the scattered disk and therefore originate from the Neptune–Pluto region whereas long period comets are from the Oort cloud and have therefore their place of birth in the Saturn–Uranus region. Such models could have been confirmed by observing compositional differences between the two comet classes, e.g. different isotopic ratios. However, so far no clear compositional differences between comets have been observed. Rather it has been observed that comets are individually chemically inhomogenous (DiSanti and Mumma 2008). Recent models show that comets can change their dynamical group quite easily (Fernandez 2007). It is therefore no longer possible to clearly distinguish the birthplace of comets either by their dynamical class or probably by there overall composition.

Comets have undergone processing by intrinsic features like radioactive isotopes and cosmic rays, but also by heating, sublimation and chemical evolution during their travel through the inner solar system. Furthermore, what we know of comets is subject to quite strong experimental biases, be it that some molecules can be observed much more easily than others or that big, new comets are accessible to many more telescopes than small, less active ones. Coma dust samples collected by the STARDUST mission have already had quite a long history before they end up in a laboratory to be analyzed and in situ measurements are restricted to very few comets which may not necessarily represent the bulk comet distribution. The ISSI workshop on "Origin and evolution of comet nuclei" had the goal to bring together experts on all stages of the "life" of a comet, from the presolar grains, the processes in the molecular clouds to the accretion in the solar nebula and the subsequent processing in the solar system.

2 Origin of Cometary Material

Comets have been accreted in the solar nebula somewhere between Jupiter and the Kuiper belt. The material itself originates from the molecular cloud from which our solar system emerged. This cloud got its material from stars and supernovae which ejected gas and dust into interstellar space. In the solar nebula material was processed by the young sun and by heating through the accretion shock. Material was flowing inwards and outwards with time. Material was subsequently altered by heat from the Sun, from radioactive isotopes or from chemical processing such as crystallization of water ice or sublimation processes. Which traces can we find in comets from which period?

2.1 How Many Presolar Grains Do We Find in Comets?

It is well established that primitive meteorites and interstellar dust particles contain small amounts of dust grains with highly anomalous isotopic compositions (Hoppe 2007). So far, a few of these grains have also been detected in comet 1P/Halley (Jessberger and Kissel 1991). The only other comet where such studies can be performed is comet 81P/Wild 2. To date, only one so-called presolar dust grain has been found among the many STARDUST grains collected. This may of course be an experimental bias. Presolar grains are very often very fragile and fluffy. They may not have survived the impact of a few km/s into the aerogel of the STARDUST dust collector (Brownlee et al. 2006). Elemental abundance measurements of Halley dust (Jessberger and Kissel 1991) show, for heavy elements, the same abundance as C1 meteorites within a factor of two. The light elements H, C, O and N are clearly overabundant in Halley dust. From STARDUST we know that the elemental abundance for refractory elements of individual grains, however, vary a lot, up to a factor of 10000

(Stephan 2007). How many of the grains survived the accretion into the solar nebula and are therefore also “presolar” grains although they may not exhibit anomalous isotopic ratios, remains to be investigated.

2.2 Traces of the Molecular Cloud in Comets

How do we recognize a dark molecular cloud origin of cometary material? Table 1 lists some of the evidence collected so far.

The strongest argument for a dark molecular cloud origin of cometary matter is probably the high deuterium content in water ($D/H = 300 \times 10^{-6}$) in comets (e.g. Balsiger et al. 1995). Water in the solar system cannot be a product of thermal (neutral) reactions occurring in the solar nebula (Robert et al. 2000; Drouart et al. 1999). According to these authors water was initially synthesized by interstellar chemistry with a high D/H ratio $\geq 720 \times 10^{-6}$ which corresponds to the highest D/H value found in meteorites (in clay minerals from LL3 chondritic meteorites). When in the solar nebula, the D/H ratio decreases via an isotopic exchange with H_2. The isotopic homogenization of the solar nebula was completed in no more than 10^6 years, reaching a D/H ratio of 88×10^{-6} (found in chondrules of LL3 chondritic meteorites). Cometary water has suffered a partial isotopic re-equilibration with H_2 before its condensation but still contains the signature of a molecular cloud origin.

Another puzzling isotopic ratio is the $^{14}N/^{15}N$ in CN in comets. Whereas this ratio is 120–160 in the CN radical it is twice as high in HCN (Schulz 2007, and references therein). This points to a different parent for at least part of the CN. So far this parent is unknown.

Table 1 Evidence for a dark molecular origin of cometary material (after Altwegg and Huntress 2001)

Observed species	Evidence for interstellar origin
H_2O	Low spin temperature (ortho/para ratio of 2.45 for water, e.g. Weaver et al. 1987 and 3.03 for NH_2, Kawakita et al. 2001)
DHO/DCN	High deuterium content in water and HCN
Carbon abundance	• Large part of the carbon is in complex organic molecules • Molecular abundance is very similar to abundance in molecular clouds and hot cores • Distribution among saturated and unsaturated species is consistent with interstellar origin. • Distribution between dust and gas is consistent with interstellar origin.
CO	• Abundance is consistent with interstellar origin and with a condensation temperature of 25–50 K.
CH_4	• Low abundance not compatible with origin in solar nebula.
CO/CH_4	High ratio compatible with interstellar origin.
H_2CO	• Abundance is compatible with interstellar origin and is higher than expected for a solar nebula origin. • Polymer as a source for formaldehyde points to an interstellar origin.
CH_3OH	Abundance not compatible with solar nebula origin.
N	Low nitrogen abundance is consistent with interstellar origin where nitrogen is most abundant in the form of N_2. The sublimation temperature of N_2 is 25 K. So it was most probably not condensed in comets or it was lost during the comet lifetime. In the solar nebula one would expect a much higher NH_3 abundance.

This parent has to have a very low $^{14}N/^{15}N$ ratio which again points to a unequilibrated chemistry and therefore to molecular cloud origin.

It is well known that dark molecular clouds and hot cores contain a large reservoir of organic molecules. The chemistry is governed by gas-phase chemistry, accretion on grains and post-evaporation gas chemistry (Rodgers and Charnley 2003). So far 230 species have been detected in space http://www.astrochemistry.net/. 50 of these species have also been detected in comets. There is a strong similarity between the abundances in young stellar objects (YSO) and comets with a few notable exceptions (Charnley and Rodgers 2008).

The physics and chemistry of low-mass star formation provides the boundary conditions for the chemical evolution of both protostellar and protoplanetary disks (e.g. Van Dishoeck and Blake 1998). It is now possible to observe in detail the organic composition of each phase prior to disk formation, a chemical sequence analogous to that which led to the protosolar nebula (Charnley 2001). The organic chemistry of protoplanetary accretion disks is of fundamental importance for understanding the composition and origin of comets and meteorities. Future theoretical models of disk fractionation chemistry will be important to highlight the differences and similarities between the molecular inventory of the natal cloud, the disk, and that detected in primitive solar system material.

2.3 Processing and Mixing of Cometary Material in the Solar Nebula

Elemental abundance measurements for dust captured by STARDUST at comet 81P/Wild 2 show an almost solar abundance of elements which have not a high volatility (Stephan 2007), at least if averaged over a lot of dust grains. The author draws the conclusion that the early solar system did not show a large-scale element fractionation. Individual grains, however, show quite a large diversity in elemental abundance. Furthermore CAIs (Ca, Al-rich inclusions) have been identified in the STARDUST sample which are attributed to high temperature phases and therefore to coming from the innermost solar system. This points to a strong mixing of at least some of the material in the early solar system, but contradicts for example the high deuterium content in cometary water. Another, possibility for the existence of CAIs far out in the solar system is given by Shu et al. (2001). Ordinary CAIs and chondrules might have formed by flare heating of primitive rocks interior to the inner edge of a gaseous accretion disk that has been truncated by magnetized funnel flow onto the central proto-Sun. The evaporation of the moderately volatile mantles above large refractory cores, or the dissolving of small refractory cores inside thick ferromagnesian mantles before launch, plus extended heating in the X-wind produce the CAIs or chondrules that end up at planetary distances in the parent bodies of chondritic meteorites or comets. The physical addition of the hot rock components into a reservoir of cool rock and unequilibrated volatile components results from the action of the X-wind.

A puzzling aspect of cometary composition is the parallel existence of crystalline and amorphous silicates. ISM's (interstellar material) and molecular cloud cores contain about 1.1% crystalline silicates compared to amorphous silicates (Kemper et al. 2005), which are in the form of amorphous Mg–Fe silicates. Comets on the other hand show distinct features of crystalline silicates. Silicates in comets appear to be a mix of high-temperature crystalline enstatite and forsterite plus glassy or amorphous grains that formed at lower temperatures (Hanner 1999). The mineral identifications from the 10 and 20 μm cometary spectra are consistent with the composition of anhydrous chondritic aggregate IDPs (interplanetary dust particles) (Wooden 2008). The origin of the cometary silicates remains puzzling. If they formed in the inner solar nebula, then their presence in comets requires significant mixing in the solar nebula. If they are circumstellar in origin, one has to explain why their spectral features are not visible in interstellar dust. Oort cloud comets seem to contain a much higher abundance of crystalline silicates than Jupiter family comets' (crystalline/crystalline+amorphous = 0.7 vs. 0.3). Furthermore, the observed crystalline feature in comets varies with heliocentric distance and with jet activity. In 9P/Temple 1 there was no crystalline feature observable before the impact of the Deep Impact probe. Shortly after the impact a clear crystalline signature could be observed which later on disappeared again (Wooden 2008). Crystals therefore seem to originate from below the mantle of comets and are not uniformly distributed in cometary nuclei. This could be at least partly due to an observational bias because of the grain size distribution as the grains lifted by the impact and probably also in jets are smaller than the undisturbed grain size distribution observed in relatively inactive comets.

2.4 The Last 4.5 Gy

Once cometesimals have formed their material can be altered by many processes. It is quite obvious from the four different comet nuclei observed so far at close distances that the morphological diversity among comets is large (A'Hearn 2008; Basilevsky and Keller 2006).

The first steps in the life of a comet after the condensation of its material were the accumulation from small dust and icy grains into cometesimals and finally into comets. It is not clear if the region where cometesimals formed is identical to the region where finally the comet formed.

9P/Temple 1 points to a very gentle accumulation of small cometesimals into a comet nucleus (A'Hearn 2008). Other scenarios also include cometary nuclei which are the result of collisions of bigger parent bodies (Fernandez 2007). It is entirely possible that the compositional and structural differences between comets and even within comets are quite large: from very low density, fluffy, porous objects with very low tensile strength to much more compact objects. The origin of the individual cometesimals forming a comet may have been at quite different locations in the solar nebula and may thus reflect samples of a radially inhomogenous disk.

Once comets have formed they are subject to heating by incorporated radioactive material which may even have led to liquid water in the interior of large (>10 km) comets (Prialnik et al. 2008). Their surfaces are changed by cosmic rays and, once inside the Jupiter orbit, also by solar UV. So far, little is known about their initial state and each model which describes their evolution faces the problem of selecting the "right" initial structure (e.g. rubble pile, capillary tubes, aggregation of grains).

One of the big, still open questions is the nature of the surface layer of a comet. Sublimation of a comet in the inner solar system is rapid. Balancing energy input and latent heat, rates of 10^{22} molecules $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$ are typical, leading to depth loss rates of 1 cm per few hours (Thomas et al. 2008). The thermal inertia of the uppermost layer is extremely low (Groussin et al. 2007). The thermal skin depth is of the order of 2 cm. Sub-surface chemical heterogeneity cannot be ruled out. That means that the surface must be disrupted every few hours to maintain the observed constancy/repeatability of emission (e.g. the emission of 1P/Halley observed by HMC (Halley Multicolor Camera) was constant to 1% over 3 hours). The surface layer must therefore have the following qualities (Thomas et al. 2008; A'Hearn 2008):

- Surface layer thickness: $\sim$cm at most
- Very good insulation properties
- But, sub-surface sublimation must be occurring to explain the limited surface area coverage of water ice seen by Deep Impact (Sunshine et al. 2006). The depth below the surface of sublimation is therefore limited to a few centimetres at most.

- Sublimation from a sub-surface layer below 1 thermal skin depth cannot match cometary production rates.

The observed inhomogeneity in comets gives an enormous number of additional free parameters for thermo-physical modelling. This implies that, at the present time, our knowledge is so limited that essentially any realistic structure can be produced by using the correct mix of input parameters (Thomas et al. 2008). Laboratory experiments on amorphous ice (Bar-Nun et al. 2008) agree quite well with Deep Impact data (A'Hearn 2008; A'Hearn et al. 2005). Both result in an extremely low tensile strength of a few hundred Pa. On the other hand, the tensile strength could also be much bigger, up to 12 kPa (Holsapple and Housen 2007) for 9P/Temple 1 and the measurements done on amorphous ice in the lab suffer from the unknown influence of gravity.

The nature of the insulation layer is not yet understood. It is an open question if indeed, as has been postulated after the Halley encounter, the material on top of a comet could contain Polyoxymethylene (POM) (Huebner et al. 1987). Laboratory measurements show that the extended formaldehyde source (Eberhardt 1999) at comet Halley would be compatible with POM's (Cottin 2008), but this is clearly not a proof for a surface layer consisting of POM's.

3 Experimental Biases

What we know of comets is limited and is subject to many significant observational biases, e.g.:

- Not all molecules can be detected by remote sensing
- Bright comets can more easily be observed than faint comets
- STARDUST samples may be contaminated by the impact (e.g. Spencer and Zare 2007), they have already a history of heating before they are captured (what we see is only what is left over), it is unclear which part of the nucleus they represent.
- Spectrophotometric observations depend heavily on models
- The coma of a comet is not fully representative of the nucleus
- In situ measurements are limited to very few comets which may have a very different origin in the solar nebula and a very different history since.
- Models, especially nucleus models suffer from an unknown initial state and too many free parameters.

These shortcomings have to be balanced by a strong interdisciplinary community effort including e.g.:

- Studies of mineralogy and organic volatility versus heliocentric distance r_h in select Jupiter family and Oort Cloud comets (amorphous vs. crystalline ice)
- Measure thermal conductivity of porous material in the lab (restrict evolution models)
- Look for the extended CN source and for possible parents of the anomalous $C^{14}N/C^{15}N$ in comets with lab experiments
- Revisit data used for analyzing spectroscopic measurements
- Measure changes of surface during one comet orbit!
- Look for "interstellar" molecules in comets (there are more than 1000 unidentified lines waiting for a patient researcher to be identified!). Look for molecules detected in cometary analogues.

New instrumentation for remote sensing on the Earth and space like e.g. ALMA and JWST (James Webb Space Telescope) will help to overcome some of the experimental biases.

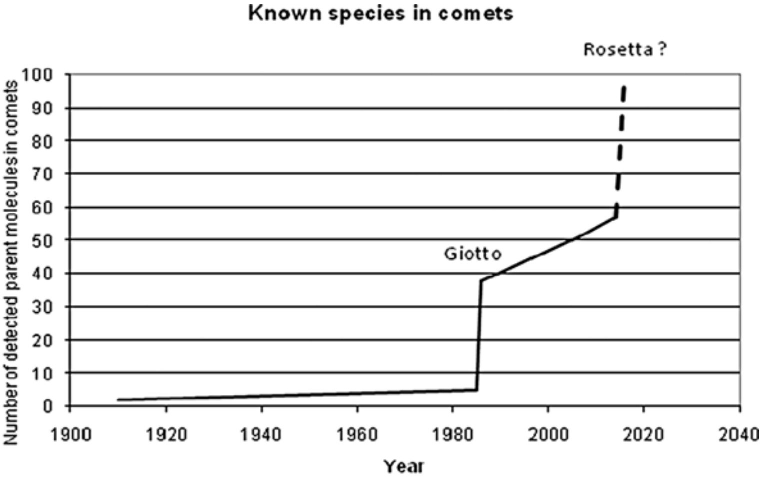

Fig. 1 Number of detected parent molecules in comets as a function of time

4 What Answers Can We Expect from Rosetta

The European spacecraft Rosetta on its way to comet 67P/Churyumov-Gerasimenko will for the first time study a Jupiter family comet in situ over almost a full orbit (Glassmeier et al. 2007). This spacecraft is well equipped with instruments to study the composition of the comet. Spectrometers from the UV to the microwave region will cover the lines of many molecules and minerals. Mass spectrometers will be able to detect molecules, isotopes and elements with very high mass ranges and mass resolutions of the volatiles as well as in the dust particles (Gulkis and Alexander 2008). Figure 1 shows the evolution of detected parent molecules in comets so far. It is evident that already the Giotto mission to comet 1P/Halley was extremely successful in identifying parent molecules as well as elemental and isotopic abundances in a comet. Rosetta's capabilities are far superior. With the Rosetta lander we hope to get "ground truth" for the first time. All measurements so far on composition have been made in the coma, or as in the case of STARDUST, on particles which have spent quite some time in the coma and which have furthermore been altered by the impact. The Rosetta lander will sample the nucleus material directly Of course also the lander has its limits. It will sample only one very small portion of the nucleus. It will sample material only from the nucleus surface or very close to it. But together with the measurements in the coma it will at least help to unravel the mystery of the comet surface layer and the near subsurface composition.

5 Open Questions

The ISSI workshop on "Origin and evolution of comet nuclei" made it very clear that there are plenty of open questions in cometary science. Some of them will be answered by Rosetta or by forthcoming remote sensing, but there will remain quite a few for future generations of cometary scientists. Below is a list of open questions. This list is not complete by far and it is clear that the list will even get longer, once Rosetta reaches its goal.

- Inhomogeneity of nuclei (between nuclei and in one single nucleus)

Table 2 Most important molecules detected in young stellar objects (YSO) and comets. In bold are the few species where there is a discrepancy between the abundances in YSO's and comets

	High-mass YSO	Low-mass YSO	Comets
H_2O	100	100	100
CO	1–20	1–60	5–20
CO_2	~20	15–40	2–10
CH_4	1–4	–	0.2–1.2
CH_3OH	1–35	**1–30**	**0.3–2**
H_2CO	3	–	0.2–1
OCS	**0.05–0.18**	**<0.08**	**0.5**
NH_3	<5	–	0.6–1.8
C_2H_6	<0.4	–	0-4–1.2
HCOOH	**3**	**9**	**0.05**
O_2	<20	–	0.5, upper limit
N_2	?	?	?
XCN	0.3–2.9	–	–
HCN	<3	–	0.2

- N_2 and CO have the same vapor pressure, but only CO is condensed
- $^{15}N/^{14}N$ ratio in HCN and CN differ by a factor of 2. What is the parent of CN?
- What is the parent of the extended CN emission?
- Silicates: where do the crystals come from (transport / annealing)
- Why are the crystalline and the amorphous silicates unevenly distributed in comets
- GEMS: Why are they sub-chondritic in composition (S, Mg, Ca, Fe compared to Si) (large flux of solar cosmic rays?)
- Evolution of nuclei
  - Surface layer:
    - Thickness
    - Composition
  - Dust emission
  - Porosity
  - Thermal conductivity
- What part of the nucleus is represented in the coma?
- Why is the dust production of comets stable over very long times?
- The dust ejection mechanism remains a subject of speculation
- What is the mass of a comet (depends on models) and with it what is the density, the porosity and the gravitation?
- What is the dust/ice ratio in comets?
- Etc., etc.

6 Conclusions

During the ISSI workshop on "Origin and evolution of comet nuclei" the life of a comet from the origin of the cometary material through the accretion of cometesimals in the solar nebula and to the evolution during its stay in the inner solar system was analyzed. Comets show a much bigger variety of morphological structures than previously assumed. However, their overall composition so far shows not much diversity, even when comparing Oort cloud with Jupiter family comets. It became evident that a comet can be quite inhomogenous by itself, at least from a morphological point of view. It remains to be investigated if comets also show a chemical inhomogeneity inside their nuclei. STARDUST results point to a good mixing of solar nebula material while isotopic ratios of water and CN point to unaltered molecular cloud material. One of the most puzzling aspects is the surface layer of comets which has to be an extremely good thermal insulator while at the same time allowing outgassing from subsurface layers. It is still not clear if a comet surface is “hard” or very “fluffy”. This question has to be solved by the Rosetta lander, at least for one comet Another unsolved mystery is the amorphous versus crystalline silicates found in comets. There remain plenty of open questions; some of them will be addressed by Rosetta whereas others will only be solved by future interdisciplinary community efforts in remote sensing, experimental laboratory work, models and in situ analyses.

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