8 Comets: Potential Sources of Prebiotic Molecules for the Early Earth

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“Of Ice and Men. . .”

Why should we be interested in comets when studying the origin of life on Earth? First, comets are rich in water and carbon, two essential constituents of terrestrial life; part of Earth’s water and carbon might be of cometary origin. But comets might also have brought Earth one step further on the way to the emergence of life.

Early last century, Chamberlin and Chamberlin proposed that infalling carbonaceous chondrite meteorites could have been an important source of terrestrial organic compounds (Chamberlin and Chamberlin 1908). Oró was the first in 1961 to propose from observations of carbon- and nitrogen-containing radicals in cometary comae that comets may have played a similar role (Oró 1961):

“I suggest that one of the important consequences of the interactions of comets with the Earth would be the accumulation on our planet of relatively large amounts of carbon compounds which are known to be transformed spontaneously into amino acids, purines and other biochemical compounds.”

It is now quite obvious, from observations and laboratory experiments, that comets are important reservoirs of a wide variety of organic compounds.

Comets will be considered in this chapter mainly as potential reservoirs of carbon and organic molecules for the early Earth. We present first their general characteristics, then the chemical composition of cometary matter as deduced from observations and constrained by laboratory experiments, the origin and evolution of this matter – and of comets themselves – the various cometary contributions to the early Earth, and the main future of ground-based and space developments for comet science. We conclude with a list of important questions for which answers should and will be sought in the forthcoming years.

The book “Comets and the Origin and Evolution of Life”, edited by Thomas et al. (1997), is a basic reference on the topic. Comets have been discussed as possible sources of prebiotic molecules by Delsemme (2000), Greenberg (e.g. 1982, 1993, 1998) and Chyba and Sagan (1997). Despois et al. (2002) and Crovisier (2004) have discussed recently the observed molecular content of comets in this perspective, while Whittet (1997) and Ehrenfreund et al. (2002) relate more generally astrochemistry to the origin of Life. Recent general reviews on cometary

science are Irvine et al. (2000), Festou et al. (1993a,b), and Bockelée-Morvan et al. (2004); the book *Comets II* (in press) edited by Festou, Keller and Weaver will present up-to-date information on many aspects of comets. In this book, Petit and Morbidelli (2004) survey the Solar System formation, and discuss the origin of water on Earth. Chapters of the French edition of this book (Gargaud et al., 2001, 2003), not included in this English edition, also contain much information on related topics only briefly alluded to here: build up and evolution of the Earth atmosphere (Marty; Selsis and Parisot), build up of the hydrosphere and D/H ratio (Robert), micrometeorites (Maurette). Recent related papers in English are Kasting (1993, 2003), Dauphas et al. (2000), Robert (2002), and Maurette (1998, 2000).

8.1 General Description of Comets

“Comets are small bodies of the Solar System, made of a mixture of ices and dust.”

8.1.1 The Cometary Nucleus

The definition above describes in fact a specific part of comets, the cometary nucleus. Comets are most of the time far from the Sun and reduced to this nucleus, a solid body named a “dirty ice snow-ball” by Whipple (1950); it is only when comets get close enough to the Sun (less than a few UA) that they develop their other more spectacular and better known components – coma and tail – described below. Comet 1P/Halley¹ is the first of the only three comets whose nuclei have been closely observed by a space probe (the other two are 19P/Borrelly, observed from 3400km by the Deep Space 1 spacecraft in September 2001, and P/Wild 2 observed by the Stardust spacecraft from 236km in January 2004). In 1986, several probes were sent to observe comet Halley, among which the European Space Agency probe “Giotto” passed within approximately 500km from the comet nucleus. The pictures taken by Giotto (Fig. 8.1) revealed an irregular-shaped body $8 \times 8 \times 16$ km by size, whose volume is roughly equivalent to a sphere of 10km in diameter (see Newburn et al., 1991). The bright comet C/1996 B2 Hyakutake, which appeared in 1996 and passed rather close to the Earth (~ 0.1 AU), had a relatively small nucleus, about 3km in diameter. Another comet, C1995 O1/Hale–Bopp, was detected for the first time during summer 1995 and became quite visible in spring 1997; although passing ten times further from the Earth, it has been more spectacular than Hyakutake due to its much larger diameter, approximately 45km (see Weaver and Lamy 1999).

¹ 1P/Halley is the official complete name of the comet, according to the International Astronomical Union – see ref. CBAT for a description of the naming rules; the familiar names (e.g. “comet Halley”) are also used in this chapter and should be considered as abbreviations.

Fig. 8.1. (a) The nucleus of comet Halley, as seen by the ESA probe Giotto in 1986. (© ESA and MPIfA) (b) the nucleus of comet P/Borrelly observed by NASA probe Deep Space 1 in 2001 (© NASA) (c) the nucleus of comet P/Wild 2 recently observed (Jan. 2004) with a resolution of 20m by Stardust, the NASA probe that will return dust samples collected during the flyby (© NASA)

The density of cometary nuclei is difficult to measure precisely: some estimates are as low as 0.2g/cm^3 or as high as 1.8g/cm^3 . However, most values are in the range $0.5\text{--}0.9\text{g/cm}^3$ (e.g. Ball et al., 2001). This is lower than the density of water ice, and would confirm the image of the “dirty snowball”. Using this density, the mass of comet Halley is about 10^{18}g (1000 billion tonnes).

The cohesion of cometary nuclei is low at least in some cases, as shown by comet D/1993 F2 Shoemaker-Levy 9: when the comet passed near Jupiter, the tidal forces let the nucleus split up into a swarm of more than 20 major pieces, which later crashed onto the planet (see Noll et al., 1996). The fact

that cometary nuclei have irregular shapes shows that these bodies were never molten – otherwise they would be shaped according to the equilibrium figure of a liquid body: a sphere or, if the body rotates, an ellipsoid.

What are the ices and dust mentioned in the definition of a comet made of? Cometary ices are water ice mostly, mixed with smaller quantities of other species like methanol (CH_3OH), CO , CO_2 , ... – the detailed composition is given below (Sect. 8.2.1 and Table 8.1). As for the dust grains, they are made of small particles of carbon, organic matter or silicates. The total mass of dust is roughly comparable to the mass of ices, within a factor of 10: some comets are “dusty”, while other are “gaseous” (e.g. Rolfe and Battrick, 1987). Despite the presence of a large amount of ice inside the nucleus, the surface itself appears quite dark: for comet Halley, the proportion of reflected light (called *albedo*) is only 4%.

8.1.2 Comet Motion

Comets move around the Sun following orbits that are in most cases ellipses (the Sun being at one focus); in some cases the orbit may be parabolic or slightly hyperbolic (e.g. Festou et al., 1993a). The eccentricity is generally high, and often near 1 (parabola) or even slightly higher (hyperbola). For comparison, the eccentricity of a circle is zero, and that of the quasicircular orbit of the Earth is 0.017 (at present). The comet speed in the region of the Earth’s orbit (i.e. at one AU from the Sun) is about 45 km/s (or 162 000 km/h). Combining (vectorially) this speed with Earth’s own motion around the Sun (~ 30 km/s) leads to relative speeds ranging between 15 and 75 km/s. This confers a large kinetic energy to cometary particles entering the Earth’s atmosphere and leads to dramatic effects when the nucleus itself impacts the Earth.

Comets are classified into various families according to their orbits. Long-period comets are defined as having an orbital period above 200 years. Among the long-period comets, one commonly calls “new comets” those for which aphelion (point of the trajectory furthest away from the Sun) is located beyond approximately 1000 AU and for which eccentricity is close to 1. This is not an official, well-defined, comet category; as these comets have periods above 10 000 years (and up to tens of Myr), no historical record of previous passages exists, and they appear “new” to us. Their orbits are very elongated ellipses, which, when they pass close to the Sun, look very much like parabolas. Comets with periods below 200 years are called short-period comets. Among those, one finds the *Halley family*, with periods from 20 to 200 years, and random inclinations of their orbital plane with respect to the ecliptic, and the *Jupiter family*, with periods of approximately 6 years, and small inclinations to the ecliptic.

8.1.3 Comet Reservoirs: Oort Cloud and Kuiper Belt

To explain the present number of observed comets (despite the rapid sublimation of the ice (see Sect. 8.1.5) and the origin of the various orbital families, the existence of two comet reservoirs is required.

The classical or *outer Oort cloud* (Oort, 1950) is a spherical reservoir situated between $\sim 20\,000$ and $100\,000$ AU; the inner radius is loosely defined (see below), whereas the outer radius corresponds to half the distance to the nearest stars, beyond which an object can no longer be considered gravitationally linked to the Sun. Oort Cloud comets are thought to be icy planetesimals scattered by the giant planets, originating mostly from the Uranus–Neptune zone and to a lesser extent from the Jupiter–Saturn zone.

Due to stellar encounters, or to the effect of the gravitational potential of the Galaxy, some of these objects are regularly sent back towards the planet zone with nearly parabolic orbits (“new” comets). The possible quantitative importance of a more tightly bound *inner Oort cloud* ($3000\text{--}20\,000$ AU), has been recently underlined (Fernandez, 1997, Levison et al. 2001) considering the very probable option that the Solar System and its Oort cloud formed in the dense stellar environment of a young open star cluster. Formation scenarios of the Oort cloud (e.g. Duncan et al., 1987) are still very uncertain, at least quantitatively. The total number of comets in the Oort cloud could be on the order of $10^{12}\text{--}10^{14}$ depending on the model and the size distribution, while the total mass estimate ranges from 1 to $250\,M_{\text{Earth}}$.

While the Oort cloud hypothesis explains quite well the long-period comet distribution, numerical simulations (Fernandez 1980) have stressed the importance of another reservoir, the *Kuiper Belt*, to explain the number of short-period comets. The existence of this belt was proposed first by Leonard (1930) and Edgeworth (1943), (the history of the concept, including the Kuiper (1950) paper and the later role of Cameron and Whipple, is discussed in Green 1999). The region has the shape of a thick torus and contains many small icy bodies beyond the orbit of Neptune. Since the discovery of the first Kuiper Belt object (KBO) by Jewitt and Luu in 1992, much observational and theoretical work has been undertaken (see Morbidelli and Brown (2004), Jewitt (2002) and de Bergh (2004) for recent reviews on the dynamical and physical properties of KBOs). Collisions in the Kuiper belt are thought to produce fragments, which are later scattered by Neptune and the other planets towards the inner Solar System, first as Centaurs, then as Jupiter Family comets. From the ~ 800 objects now observed (summer 2003) a total population of $70\,000$ bodies larger than 100 km in diameter is estimated, and 1 to 10 billion bodies larger than 1 km . Several families, with probably different origin, are recognized in the Kuiper Belt (see Morbidelli and Brown 2002 and Jewitt 2002 for details). A subpopulation, the plutinos, is in a collision-avoiding resonant orbit with Neptune, and encompasses Pluto itself (and its satellite Charon). Pluto is considered as the largest KBO (with $D \sim 2500\text{ km}$), and several other large objects are known (Quaoar, $D \sim 1300\text{ km}$; Charon, $D \sim 1200\text{ km}$; Varuna, $D \sim 900\text{ km}$).

The formation of these reservoirs has been accompanied by substantial scattering of comets towards the zone of the terrestrial planets; these comets possibly supply carbon and organics to their surfaces (see Sect. 8.5) but probably make only a limited contribution to Earth’s water (see Chap. 2, Part I by Petit and

Morbidelli). The composition of the comets coming from the two reservoirs is expected to differ more or less strongly according to the various formation models. Understanding the formation scenario of comets is vital for any considerations on the ubiquity (or scarcity) of terrestrial planets favourable to life development elsewhere in the Universe.

8.1.4 The Active Comet

When a comet approaches the Sun, it enters the active phase. A coma develops around the nucleus, which consists of a roughly spherical halo of neutral gas and dust particles. The radius of the coma depends on the chemical species, and ranges between less than a thousand to more than one million km (e.g. Crovisier and Encrenaz, 2000) (Fig. 8.2). What we call here “radius” is indeed a characteristic length describing the progressive decrease of the spatial density of particles. Beyond this coma, an atomic hydrogen cloud is produced by the photodissociation of a number of species, mainly H_2O and OH ; this cloud can reach 1 to 10 million km. Starting from the nucleus and the coma, three types of cometary tails develop: a plasma tail, a dust tail, and a tail of neutral sodium

Fig. 8.2. Schematic view of an active comet. The Sun is (approximately) in the direction opposite to the ion tail, whose shape is due to the interaction with the rapid (~ 400 – 800 km/s) charged particles of the solar wind. The dust particles that were previously released from the nucleus are slowly pushed away by the pressure of the solar photons, which, combined with the comet motion (here toward the left) explains the shape of the dust tail (see e.g. Festou et al., 1993b)

atoms – the latter clearly seen recently in observations of comet Hale–Bopp (Cremonese et al., 1997).

The plasma tail is made of (atomic and molecular) ions and electrons. It has a characteristic blue colour due to the CO^+ ions, a very rectilinear shape and is almost perfectly opposed to the Sun's direction. It is produced by the interaction of the solar wind – itself made of protons and charged particles – with the ions produced in the coma (Fig. 8.3). The yellow-white dust tail consists of small grains that have typically a diameter between 1 and 10 micrometres, and that reflect and scatter the light of the Sun. Its shape depends on the balance between the gravitational force from the Sun, and the radiation pressure due the photons of the solar radiation.

An antitail is seen in some comets, looking like a narwhal tusk pointing toward a direction opposite to the other tails. It is in fact always present, but not always visible. It reveals the presence of an accumulation of particles in the orbital plane of the comet. These particles are larger than those of the normal dust tail, and have thus been ejected at low speed from the cometary nucleus (they are less easily lifted by the gas flow) and are less sensitive to solar-radiation pressure (their mass/surface ratio is larger). By a projection effect, these particles appear as a spike at the head of the comet, when the Earth happens to cross the comet orbital plane. This feature usually appears only on the Sun side, but

Fig. 8.3. Image of a comet with well-developed tails (Hale–Bopp). The plasma tail (thin, rectilinear and bluish) is clearly recognized from the dust tail (diffuse, curved and white-yellow). (© Photo R. Lauqué)

Fig. 8.4. Brownlee particle (interplanetary dust collected in the stratosphere). For the fluffiest of these particles, the origin is probably cometary

can sometimes also be distinguished as a thin line in the antisolar direction, superposed to the normal dust tail. The “neck-line” recently observed on comet P/Churyumov-Gerasimenko is an antitail (Weiler et al., 2004).

Cometary dust particles disperse more or less rapidly into the interplanetary space, according to their shape, nature and initial velocity. Some of them cross the path of the Earth; if large enough they produce meteors. One can get an idea of cometary dust particles by looking at particles collected in the Earth stratosphere (“Brownlee particles”, or stratospheric interplanetary dust particles – SIDP). Many of these particles have a large surface to mass ratio and a very irregular, and somewhat fractal-like structure (Fig. 8.4). All collected particles are, however, not as irregular: one finds also among SIDPs more compact particles, similar to small blocks of clay. It is tempting – but perhaps too simplistic – to attribute to the most irregular particles a cometary origin, whereas the most compact ones would come from asteroids.

The third cometary tail, the sodium tail, made of neutral sodium atoms, was discovered for the first time in the Great Comet C/1910 A1, and reobserved more recently in comets C/1957 P1 (Mrkos) and Hale–Bopp. Sodium is pushed away in the antisolar direction by the radiation pressure, in a way similar to what happens for dust particles.

8.1.5 Gas and Dust Production

The weakest H_2O production rates currently detected in comets are of 10^{26} molecules/s (3 kg/s) when the comet is favourably situated. In comet Hale–Bopp

at perihelion, the production rate reached up to 10^{31} molecules/s, which corresponds to 300 tons/s. These rates imply that a bright comet typically loses a 1-m thick sheet at each perihelion passage. Thus for a nucleus of about a few tens km in diameter, one expects the comet to disappear after a few thousand passages close to the Sun. This implies that today short-period comets ($P < 200$ yr) cannot have occupied their present orbit since the beginning of the Solar System.

The expansion speed of most molecules in the coma is about 1 km/s. Photodissociation reactions take place, for example $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$, followed by $\text{OH} \rightarrow \text{O} + \text{H}$. For the photodissociation fragments, the speeds can reach several km/s (8 and 21 km/s in the case of H produced from H_2O). The matter ejected by comets is almost equally distributed in mass between volatiles (mainly H_2O) and dust – within a factor 10. It is possible that the dispersion of the gas/dust ratio between comets represents a variation in the initial composition of the cometary nucleus; alternatively, it can also be an effect of evolution after many passages close to the Sun.

The dark surface observed on comet Halley’s nucleus may consist of an accumulation of dust, and/or of complex refractory organic molecules. This crust may be broken by the explosion of gas pockets heated under the crust: this would enrich the coma in dust particles, and appear as an outburst of the comet.

8.1.6 Remote Activity, Outbursts and Split Comets

The activity of comets strongly depends on the distance to the Sun. It has long been thought that cometary activity developed only when the comet was closer than 4 AU from the Sun, because the “dirty snow ball” model of the nucleus suggested that water, the major volatile, controlled the emission of other molecules and of solid particles. The sublimation of H_2O ice is important only at heliocentric distances smaller than 4 AU and drives the coma development for such distances. However, a preperihelion cometary activity was detected in comet Hale–Bopp as far as 7 AU from the Sun. This activity has been attributed to the sublimation of carbon monoxide. CO is indeed present in large quantities with respect to H_2O , from 5% to above 20% – depending on the authors, the measurement techniques and the circumstances (type of comet, distance to the Sun). CO outgassing can, by a process similar to H_2O outgassing, lift dust particles and create a coma (Bockelée-Morvan and Rickman, 1999). After its passage at perihelion, comet Hale–Bopp was still outgassing CO as far as 14 AU.

Cometary matter is usually divided into two components: “refractories” and “volatiles”; the word “refractories” applies to species that do not sublimate. This classification is sometimes refined, introducing “hypervolatiles” (Ar, N_2 , ...), and “semirefractories” (e.g. organic refractories, as opposed to more refractory species like silicates). Note here that water, traditionally ranking as the major volatile species in comets, behaves at 7 AU like a refractory.

A peculiar comet, 29P/Schwassmann-Wachmann 1, which follows an almost circular orbit at 6 AU from the Sun (i.e. somewhat beyond Jupiter), harbours intense and unpredictable outbursts; here also, CO is at the origin of this activity. Comet Halley showed an activity outburst after its perihelion passage, when it was already 14 AU from the Sun. Because of the lack of spectroscopic information, one does not know for sure if this outburst was also due to CO; on the pictures, only the development of a coma was noticed.

Breakup of cometary nuclei (see Boehnhardt 2002) is not uncommon. Some comets break into a few pieces (C/1975 v1 West), some into many pieces (57P/du Toit-Neujmin-Delporte in 2002), some even vanish (C/1999 S4 LINEAR). 90% of the Sun-grazing comets observed by the SOHO satellite belong to same orbital family: Kreutz family (Lamy and Biesecker 2002). They may have their origin in the splitting of one large comet. Depending on their size, the fragments have a lifetime between hours and years. The rate of splitting events of periodic comets has been evaluated to 0.01/yr/comet (Chen and Jewitt 1994). This makes splitting an important mass-loss factor, comparable to ordinary activity, and an important cause of comet death. While tidal forces close to Jupiter were clearly responsible for the breakup of Shoemaker-Levy 9, the other cases of splitting can occur at any place along the orbit, generally far from any planet. Other explanations (beside tidal forces – when applicable) involve thermal stress and gas explosions, possibly linked to runaway exothermic transformation of amorphous to crystalline ice, rotational breakup due to centrifugal force (Jewitt 2002) and fragmentation due to a collision with another small Solar System object.

Splitting events are an important source of information on the internal structure of comets. During the complete splitting of C/1999 S4 LINEAR, Bockelée-Morvan et al., (2001) detected no change in the relative molecular abundances, which pleads in favour of a rather homogeneous composition of the nucleus. Encounters with split cometary nuclei are a likely explanation for impact-crater chains seen on giant planet satellites, and that probably occurred on Earth too.

8.1.7 Nucleus Modelling: Outgassing and Internal Temperatures

Detailed modelling of the physical processes involved in nucleus formation, evolution and outgassing is a key tool to address important issues such as the pristine character of cometary matter, and the relation between abundances in the nucleus and those measured in the coma (see Sect. 8.2.1.4). Important phenomena and comet parameters include: ice sublimation; porosity of the cometary matter, which decreases from small to large objects, contributing to the density variation of icy bodies (from $\sim 0.5 \text{ g/cm}^3$ for small comets to 2 g/cm^3 for Pluto); heat transport by sublimated gases in the pores, which usually dominates solid thermal conductivity; radioactive heating by long-period elements like ^{235}U , ^{238}U , ^{40}K ; disruptive and shattering collisions between comets; amorphous to crystalline ice transition, with possible release of trapped gas; surface

processing by solar and galactic photons and particles. In the formation phase, heat from the short-period element ^{26}Al and heat due to accretion itself may be critical, but their role and magnitude vary greatly from one model to another. The difference between the production rates of CO (highly volatile) and H_2O as a function of distance to the Sun is well reproduced by models (e.g. Prialnik 1999, 2002, Enzian 1999, Coradini et al., 1997a,b, Capria 2002, Benkhoff 1999, Huebner and Benkhoff 1999a); a review of those models is presented by Huebner et al., (1999b). However, several other phenomena take place that lead to the observed abundance in the coma; they make the link between nucleus and coma abundances for some species more complex (HNC , H_2CO , ...), whereas not preventing in other cases a simple connection, as shown by species whose release closely follows that of H_2O , without significant effects of differential sublimation (see Sect. 8.2.1.4 and Fig. 8.5).

Fig. 8.5. This diagram displays the production rate Q_X of various cometary molecules as a function of heliocentric distance r_H (Biver et al. 2002). In this logarithmic scale Q_X shows, in general, a linear trend, corresponding to a power law in r_H . Whereas some species clearly depart from the mean behaviour (HNC , H_2CO , CO , CS – see discussion in text), the variation of the remaining species (e.g. CH_3OH , HCN , H_2S , CH_3CN) are roughly parallel ($\sim r_H^{-2}$), which sets a limit on the importance of differential sublimation effects for these species

8.1.8 Internal Temperature and the Case for Liquid Water

A crucial issue for prebiotic chemistry and exobiology is the maximum temperature reached by cometary matter during its history. Prialnik and Podolak (1999) consider that comets form rapidly, which leads to a key role of ^{26}Al decay in heating the interior of that comet. The maximal temperature reached somewhere in the nucleus ranges from low (35–90K for a small 1-km radius comet with low/ high (0.1/0.9) porosity) to 270–210K for a 100-km radius object. A very different situation is found in McKinnon (2002), who modelled the thermal history of large icy bodies in the outer solar nebula (Kuiper Belt). The accretion there is slow enough for ^{26}Al to have mostly decayed, and collisional accretion is the main heat source. The temperature remains below 100K in most places for radii below 100km, but reaches more than 250K in the case of KBO Varuna ($R \sim 400\text{km}$).

The prospect for high temperature inside the nucleus raises the question of possible liquid water inside comets or Kuiper Belt objects. Liquid water is a key parameter for chemical evolution toward prebiotic molecules, such as amino acids more complex than glycine. Therefore liquid water events on comets might allow the synthesis of more molecules than those one would expect in “dry” comets. From the model quoted above, liquid water seems excluded at present times in the bodies of modest size ($< 100\text{km}$ diameter) reaching the zone of terrestrial planets. Conditions were more favourable in the past but only a very limited parameter range would allow liquid water to be present for some time (Podolak and Prialnik 1997); in the case of KBOs, the body should be among the largest (Pluto?).

8.2 Chemical Composition of Comets as Deduced from Observations

8.2.1 Volatiles

8.2.1.1 Observations

Many observations and new discoveries concerning cometary volatiles were made recently, particularly thanks to the development of new instruments (large millimetre-wavelength radio telescopes, among which the IRAM 30-m dish on Pico Veleta and the Plateau de Bure interferometer have proven especially useful; infrared instruments, either ground-based or space-borne: Keck Telescope with NIRSPEC, and ISO satellite) and with the presence of very active comets: Hyakutake in 1996 and Hale–Bopp in 1997 (Bockelée-Morvan 1997, Despois 1999, Crovisier 1999, Bockelée-Morvan et al., 2000). Ten years before, the passage of comet Halley in 1985–86 had already brought considerable progress, from ground-based observations as well as from space probes, in particular Giotto and Vega 1 and 2 (Crovisier and Schloerb 1991, Encrenaz and Knacke 1991).

The majority of new detections of parent molecules (i.e. molecules coming directly from the nucleus) have been performed through radioastronomical observations. This technique provides very safe identifications of the molecular species through very high resolution study ($R = \lambda/\Delta\lambda \sim 10^7$ or better) of their rotational spectrum. Molecular abundances from radio data are usually considered to be accurate within 10–20% (calibration uncertainties), provided the excitation model for the molecule is correct. When comparing various techniques (UV, IR, radio), abundances agree usually well (within a factor of 2 at most). Among the species detected for the first time in Hale–Bopp, formamide (NH_2CHO) – a species already complex for astronomers! – already bears some resemblance to glycine $\text{NH}_2\text{-CH}_2\text{-COOH}$.

8.2.1.2 Molecular Abundances in Cometary Ices

Molecules detected in comets are given in Table 8.1; abundances – by molecule number – are expressed in per cent with respect to H_2O . The majority of the values are from Hale–Bopp observations. The next columns indicate, where available, the comet-to-comet variation range, and the number of comets observed (detected + undetected; Biver et al., 2002). The meaning of these abundances is discussed below (Sect. 8.2.1.4).

The most abundant species, with abundances around 10% of H_2O , are carbon monoxide CO (from 1 to 30%, see below), carbon dioxide CO_2 (5%) and methanol (1–5%). At the $\sim 1\%$ level one finds the first sulfur-bearing species, H_2S , formaldehyde H_2CO (its exact abundance is hard to determine, due to the extended source problem discussed below), and the first nitrogen-bearing species: ammonia NH_3 (0.6%). Then, three hydrocarbons that are observable only in the infrared: methane CH_4 and ethane C_2H_6 (0.6%) and acetylene C_2H_2 (0.1–0.5%). With 0.25%, ethylene glycol $\text{CH}_2\text{OHCH}_2\text{OH}$ is the second alcohol. One also finds at these levels other sulfur species like SO_2 (0.1%), OCS and CS_2 , and HCN (0.2%). SO (0.2–0.8%) is probably mostly a product of SO_2 photodissociation (estimated itself around 0.1%). The least abundant currently detectable species have a relative abundance of approximately 10^{-4} . Among them, isocyanic acid HNCO , formic acid HCOOH , the disulfur S_2 , methylformate HCOOCH_3 , HNC (see below), methyl cyanide CH_3CN and cyanoacetylene HC_3N (in comparable abundances), thioformaldehyde H_2CS and formamide NH_2CHO .

8.2.1.3 A Few Important Cases

• *Newly Found Species*

Bockelée-Morvan et al., (2000, note), and Bockelée-Morvan and Crovisier (2002) report the identification of acetaldehyde CH_3CHO , with an abundance of about 0.02% relative to H_2O from a reanalysis of comet Hale–Bopp data. Recently, $\text{CH}_2\text{OCH}_2\text{OH}$ (ethylene glycol – commonly “antifreeze”) has been identified

Table 8.1. Relative production rates of molecules in the coma, expressed by molecule number and in % relative to water ice (adapted from Despois et al., 2002). These rates are believed to be good tracers of molecular abundances in cometary ices, except for some species, like CO, H₂CO, HNC (see text). The values are for comet Hale–Bopp (Bockelée-Morvan et al., 2000, Crovisier et al., 2004a,b), except when indicated Hya. (Hyakutake) or I–Z (Ikeya–Zhang). When the molecule has been measured in several comets a range (Biver et al., 2002) is given

Molecule	Abundance (H ₂ O = 100)	Intercomet variation	Detected comets + upper limits	Notes
H ₂ O	100			
H ₂ O ₂	< 0.03			
CO	23	< 1.7 – 23	5 + 4	Var.
CO ₂	6 (various)			
CH ₄	0.6			
C ₂ H ₆	0.6			
C ₂ H ₂	0.2			
C ₄ H ₂	0.05?(I–Z)			Prelim.
CH ₃ C ₂ H	< 0.045			
CH ₃ OH	2.4	< 0.9 – 6.2	15 + 2	
H ₂ CO	1.1	0.13 – 1.3	13 + 2	Extend.
CH ₂ OHCH ₂ OH	0.25			
HCOOH	0.09			
HCOOCH ₃	0.08			
CH ₃ CHO	0.025			
H ₂ CCO	< 0.032			
c-C ₂ H ₄ O	< 0.20			
C ₂ H ₅ OH	< 0.10			
CH ₂ OHCHO	< 0.04			
CH ₃ OCH ₃	< 0.45			
CH ₃ COOH	< 0.06			
NH ₃	0.7			
HCN	0.25	0.08 – 0.25	24 + 0	
HNCO	0.10			
HNC	0.04	< 0.003 – 0.035	5 + 2	Extend.
CH ₃ CN	0.02	0.013 – 0.035	4 + 0	
HC ₃ N	0.02			

Table 8.1. (continued)

Molecule	Abundance (H ₂ O = 100)	Intercomet variation	Detected comets + upper limits	Notes
NH ₂ CHO	0.015			
NH ₂ OH	< 0.25			
HCNO	< 0.0016			
CH ₂ NH	< 0.032			
NH ₂ CN	< 0.004			
N ₂ O	< 0.23			
Glycine I	< 0.15			
C ₂ H ₅ CN	< 0.010			
HC ₅ N	< 0.003			
H ₂ S	1.5	0.12 – 1.5	11 + 3	
OCS	0.4			Extend.
SO	0.3			Extend.
CS ₂ (from CS)	0.17	0.05 – 0.17	9 + 0	
SO ₂	0.2			
H ₂ CS	0.02			
S ₂	0.005 (Hya)			
CH ₃ SH	< 0.05			
NS	0.02			Parent?
PH ₃	< 0.16			
NaOH	< 0.0003			
NaCl	< 0.0008			

Notes (see text for discussion):

- Extend.: extended source – in this case the abundance depends somewhat on the model adopted for the spatial distribution of the source
- Var.: CO shows large variability in a given comet along the orbit, and from comet to comet
- C₄H₂ values are preliminary
- NS is probably a photodissociation product from an unknown parent.
- CS₂ abundance indirectly deduced from CS abundance
- CO₂ measured to be 20% in Hale–Bopp at a distance of 2.9 UA by the ISO satellite
- Glycine is a compound with a very low volatility. Nondetection in the gaseous phase does not imply absence from the refractory component. Glycine I refers to one of the two most stable conformers of the molecule.

from the same archive spectra (Crovisier et al., 2004b); surprisingly, its abundance (0.25%) is higher than the upper limit for ethanol (0.1%), which may be an important constraint on the formation processes of cometary molecules. C_4H_2 has been possibly identified in the near infrared (NIR) spectrum of comet C/2002 C1(Ikeya-Zhang) (Magee-Sauer 2002). NS ($x \sim 0.02\%$), a radical, probably a dissociation product, has been detected in comet Hale-Bopp (Irvine et al., 2000b); its parent is not yet known: HNCS, HNSO, NH_4SH have been suggested.

- *Supervolatiles*

Very volatile (“supervolatile”) species, like Ar, N_2 , H_2 , CO are important to set an upper limit to the highest temperature ever reached by the cometary nucleus and thus its degree of thermal processing. Bockelée-Morvan and Crovisier (2002) report doubts on the detection of Ar and N_2 (from N_2^+). H_2 appears to be a product of water dissociation, not a nuclear species. To date, the most volatile species are thus CO and CH_4 .

- *Glycine Upper Limit in Volatiles*

Table 8.1 includes upper limits from radio observations of the coma (Bockelée-Morvan and Crovisier 2002). The limit ($x < 0.15\%$ or ~ 0.004 by weight or 6×10^{-5} mol/g) on glycine (the simplest amino acid, and one of the 20 that are the building blocks of proteins) is not very stringent, due to the intrinsic weakness of its radio lines. Furthermore, this limit concerns only the fraction of glycine molecules that could be released from the nucleus due to ice sublimation. Note that pure solid glycine itself is a refractory compound (T_{subl} is ~ 500 K for 1 atm pressure) and that thermal destruction occurs at a similar temperature. In the CM carbonaceous chondrite meteorite Murchison, glycine abundance (here with respect to refractories) is about 10^{-7} mol/g (Cronin and Chang 1993).

8.2.1.4 Are Coma Abundances a True Image of Ice Composition in the Nucleus?

On a plot of their production rates according to the distance to the Sun (Fig. 8.5 “Christmas tree plot” Biver et al., 2002), a majority of individual molecules vary in a similar way, which suggests that most of the cometary material escapes as a whole, without strong differentiation between chemical species. A few species (most notably CO, H_2CO , and HNC) harbour, however, a peculiar behaviour, and require additional phenomena to be taken into account: differential sublimation, extended source, and coma chemistry.

- *Differential Sublimation*

The great volatility of CO induces an important variation of the CO/ H_2O ratio with heliocentric distance. CO can not only move through the micropores present in the ice, but even through the structure of crystalline ice itself; as a result, the surface layers of the nucleus can, according to cases, be either depleted or enriched in CO. This phenomenon has been modelled in detail (see Sect. 8.1.7).

- *Extended Sources*

Some coma molecules do not appear to be emitted directly from the nucleus, but are more probably secondary products of photo- or thermal degradation of larger species, or products of chemical reactions in the coma. Thus they appear to come from an extended source surrounding the nucleus. Bockelée-Morvan and Crovisier (2002) summarise different indicators of extended source (spatial distribution, line shape, production behaviour with distance to the Sun). The best established cases are H_2CO and CO . Recent observations indicate that SO , CS , OCS and HNC harbour extended source characteristics. Photodissociation is likely to explain the case of SO (from SO_2) and CS (from a yet uncertain parent, maybe CS_2). HNC may be partly chemically produced (see below). The origin of H_2CO is not only in the nucleus, but also in the coma, where it is released from a “carrier”: maybe organic CHON grains, maybe polymers (polyoxymethylene – POM, which has been detected after experimental simulations of cometary ice analogs), maybe both. The degradation of polyoxymethylene (POM) has been studied in the laboratory and is found to be a possible source for H_2CO (Cottin et al., 2001, 2004). Various CN-bearing compounds including hexamethylenetetramine (HMT, see Fig. 8.13) and poly-HCN are possible sources of extended CN radical in the coma (Fray et al., submitted) in addition to the photodissociation of HCN.

- *Coma Chemistry*

HNC is a case for which coma reactions (other than photodissociation) can affect molecular abundances. The peculiar behaviour of the production rate of this species in comet Hale–Bopp, with its strong increase when the comet approached the sun, leads to the proposal of its production from HCN through chemical reactions in the coma as an explanation. Rodgers and Charnley (2001a) shows that reactions between HCN and high-speed (“suprathermal”) hydrogen (from H_2O dissociation) could explain HNC production in comet Hale–Bopp. This process, however, is not efficient for smaller comets such as comet Hyakutake, for which the origin of HNC is still an open question (Irvine et al., 2003, Rodgers and Charnley 2001, Charnley et al., 2002a,b). It should be noted that in interstellar clouds, and thus perhaps also in protosolar nebulae, HNC and HCN are both present, and that HNC is stable in ice at sufficiently low temperature. Therefore, the presence of some HNC in the nucleus is not excluded.

Are some other minor species due to reactions in the coma? Rodgers and Charnley (2001b) show it cannot be the case for the detected species HCOOCH_3 and HCOOH , which are then expected to be directly released from the nucleus.

8.2.2 Grains

8.2.2.1 Nature of Grains

The chemical composition of the grains of comet Halley has been analyzed in situ by mass spectrometry (instrument PUMA on board the Vega 1&2 space-

craft, and instruments PICCA, IMS and NMS on board Giotto spacecraft – Altwegg et al., 1999). When grains are ejected from the nucleus, any embedded ice sublimates within the first few kilometres. Therefore, we will only consider the refractory (nonvolatile) component of grains in this section. Vega spacecraft have collected particles between 80 000 and 120 000 km from the nucleus. About 5000 particles were analyzed, with mass ranging from 5×10^{-17} to 5×10^{-12} g (which means a size ranging from 0.04 to $2 \mu\text{m}$ if one assumes a density equal to 1). The total mass that was analyzed was only a few nanograms. Their elemental composition shows that the particles are made of a mixture of silicates and organic material. In comet Halley’s coma, when Giotto made its measurements, the ratio between silicates and organic matter was found to be between 1 and 2. When organic matter is very abundant, the grains are called “CHON” grains (i.e., compounds of C, H, O and N). According to some models, the small mineral particles might be embedded in a matrix of carbonaceous matter (Greenberg 1982); however, mass spectrometer measurements show the existence of pure silicate and pure organic grains, beside grains of mixed composition (Fomenkova, 1999).

Figure 8.6 shows the production of grains in mass and number for comet Halley as derived by Crifo (Crifo 1995, Crifo and Rodionov 1997) from in situ measurements presented in McDonnell et al. (1991). It must be noted that data up to 1 mm are direct in situ measurements, whereas higher values are extrapolations (relevant within an order of magnitude of uncertainty).

The temperature of grains can be derived from observations, but the best estimations are reached through calculations based on hypotheses about their shape and composition (Crifo 1988). Two extreme temperatures for each grain

Fig. 8.6. Dust-grain production from comet Halley nucleus assuming a density of 1 g cm^{-3} (Cottin et al., 2004)

size are achieved, depending on whether the grain is made of olivine (low temperature) or amorphous carbon (high temperature). Olivine represents the silicate nucleus of grains with a very low absorbance in the visible; it is a lower temperature limit for grains. Amorphous carbon (aC) is representative of dark material, and stands as an upper limit for a strongly absorbing organic component of grains. As grain composition is poorly known, one cannot pretend to better constrain their temperature than between those two extremes. Grains temperatures are presented on Fig. 8.7 for a spherical shape; these temperatures are reached within the first few tens of kilometres from the nucleus (Crifo 1991). For porous or nonspherical grains the temperature tends to be higher.

Fig. 8.7. Grain temperature as a function of size and composition (Cottin et al., 2004)

8.2.2.2 Organics in Grains

The most fruitful works related to the organic composition of grains have been reported in Kissel and Krueger 1987, and Krueger and Kissel 1987). To interpret the PUMA's mass spectra, they consider that all sudden dissipation processes near solid surfaces after an impact are governed by the same rules of molecular ion formation (Fig. 8.8). Such impacts occur when a dust particle hits the mass spectrometer's target. This hypothesis yields a good agreement between their predictions and other observations for small molecules (e.g. HCN, CH₃CN).

For larger molecules the problem is more complex, as they cannot survive the impact process without fragmentation. In addition to the difficulty of assembling correctly the fragments to reconstitute the original molecule, the nature of the fragments themselves is uncertain, several fragments having the same mass (to the resolution of the spectrometer). Thus the identification by these authors

Fig. 8.8. Cumulated mass spectra collected in comet Halley by instrument PUMA on board VEGA-1 spacecraft and tentative interpretation. Adapted from Kissel and Krueger (1987)

of purines and adenine, for example, should be considered as very tentative. However, what is clearly shown by PUMA mass spectra is that compounds with complex structure and large molecular masses (at least with m/z up to 160 g mol^{-1}) are present on grains.

First interpretations of the heavy-ion mass spectra from the PICCA instrument led Huebner (1987) to conclude the presence of polyoxymethylene (POM) in comet Halley. After further analyses, Huebner et al., (1989) discussed the presence of POM derivatives such as sulfur copolymers. As already stated in this chapter, the presence of POM in comets is coherent with the detection of extended sources of H_2CO in the coma. Indeed, this molecule could be the degradation product of POM. The authors also suggest the presence of HCN polymers such as polyaminocyanomethylene (PACM: $(\text{NH}_2\text{--C--CN})_n$), even though these polymers are very difficult to detect because in the coma $\text{HCN}/\text{H}_2\text{CO} \sim 0.1$ and because from thermodynamic considerations N-containing polymers should be less volatile than O containing polymers (Krueger et al., 1991). The presence of HCN/ H_2CO copolymers could also be suggested on comets because these two molecules polymerize very easily by themselves.

Later, however, Mitchell et al., (1992) showed that the mass spectrum pattern that led Huebner to announce the detection of polyoxymethylene is only characteristic of a mixing of molecules composed of C, H, O and N atoms (CHON molecules). Therefore PICCA mass spectra do not imply the presence of POM, but only of a large diversity of CHON molecules, among which POM could be present. The most we can say, if we consider laboratory simulation results presented latter in this chapter and the detection of an extended source of formaldehyde, is that the presence of POM on cometary nuclei is possible.

Beside polymers, heteropolymers and large CHON molecules, other compounds have been suggested: pure carbon grains, PAHs (polycyclic aromatic hydrocarbons, i.e. aromatic cycles linked together), very “branched” aliphatic hydrocarbons (Fomenkova 1999). PAH detection from in situ UV spectroscopy in Halley was announced (Moreels et al., 1994); PAHs were not seen in the ISO spectra of Hale–Bopp, possibly due to the lower temperature of the comet at the time of these observations (Crovisier 1999). A weak residual feature at $3.28\mu\text{m}$ was, however, seen by Bockelée-Morvan et al., (1995) in various comets, and especially the dustier ones, which might be due to PAHs; this would correspond to a relative abundance to water 1.5 to 10×10^{-6} , at least 100 times below that deduced from UV data. A list of compounds probably and possibly detected in comet Halley grains by mass spectroscopy is reported in Table 8.2.

Table 8.2. Organic molecules inferred from mass spectra of gas and dust particles in comet Halley. The confidence levels of detections by MS are established as follows: – Confirmed: Molecule also detected by remote observations; – High: Molecule not detected by remote observations but present after laboratory irradiations of cometary ice analogs; – Medium: Molecule detected only by mass spectroscopy with a good confidence level according to the authors; Low: Molecule only inferred by mass spectroscopy with a low confidence level according to the authors

Molecule	Family	Mass spectrometer	Confidence level	Ref.
Hydrocyanic Acid	C–N–H	PUMA, PICCA	Confirmed	1, 2, 3
Methyl cyanide	C–N–H	IMS	Confirmed	7
Acetonitrile	C–N–H	PUMA, PICCA	Confirmed	1, 2, 3
Methanol	C–O–H	NMS	Confirmed	6
Formaldehyde	C–O–H	PUMA, PICCA	Confirmed	3
Formic acid	C–O–H	PUMA	Confirmed	1, 2
Acetaldehyde	C–O–H	PUMA, PICCA	Confirmed	1, 3
Ammonia	N–H	PUMA	Confirmed	2
Isocyanic acid	C–N–O–H	PUMA	Confirmed	1, 2
Ethane	C–H	NMS	Confirmed	8
Acetylene	C–H	NMS	Confirmed	8
Acetic acid	C–O–H	PUMA	High	1
Polyoxymethylene	C–O–H	PICCA	High (itself or derivatives)	4, 5
Ethene	C–H	NMS	High	8
Iminoethane	C–N–H	PUMA	Medium	1, 2
Aminoethene	C–N–H	PUMA	Medium	1, 2
Pyrroline	C–N–H	PUMA	Medium	1

Table 8.2. (continued)

Molecule	Family	Mass spectrometer	Confidence level	Ref.
Pyrrole	C–N–H	PUMA	Medium	1, 2
Imidazole	C–N–H	PUMA	Medium	1
Pyridine	C–N–H	PUMA	Medium	1, 2
Pyrimidine	C–N–H	PUMA	Medium	1, 2
Ethyl cyanide	C–N–H	IMS	Medium	7
Pentyne	C–H	PUMA	Low	1
Hexyne	C–H	PUMA	Low	1
Butadiene	C–H	PUMA	Low	1
Pentadiene	C–H	PUMA	Low	1
Cyclopentene	C–H	PUMA	Low	1
Cyclopentadiene	C–H	PUMA	Low	1
Cyclohexene	C–H	PUMA	Low	1
Cyclohexadiene	C–H	PUMA	Low	1
Benzene	C–H	PUMA	Low	1
Toluene	C–H	PUMA	Low	1
Propanenitrile	C–N–H	PUMA	Low	1
Iminomethane	C–N–H	PUMA	Low	1
Iminopropene	C–N–H	PUMA	Low	1
Purine	C–N–H	PUMA	Low	1, 2
Adenine	C–N–H	PUMA	Low	1, 2
Polyaminocyanomethylene	C–N–H	PICCA	Low	5
Methanolitrile	C–N–O–H	PUMA	Low	1
Methanalimine	C–N–O–H	PUMA	Low	1
Aminomethanol	C–N–O–H	PUMA	Low	2
Aminomethanal	C–N–O–H	PUMA	Low	2
Oxyimidazole	C–N–O–H	PUMA	Low	1
Oxypyrimidine	C–N–O–H	PUMA	Low	1
Xanthine	C–N–O–H	PUMA	Low	1

1 (Kissel and Krueger 1987); 2 (Krueger and Kissel 1987); 3 (Krueger et al., 1991); 4 (Huebner 1987); 5 (Huebner et al., 1989); 6 (Eberhardt and Krankowsky 1995); 7 (Geiss et al., 1999); 8 (Altwegg et al., 1999)

8.2.2.3 Cometary Silicates

The nature of other refractory components is constrained by infrared observations of comets. Identification is achieved through a comparison of observations with laboratory spectra of different kinds of silicates and possibly carbonaceous

grains, and it should be noted that there is no unique solution to the fitting problem. It appears that grains are made of a mixture of crystalline and amorphous silicate (Brucato et al., 1999, Crovisier et al., 1997, Harker et al., 2002, Hayward and Hanner 1997, Nuth et al., 2002, Wooden et al., 2000).

Crystalline forsterite (a magnesium-rich olivine) has been detected thanks to the ISO infrared satellite (Crovisier et al., 1997). Ground-based telescopes have enabled a study of the infrared spectrum around $10\mu\text{m}$, and determined the ratio pyroxene/olivine. According to Harker et al., (2002) amorphous silicates make up about 70% (by mass) of the submicrometre-sized ($\leq 1\mu\text{m}$) silicate dust grains in Hale-Bopp's coma, and are distributed roughly equally between olivine and pyroxene composition, and between Fe-rich and Mg-rich species; the remaining 30% are predominantly Mg-rich crystalline silicates with a crystalline

Fig. 8.9. Comparison of the infrared spectrum of Hale-Bopp obtained by ESA's Infrared Space Observatory ISO (Crovisier et al., 1997) with that of a young star of type AeBe (e.g. Malfait et al., 1998). The features in the comet spectrum lead to the identification of a crystalline silicate, forsterite, a magnesium-rich olivine. The AeBe stars are slightly more massive than the Sun, but the dust that surrounds them and that is responsible for this IR emission is considered to be similar to dust in the protosolar nebula. In HD100456, the similarity is even more striking and points towards a high crystalline mass fraction and small particle size ($< 10\mu\text{m}$) in both cases (Bouwman et al., 2003)

olivine:orthopyroxene ratio about 4 to 5 : 1 that seems to vary slightly with heliocentric distance. Figure 8.9 shows a comparison between the infrared spectrum of Hale-Bopp and circumstellar matter around a young star. However, data of such a high quality is only available for one comet (Hale-Bopp).

8.2.3 Elemental and Isotopic Composition

8.2.3.1 Elements

The composition in elements that can be deduced by combining dust and gas measurements (Geiss 1988) leads to abundances normalized to silicon close to solar abundances for carbon and oxygen. However, one notes a depletion (underabundance) of hydrogen of about 600, due to the high H_2 volatility and a depletion of 2 for nitrogen, which is explained in the same way by the fact that nitrogen is often in the form of N_2 , a very volatile gas, too (Fig. 8.10). The

Fig. 8.10. Comparison of elemental abundances in the Sun, comet Halley, and (C1, C2) meteorites (Geiss 1988). The element abundance ratios in P/Halley are uncertain by a factor of about two (excluding the variability and uncertainty in the gas/dust ratio)

gas:dust ratio derived in the case of Halley is 1:2 in mass (Jessberger and Kissel 1991); note that the computation of the elemental composition for the whole comet uses this ratio and is quite sensitive to it.

In Fig. 8.10, the elemental composition of comets is also compared with that of carbonaceous chondrites (Geiss 1988). Elements of the series Mg–Al–Ca, as well as oxygen have comparable abundances within a factor of 2. On the other hand, in comet Halley, abundances of carbon, hydrogen, nitrogen and of any other element appearing mostly in volatile compounds are larger than in carbonaceous chondrites. This leads us to say that cometary matter is more “pristine” than that of carbonaceous chondrites, in the sense that it underwent less heating and thus was less processed.

8.2.3.2 Isotopic Abundances

Much of the information on the origin of cometary matter and on the importance of the cometary contribution to the Earth’s water content derives from the study of isotopic abundances, which have been recently reviewed by Altwegg and Bockelée-Morvan (2003). The D/H ratio in particular is very important data to investigate the origin of cometary matter (e.g. Bockelée-Morvan et al., 1998, Mousis et al., 2000, Robert 2002) and its delivery to the Earth (Dauphas et al., 2000; see Sect. 8.5.3). It was measured for two species: HDO/H₂O (D/H $\sim 3 \times 10^{-4}$) and DCN/HCN (D/H $\sim 2.3 \times 10^{-3}$); upper limits on the order of 10^{-2} or below have also been set for deuterated formaldehyde, methanol, ammonia and H₂S. Molecules appear enriched in deuterium: as can be seen in Fig. 8.11, D/H in water for the 3 comets for which it has been measured is twice the ocean SMOW value, and an order of magnitude higher than the protosolar value of 2.5×10^{-5} . This enrichment is however not as high as in the interstellar gas (where multiply deuterated species like D₂CO and even ND₃ have been observed). Measurements of the O, C, N and S isotopes display, in general, abundances very close to solar abundances (e.g. Jewitt et al., 1997, Lecacheux et al., 2003), which confirms that the comets are Solar System objects. This does *not* contradict the assumption of an interstellar origin of the cometary matter discussed below. Indeed, the Sun and the Solar System as a whole were formed from a homogeneous clump of interstellar matter and it is from the same fragment of IS matter that the comets were made.

Some carbonaceous grains analyzed by in situ mass spectroscopy in Halley (Jessberger and Kissel 1991) showed a very high ratio ¹²C/¹³C, rising up to 5000, whereas the normal ratio in Solar System objects is 89. These small grains would have been formed in the envelope of certain stars known as AGB stars (asymptotic giant branch) and would then have been injected into the interstellar medium. They thus would have been mixed with the interstellar cloud fragment that condensed to form the protosolar nebula, then later incorporated as such in the matter of forming comets. As this high departure from solar ¹²C/¹³C values is concentrated in very small grains, which do not represent a large quantity

Fig. 8.11. D/H ratios in the Solar System. For comets, only measurements of D/H in water are shown (from Hersant et al., 2001)

of carbon, the average value of the cometary $^{12}\text{C}/^{13}\text{C}$ ratio remains close to the solar value, namely approximately 89. An intriguing measurement has been made in CN (Arpigny et al., 2003) suggesting the existence of parents of the CN radical other than HCN – possibly solid organic compounds – with strongly nonsolar N isotopic ratios.

8.2.4 Are All Comets Similar?

Abundance variations are observed from one comet to another, in particular for CO (from less than 1% to more than 30% according to comets and to the distance from the Sun) and CH_3OH (1 to 5%; e.g. Bockelée-Morvan 1997). This composition is deduced from gas abundances measured in the coma, making assumptions on the spatial distribution of the molecules, the limited chemistry in the coma, and the sublimation process.

That all comets are not similar already has observational evidence, as seen from dust content and daughter species C_2 , CN (A'Hearn et al., 1995, Rolfe and Battrick 1987). Column 3 in Table 8.1 shows the range spanned by the observed molecular abundances in a sample of comets (Biver et al., 2002). Different compositions are expected, to some extent, between comets coming from the Oort cloud and the Kuiper Belt due to their different formation zone (respectively Jupiter–Neptune versus mostly transneptunian, see Sect. 8.4 and Morbidelli and

Table 8.3. Molecules detected during experimental simulations of cometary ice analogs. *Italic letters* refer to molecules actually detected in comets. (t) means tentative detection only in the analogs. Amino acids (alanine, AIB, ... except glycine) were detected after acid hydrolysis of the room temperature residue. Updated from Cottin et al., 1999

Hydrocarbons: CH_4 C_2H_2 , C_2H_4 , C_2H_6 C_3H_8 , C_4H_{10} C_5H_{10} , C_5H_{12} C_6H_{12} , C_6H_{14} C_7H_{16}	Ketones: CH_3COCH_3 $HOCH_2COCH_3$ $HOCH_2CH_2COCH_3$	Alcohols: CH_3OH CH_3CH_2OH $HOCH_2CH_2OH$ $HOCH_2CH(OH)CH_2OH$ $C_4H_8(OH)_2$ C_5H_9OH (t) $C_5H_{11}OH$
Amides: NH_2CHO CH_3CONH_2 $HOCH_2CONH_2$ $NH_2(CO)_2NH_2$ $HOCH_2CH(OH)CONH_2$	Carboxylic acids: $HCOOH$ CH_3COOH (t) $HOCH_2COOH$ $HOCH_2CH(OH)COOH$ $HOCH_2CH_2COOH$ $NH_2COCOOH$	Amino Acids: NH_2CH_2COOH (Glycine) $NH_2CH(CH_3)COOH$ (Alanine) $CH_3CH_2CH(NH_2)COOH$ (α ABA) $CH_3CH(NH_2)CH_2COOH$ (β ABA) $(CH_2NH_2)(CH_3)CHCOOH$ (AIBA) Sarcosine Ethylglycine Valine, Proline, Serine Aspartic acid Diaminopropanoic acid Diaminobutyric acid Diaminopentanoic acid Diaminohexanoic acid
Amines: $HOCH_2CH_2NH_2$ $HCNH(NH_2)$ Diaminopyrrole Diaminofurane Triaminopropane $(CH_2)_6N_4$ (HMT)	Aromatic Compounds:
Aldehydes: H_2CO CH_3OCH_2CHO (t)	Ethers: $CH_3OCH_2OCH_3$ (t) $C_3H_6O_3$ (Trioxane) (t) $(-CH_2-O-)_n$ (POM)	Esters: $HCOOCH_3$ CH_3COOCH_3 $CH_3CH_2COOCH_3$

Others: CO , CO_2 , C_3O_2 , H_2O_2 , H_2CO_3 , N_2H_4 , $HNCO$, NH_2CONH_2 , $NH_2CONHCONH_2$

Brown 2004). Observational evidence has been claimed for variations in the C_2H_6/H_2O and CH_4/H_2O ratios (Mumma et al., 2002, and Gibb et al., 2003, respectively), but the statistics is still limited.

8.3 Laboratory Simulation of Cometary Matter

8.3.1 Experimental Simulations

Only volatile molecules have been detected so far in cometary atmospheres, as no direct cometary sample has ever been analyzed (except for IDPs, whose origin cannot, however, be uniquely assigned to comets). For a better insight into more complex, less volatile material, one has to turn to experimental laboratory work. The principle of such experiments is the following: from observations of the most abundant species in comas and in the interstellar medium, one can infer the

probable composition of the nucleus ices. A gaseous sample of the key species is deposited under vacuum on a cold substrate and irradiated during or after deposition by UV photons or charged particles. Condensed ices are sometimes simply warmed up slowly without irradiation. When the sample is warmed up for analysis a refractory organic residue remains on the substrate as the volatiles sublimate (Fig. 8.12). Greenberg has called this residue “yellow stuff”. Bernstein et al., (1997) have shown that the organic residue is formed only when the initial mixture of ices contains polar molecules such as CH_3OH and NH_3 .

The diversity of organic compounds synthesized is remarkable but their identification is seldom exhaustive. Table 8.3 is a simplified list of all the detected compounds. The simplest compounds such as CO , CO_2 , H_2CO and CH_4 are

Fig. 8.12. A typical experimental setup allowing the irradiation (by UV and/or energetic protons) of cometary ice analogs made by deposition of a gas mixture on a rotating aluminium mirror cooled down to 10 K in a cryostat. The ice evolution can be analysed in situ by infrared reflection spectroscopy, and the volatiles released during warming, by mass spectrometry. The room-temperature residue can be collected for further analysis such as GC-MS (gas chromatography coupled to mass spectrometry), HPLC (high-performance liquid chromatography) and many others. From Hudson and Moore (1999)

detected in almost all the experiments, if the irradiated ice contains the appropriate elements. For more complex molecules, it depends on the ice composition and the nature of the energy source.

In addition to chemical transformations, it must be mentioned that experiments on the trapping of gases during ice condensation suggest that these processes play an important role in determining the composition of the ice and could lead to important enrichment or depletion between the gaseous and solid phases (Notesco and Bar-Nun 1996, Notesco and Bar-Nun 1997, Notesco et al., 1997).

8.3.2 Energy Deposition

Three kinds of energetic processing occur on icy coated dust grains in interstellar clouds (potentially precometary ices – see Sect. 8.4) or in the outer layers of comet ices in the Solar System:

In interstellar clouds, icy coated dust particles are subjected to processing by:

- *Charged particles*: Galactic cosmic rays.
- *UV-photons*: Lyman α photons from neighboring stars (in the diffuse outer regions of a cloud), or UV-photons induced by galactic cosmic rays (in the inner regions of dense clouds).
- *Thermal processes*: Cycling between the cold centre of a dense cloud and its warmer diffuse outer regions.

In the Solar System, the outer layers of comets undergo the same processes:

- *Charged particles*: Galactic cosmic rays, mainly in the Kuiper belt and the Oort cloud. This process has the largest effect on the outer few metres of the nucleus.
- *UV-photons*: Solar-UV, mainly in the inner Solar System when the comet is close to the Sun. This process would affect the outer few micrometres of the nucleus. Also during the Solar System formation, in the external layers of the disk, when solar UV luminosity was much higher than today.
- *Thermal processes*: During the formation of the Solar System (depending on the region in which the comet accretes), and in the inner Solar System (when the comet approaches perihelion).

Due to the diversity of environments involved, constraining the degrees to which different processes affect cosmic ices is a highly convoluted problem. Differences between the products synthesized during processing, according to the energy sources, could give information on the history of cometary matter and comets. Investigations are in progress to address this question.

8.3.2.1 UV Irradiation

UV irradiation is performed using a flowing-hydrogen discharge lamp (powered by a microwave cavity) delivering mainly Lyman α photons (122nm) and a broad

band of photons centred at 160nm (see Allamandola et al., 1988, and Cottin et al., 2003) for a detailed description). The irradiated ices comprise common cometary small molecules but the initial abundances of CH_3OH , NH_3 and/or CO relative to H_2O are usually higher than those deduced for present-day comets and displayed in Table 8.1. During these experiments a wide variety of organic compounds have been identified. From an initial mix of H_2O : CO : NH_3 (ratio = 5: 5: 1), glycine, the simplest amino acid, acetamide, glyceramide, and many other molecules have been detected by GC-MS (Briggs et al., 1992). Analysis by MS-MS on the organic residues formed, leads to the detection of heavier compounds: several cyclic molecules and PAHs (Greenberg and Mendoza-Gomez 1993). The composition of the heaviest part of the residue is still unknown but an elemental composition based on the overall structure of the mass spectra is given by Greenberg and Li (1998) (C: O: N: H = 1: 0.06: > 0.001: 1.1).

Among the molecules synthesized after such irradiations of ices, one of them is of great interest. Bernstein et al., (1995) have identified abundant hexamethylenetetramine (HMT – $\text{C}_6\text{H}_{12}\text{N}_4$) in the refractory residue. This compound has exobiological implications since its acid hydrolysis products are amino acids (Wolman et al., 1971). Typically, for an initial composition of H_2O : CH_3OH : CO : NH_3 (10: 5: 1: 1), the organic residue at 300K contains HMT ($\sim 60\%$), ethers and POM-like polymers ($\sim 20\%$), ketones and amides ($\sim 20\%$). 1/5 of the carbon and 1/2 of the nitrogen from the initial ice composition remain in the refractory part (Bernstein et al. 1995). Thus a large fraction of HMT is formed (60% of the residue) whereas only 5% NH_3 is present in the ice before irradiation. A scheme of HMT production is shown in Fig. 8.13. Formaldehyde is produced by methanol UV oxidation. It then reacts with ammonia to produce methylimine and its trimer: hexahydro-1,3,5-triazine. Successive reactions with formaldehyde and ammonia result in the formation of HMT (Bernstein et al., 1995). Methanol plays a key role and it has been shown by ^{13}C isotopic substitution that it is the source of HMT's carbon. The production of HMT and some HMT family molecules has been studied in great detail by Muñoz Caro (2003).

HMT photolysis produce nitriles (HCN and RCN) and isonitriles (RNC) (Bernstein et al 1994, Cottin et al 2002). Knowing this, it is interesting to note that it has been shown that the CN radical might have an extended source in comet Halley (Klavetter and A'Hearn 1994). According to these authors, this source could be large molecules present on grains because the observed HCN cannot explain the amount of CN in comets. Other observed CN-containing compounds (HNC, CH_3CN , HC_3N) are only minor products and cannot explain the discrepancy. Thus having been produced in the interstellar ices, as we have just seen, HMT could act as a parent ($\text{HMT} \rightarrow \text{CN}$) or “grandparent” ($\text{HMT} \rightarrow \text{RCN} \rightarrow \text{CN}$) molecule for the CN extended source. As yet, there has been no observation of HMT in comets. If present, its detection in the IR would be masked by the Si–O and C–O vibration bands that are in the same region as the strongest HMT infrared signatures. Direct detection of HMT should be

Fig. 8.13. Hexamethylenetetramine (HMT) chemistry. From (Bernstein et al., (1995))

feasible by in situ measurements with the GC-MS on board the lander of the Rosetta mission.

Bernstein et al (2002) and Muñoz Caro et al (2002) have detected a great number of amino acids (such as glycine, alanine, sarcosine, valine, proline, serine, etc.) in residues obtained after UV irradiation of ice mixtures made of $\text{H}_2\text{O}:\text{NH}_3:\text{CH}_3\text{OH}:\text{HCN}$ and $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO}:\text{CO}_2$, respectively. Unhydrolyzed residues produce only a trace of glycine whose detection has already been reported by Briggs et al (1992) without any liquid water introduced to the analysis protocol. The detection of the other amino acids requires an acid hydrolysis of the residue in very strong conditions ($\text{HCl} \geq 6M$ and $T \geq 100^\circ\text{C}$). Therefore it is not clear to date if 1) amino acids are present themselves in the laboratory residues, and henceforth in cometary ices, or if “only” amino acids precursors are synthesized, and 2) if the residues’ processing (acid hydrolysis) is relevant to any chemistry that could have turned the amino acids’ precursors imported by cometary impacts in the primitive oceans of the early Earth into actual amino acids. Note that the hydrolysis conditions would break a peptidic bond; some dipeptides have been found in the extraterrestrial organic matter of the Yamato-791198 and Murchison meteorites, but only glycine-glycine dimers and with a low (10^{-4}) abundance relative to glycine (Shimoyama and Ogasawara 2002).

8.3.2.2 Irradiation by Charged Particles

Important work concerning the particle bombardment of ices has been performed by Strazzulla's team in Catania and in Marla Moore's laboratory at NASA Goddard Space Flight Center. The particles used are H^+ , He^+ , N^+ or Ar. The bombardment of a large diversity of carbon-containing ices induces an evolution toward an amorphous material called Strazzulla "ion-produced hydrogenated amorphous carbon" (IPHAC) (Strazzulla 1997; Strazzulla and Baratta 1991; Strazzulla et al 1991).

The general results are the following: up to a dose of about 10 eV/C atom the ice is partially converted into a refractory material. From 10 to 25 eV/C atom, a massive loss of H is observed and the target evolves to an organic material made of chemical chains of different sizes. For stronger irradiations (≥ 25 eV/C atom) IPHAC, the ultimate state of organic degradation, is formed (Strazzulla 1997). It has been shown by Jenniskens et al. (1993) that energetic UV (10 eV) irradiation of the organic residue of processed ices also leads to IPHAC formation, which then can be also called: "irradiation-produced hydrogenated amorphous carbon". Thus, after a typical lifetime in the interstellar medium, UV radiation and/or particles convert the organic mantle of interstellar dust into amorphous hydrogenated carbon.

A set of data comparing UV photolysis and ion irradiation of ices showed that the yield of major products was similar for a simple ice containing H_2O and CO_2 (Gerakines et al 2000), showing that the ice chemistry seems to be quite similar whether induced by photons or charged particles. Indeed, HMT production has been reported when interstellar ice analogs containing CH_3OH and NH_3 are irradiated with protons (Cottin et al., 2001), the same as with photons. The main difference is that UV photons (typically at 122 nm) only affect a few tenths of a micrometer in water-dominated ice, whereas protons can reach and alter the ice composition down to a few metres depth.

Chemical differentiation is more noticeable when molecules not dissociated by photons with a wavelength of 122 nm and above are involved in the chemical processes. This is the case for CO and N_2 . Different results are obtained if pure CO is photolyzed or proton irradiated (Gerakines and Moore 2001). Likewise N_3^+ is detected when ices containing N_2 are proton irradiated, but not after photolysis (Hudson and Moore 2002). It seems that it is more the energy level than the way it is deposited (UV or charged particles) that matters for the chemistry.

We note that in these kinds of experiment, C_3O_2 , which is sometimes evoked as an extended source of CO, has been detected after irradiation of ices containing CO or CO_2 (Brucato et al. 1997; Moore et al 1991). Kobayashi et al (1995) and Kasamatsu et al., (1997) were the first to report amino-acid production from irradiated ices. After an irradiation by 3-MeV protons of mixtures containing water, ammonia and a carbon-containing molecule (carbon monoxide, methane or propane), they detected by HPLC several amino acids: glycine, and for the first time in a cometary simulation, alanine, aminobutyric acid and aminoisobutyric

acid. These new detections were not made directly from the organic residue, but after an acid hydrolysis in water. Likewise for UV irradiation, only traces of glycine were found during the analysis of unhydrolyzed residues.

8.3.2.3 Thermal Processing of Ices

Polyoxymethylene and associated molecules and polymers have been detected when several mixtures containing formaldehyde, instead of being irradiated, were warmed slowly to room temperature (Schutte et al., 1993a, Schutte et al., 1993b).

There are many differences between the organics detected with or without UV processing of ices. Without irradiation, HMT is not detected, which is quite surprising as H_2CO and NH_3 readily react in the gaseous phase to form HMT (Bernstein et al., 1995; Walker 1964). Likewise, ketones, amides or esters, easily synthesized under irradiation, are quite rare in those thermal experiments. It seems that UV photons provide enough energy to surmount the energy barrier for formation of these molecules. Without UV, POM's production is favoured since it requires less energy.

8.3.3 Relevance and Importance of Laboratory Simulations

This section can not be concluded without discussing the relevance of experimental simulations. Of course, an irradiation of a few hours can not reproduce millions of years or more of slow evolution with complex heterogeneous chemistry in an interstellar environment that will never be completely reproduced in the laboratory. Nevertheless, in the $3.4\text{-}\mu\text{m}$ region, infrared spectra of methane and butane mixtures after a particle irradiation present a very good fit with the observations of dust particles in the diffuse interstellar medium (i.e. highly processed material), and even with spectra of residues from the Murchinson meteorite (Pendleton et al., 1994). The same results have been obtained with residues of $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{CH}_4/\text{C}_2\text{H}_2/\text{CH}_3\text{OH}$, which have been exposed to direct solar UV radiation on the EURECA space station (Greenberg and Li 1997, Greenberg et al., 1995). These are also highly processed materials. Thus Strazzulla's IPHAC appears to be similar to the refractory mantle of dust grains in the harsh conditions of the diffuse interstellar medium. The less-processed mantle formed in molecular clouds is almost certainly composed of the large range of molecules detected after experimental simulations, and the abundances of characteristic molecules like HMT or POM depends on the history of the grain and the relative contribution of the different energy sources: UV and proton irradiation lead to HMT, thermal processing to POM-like polymers. The importance of such simulations is underlined if one considers that data drawn from these simulations are necessary for the preparation of space missions to comets. A good illustration of this point is the selection and calibration of chromatographic columns for the COSAC experiment (ROSETTA mission – ESA) that requires an anticipation of the nature of the molecules to be searched for (see Sect. 8.6).

8.4 Origin and Evolution of Cometary Matter

8.4.1 Origin of Cometary Matter

We have already seen (Sect. 8.1.3) how icy planetesimals populated the two present comet reservoirs, the Oort cloud and the Kuiper Belt, in the early times of the Solar System. We address now the problem of the formation of these icy planetesimals, and the processes determining the composition of cometary matter. As underlined by Yamamoto (1991) these two steps are distinct: the chemical composition is probably fixed to a large extent early in the accretion process, well before km sized bodies are built.

Figure 8.14 summarizes the present view of Solar System formation. All the matter originates in an interstellar cloud composed of dust and gas. Close to the protosun, towards the centre of the nebula, only rocky material would condense, while volatile species remained in the gas phase. Rocky planetesimals – bodies of intermediate size, ranging between 1 m and a few km – were formed there. These rocky planetesimals represent a crucial stage in the process of planet formation; they present a great similarity with present-day asteroids. On the contrary, towards the outermost parts of the nebula, where the temperature was lower, dust and ices formed the material of icy planetesimals, similar to present-day comets.

Fig. 8.14. Diagram showing the origin and the evolution of the cometary matter

These rocky and icy planetesimals intervened in very different proportions in the formation of planets. Rocky planetesimals played the major role for the formation of the Earth and other telluric planets (Mercury, Venus, Mars), while it was mostly the icy planetesimals that took part in the formation of the cores of the giant planets Jupiter, Saturn, Uranus and Neptune. Today comets are thought to be a subset of these ancient icy planetesimals, which survived until now with no or very little evolution.

This global picture, displayed in Fig. 8.14, presents in fact several simplifications. For example, there is also a small number of short-period comets that come from the Oort cloud. Moreover, the separation between rocky and icy planetesimals is not that clear, because bodies of intermediate composition and properties have been found (e.g. Phaeton, Chiron). In addition bipolar flows (see Chap. 1, Part I by T. Montmerle), which are produced in the vicinity of the protosun, may reinject a certain quantity of matter from the protosolar nebula into the collapsing protostellar envelope, allowing material highly processed in the vicinity of the Sun to be incorporated into comets at great heliocentric distances. A similar effect is obtained in the model by Shu et al. (1996) where grains are ejected from the vicinity of the protosun towards the outer parts of the disk.

8.4.2 Cometary Ices versus Interstellar Ices: the Facts

In cold dense interstellar clouds, interstellar grains are coated with ice mantles whose composition can be observed indirectly in a few regions where they evaporate: hot cores surrounding a massive star in formation inside an interstellar cloud, such as occur, for example, in the heart of the Orion Nebula, or shocked regions along bipolar flows (e.g. Kurtz et al., 2000, Bachiller et al., 2001). In the first case, the ice mantles of the grains of the collapsing envelope are thermally evaporated close to the young massive star in formation. In the second case, it is the shock wave created by the bipolar flow propagating through the interstellar medium surrounding the young star that leads to the destruction of the ice mantles and releases the molecules to the gas phase. The good correlation of molecular abundances between cometary and interstellar ices (Table 8.4 and Fig. 8.15) is one of the arguments that leads us to conclude that the matter of comets is very close to interstellar matter, suggesting similar conditions of formation, and even possibly a direct link (comets being then a frozen piece of interstellar matter).

A more straightforward comparison should arise from direct measurements of interstellar ices. Unfortunately, these measurements can only be performed in front of strong infrared sources (e.g. Ehrenfreund and Charnley 2000 and references therein). Furthermore, identification of a precise species and quantitative determination of its abundance from its IR vibrational bands are more difficult than in the case of millimetre-wave rotation spectra of gas-phase species. Table 8.4 lists the abundances in two sets of young stellar objects (*YSO*), respectively leading to low-mass ($< 2M_{\text{Sun}}$) and high-mass stars. The former case,

Table 8.4. Cometary versus interstellar ices. Note their overall similarity. The agreement might be better in the case of ices surrounding low-mass protostars (a category to which the protosun belonged), but most of the present data are only upper limits, including NH_3 and CH_3OH . N_2 , O_2 , H_2 and rare gases are other important species whose ice abundances are not yet known. IS data are from Ehrenfreund and Charnley (2000); the range corresponds to 2 objects in each category (high-mass objects: W33A and N7538S; low-mass objects Elias16 and 29). Cometary data are from Table 8.1 (cometary volatiles); when no range is given, data refer to comet Hale-Bopp, except the O_2 limit, which comes from comet Halley. X-CN is the sum of various CN species (mainly the OCN^- ion in the case of IS ices)

Species	Interstellar ices high-mass YSO	Interstellar ices low-mass YSO	Cometary volatiles
H_2O	100	100	100
O_2	< 7	–	< 0.5 (*)
CO	9–16	6–25	1.7–23
CO_2	14–20	15–22	6
CH_4	2	< 1.6	0.6
C_2H_6	< 0.4	–	0.6
CH_3OH	5–22	< 4	0.9–6.2
H_2CO	1.7–7	–	0.13–1.3
HCOOH	0.4–3	–	0.09
NH_3	13–15	< 9	0.7
X-CN (*)	1–3	< 0.4	0.08–0.25
OCS, XCS	0.05–0.3	< 0.08	0.4

which corresponds to the Sun itself, is still very incomplete. O_2 and O_3 , for which only upper limits have been measured, may contain a substantial fraction of atomic O. The very volatile species H_2 and N_2 , and rare gases like Ar, may be present to an unknown extent in IS ices as well as in cometary ices.

Table 8.5 gives the list of the 137 interstellar and circumstellar molecules (not including isotopic variants) detected to date (January 2004) in the gas phase. Among them are ethanol $\text{C}_2\text{H}_5\text{OH}$, which has been long known, and glycolaldehyde CH_2OHCHO , whose detection has been recently claimed in the ISM (Hollis et al. 2000). Glycolaldehyde belongs to the family of molecules $\text{C}_n(\text{H}_2\text{O})_n$, which for $n > 2$ are sugars or oses. In carbonaceous chondrites (the meteorites with composition closest to comets) Cooper et al. (2001) have detected several sugar molecules. If one also takes into account the presence of H_2CO , a sugar precursor at the per cent level in comets, that sugar molecules exist in comets is a likely hypothesis.

The heaviest known interstellar molecule to date is HC_{11}N , which belongs to the family of cyanopolyynes (a succession of acetylene molecules linked one

Fig. 8.15. Correlation of cometary (Hale-Bopp) and interstellar (ISM) gas-phase abundances (here for molecular species made of C, O, and H atoms; abundances are normalized to CH_3OH). The ISM regions selected for comparison are believed to release ice mantle molecules to the gas phase due to heat or shocks (Bockelée-Morvan et al., 2000)

to another to form a linear chain, and ending with a CN radical: $\text{H}(\text{CC})_n\text{CN}$. The discovery of glycine $\text{NH}_2\text{-CH}_2\text{-COOH}$ by Snyder et al., (e.g. 1997) in the ISM was not confirmed (Combes et al., 1996). Later searches by Ceccarelli et al., (2000) and Hollis et al., (2003) also led to upper limits. Recently, a detection has been published (Kuan et al., 2003) but it is also subject to debate. Due to the similarities between comets and the interstellar medium presented above, one can legitimately think that a number of these species exist also in comets; their detection is a challenge for new telescopes and space experiments (Sect. 8.6). In the interstellar medium grain surface chemistry also takes place. Charnley (1997) proposed a whole scheme of surface reactions to explain the formation of some complex compounds in the interstellar ices.

8.4.3 Models of Cometary Matter and Comet Nucleus Formation

According to some models, the rich IS chemistry may have been kept in comets, and thus be the ultimate source of some prebiotic compounds on Earth. This issue is especially important when discussing how common is prebiotic material

Table 8.5. List of the 137 molecules detected in the interstellar or circumstellar medium (April 2003), after Wootten (2003) and PCMI website (Boulanger and Gérin). The reality of some detections (followed by “?”) is still under discussion, e.g. glycine $\text{NH}_2\text{CH}_2\text{COOH}$ (see text)

Molecules with 2 atoms:	AlF, AlCl, C_2 , CH, CH^+ , CN, CO, CO^+ , CP, CS, HCl, H_2 , KCl, NH, NO, NS, NaCl, OH, PN, SO, SO^+ , SiN, SiO, SiS, SiH, SiC, HF, SH, FeO?
Molecules with 3 atoms:	C_3 , C_2H , C_2O , C_2S , CH_2 , HCN, HCO, HCO^+ , HCS^+ , HOC^+ , H_2O , H_2S , HNC, HNO, MgCN, MgNC, N_2H^+ , N_2O , NaCN, OCS, SO_2 , c- SiC_2 , SiCN, CO_2 , NH_2 , H_3^+ , AlNC
Molecules with 4 atoms:	$\text{C}_4?$, c- C_3H , l- C_3H , C_3N , C_3O , C_3S , C_2H_2 , CH_3 , CH_2D^+ ?, HCCN, HCNH^+ , HNCN, HNCN, HNCN, HOCO^+ , H_2CO , H_2CN , H_2CS , H_3O^+ , NH_3 , c- SiC_3
Molecules with 5 atoms:	C_5 , C_4H , C_4Si , l- C_3H_2 , c- C_3H_2 , C_2H_4 , CH_2CN , CH_4 , HC_3N , HC_2NC , HCOOH, H_2CHN , $\text{H}_2\text{C}_2\text{O}$, H_2NCN , HNC_3 , SiH_4 , H_2COH^+
Molecules with 6 atoms:	C_5H , C_5O , C_5S , C_2H_4 , CH_3CN , CH_3NC , CH_3OH , CH_3SH , HC_3NH^+ , HC_2CHO , CH_2CHO , HCONH_2 , l- H_2C_4 , HC_4H , C_5N
Molecules with 7 atoms:	C_6H , CH_2CHCN , $\text{CH}_3\text{C}_2\text{H}$, HC_5N , HCOCH_3 , NH_2CH_3 , c- $\text{C}_2\text{H}_4\text{O}$, CH_2CHOH ,
Molecules with 8 atoms:	$\text{CH}_3\text{C}_3\text{N}$, HCOOCH_3 , CH_3COOH , C_7H , H_2C_6 , HC_6H , CH_2OHCHO
Molecules with 9 atoms:	$\text{CH}_3\text{C}_4\text{H}$, $\text{CH}_3\text{CH}_2\text{CN}$, $(\text{CH}_3)_2\text{O}$, $\text{CH}_3\text{CH}_2\text{OH}$, HC_7N , C_8H
Molecules with 10 atoms:	$\text{CH}_3\text{C}_5\text{N}?$, $(\text{CH}_3)_2\text{CO}$, $\text{CH}_2\text{OHCH}_2\text{OH}$, $\text{NH}_2\text{CH}_2\text{COOH}?$
Molecules with 11 atoms:	HC_9N
Molecules with 12 atoms:	C_6H_6 , $\text{C}_2\text{H}_5\text{OCH}_3$
Molecules with 13 atoms:	HC_{11}N

at the scale of our Galaxy, and the origin of chiral asymmetries (see Sect. 8.5.7 and the Chap. 3, Part II, by Cronin and Risse). However, an important point is to realize that completely different and contradictory models are still proposed in this field, none of them being devoid of problems, although some are favoured by the present authors. A very detailed account of the pros and cons of each model can be found in Irvine et al., (2000a).

Following Yamamoto (1991) we distinguish the *formation of cometary matter* from the formation of comet nuclei: to a large extent, the size increase of the icy bodies in the protosolar nebula is decoupled from their chemical evolution.

8.4.3.1 Cometary Matter Formation

The beginning of the accretion process is the most critical step in fixing the composition of cometary matter, as the small ($\sim$ micrometre-sized) particles have the highest surface/volume ratio and maximize both surface reactions and gas-grain interactions. Furthermore, being small bodies ($\sim 1-10$ km), comets did not experience substantial heating (either internal, radioactive, or external, by collisions); these processes could, however, have affected the largest KBOs, a few 100 km in diameter (see Stern (2003) for a discussion of collisions in the Kuiper Belt, McKinnon 2002 and DeSanctis et al., (2001) for models of KBO thermal evolution). The three main categories of models for the first phase differ by the degree of reprocessing of the original material.

- In the *interstellar model* of comets, cometary matter is formed very early, with no or little further processing, by sticking together *interstellar grains*, and condensing to ice volatile molecules from the original interstellar gas phase to grain mantles. This is essentially the model proposed by Greenberg (1982, 1998) and retained by Irvine et al., (1980, 1996, 2000), Yamamoto (1983, 1985, 1991), Despois (1992), Bockelee-Morvan et al., (2000). In this model ice is mostly amorphous, except in the outer layer of the nucleus heated by the Sun when the comet approaches perihelion. The strong points in favour of this model are the coexistence of oxidized (CO_2 , CO , SO_2) and reduced (H_2S , CH_4 , H_2S) species, as observed in IS clouds, the rough overall abundances correlation (see previous section), including complex species like HC_3N , NH_2CHO , HCOOCH_3 , and various indications of low-temperature processes (OPR, ortho:para ratios, in H_2O and other species, deuterium enrichment, presence of very volatile species like CO and CH_4). The syntheses occurred either in the interstellar cloud or during the protosolar phase, in the outer and cold part of the protosolar nebula, and bear testimony of ISM-like chemistry (low-temperature ion-molecule and surface reactions). Indeed the DCN/HCN and $\text{HDO}/\text{H}_2\text{O}$ ratios would mean in this hypothesis a formation temperature around 30–50 K (Meier et al., 1998), coherent with the OPR and CO volatility. Furthermore, this model is predictive to some extent, as the list of IS molecules proved to be a very good guide for the detection of new cometary species. The main problems are the presence in comets of crystalline silicates, not seen at present in the IS medium, and the deuteration level that, although high enough to imply that interstellar processes played a role, are much lower than the record values in hot cores.
- in the *pure protosolar nebula model*, or ‘*quenching*’ model (e.g. Prinn and Fegley 1989, Fegley 1993), the chemical memory has been fully or largely

lost. This model is similar in many aspects to the successful models of the inner solar nebula (terrestrial planet zone). The comet-forming material is supposed to have experienced high temperatures in a hydrogen-rich nebula in thermochemical equilibrium (temperatures above $\sim 500\text{K}$), which favours CO over CH_4 . The concept of “kinetic inhibition” of the CO to CH_4 conversion (Lewis and Prinn 1980, Prinn and Fegley 1981) leads to quenched thermochemistry: the hot-gas composition remains in chemical equilibrium when the gas cools down, until a quenching temperature below which reactions become too slow and the composition remains unchanged. This allows CO to be the major C-bearing volatile, despite the higher thermodynamical stability of CH_4 at low T . However, species predicted as abundant by the model are not observed (NH_4HCO_3 , $\text{NH}_4\text{COONH}_2$), the observed complex species like HCOOCH_3 are not predicted, and explaining the cometary volatiles’ chemical composition requires mixing contributions from IS gas, protosolar disk gas, and gas from the giant planet subnebulae in the right proportion (Prinn and Fegley 1989). Thus, an increasing complexity is required to explain even the gross features (e.g. oxidized/reduced species ratio) of the observed volatile composition.

- the *partially reprocessed IS matter model* is proposed by Lunine, Gautier and coworkers (e.g. Iro et al., 2003 and refs. therein). This aims at explaining several features of the Solar System besides cometary composition, such D/H ratios and rare-gas abundances in the giant planets. The solar nebula is initially rather hot (600K at 1AU) and cools down with the decrease of the disk accretion rate from 10^{-5} to $10^{-8}M_{\text{Sun}}/\text{yr}$. The nebula is supposed to be already isolated from the parent cloud (protostellar envelope). A key feature is that a significant fraction (depending on the heliocentric distance) of ice mantles of infalling interstellar grains vaporize through an accretion shock before reaching the nebula; the molecules then recondense as crystalline ice (as in the preceding pure protosolar nebula models), which incorporates minor species as gas clathrates or stoichiometric hydrates. The chemical composition of the gas is supposed to be unaltered, whereas the deuteration is diminished by interaction with the H_2 of the nebula. Gas composition and clathrate/hydrate stoichiometry control the final composition of cometary ices (clathrates are a class of solids in which small gas molecules like CH_4 , CO_2 or noble gases occupy “cages” made up of hydrogen-bonded water molecules; other species like NH_3 form solid hydrates with well-defined composition $(\text{NH}_3)(\text{H}_2\text{O})_n$). Another essential feature is turbulence across the disk that can transport the silicate grains processed (crystallized) in the vicinity of the Sun to the cold regions where the ice forms.

8.4.3.2 The Building of the Nuclei

In the continuous accretion process leading from $0.1\text{-}\mu\text{m}$ grains to km-sized bodies, there is a scale level, probably close to $1\text{--}10\text{m}$, after which the chemical com-

position of the matter is almost fixed (note, however, that very small molecules like CO could diffuse through the ice if warmed enough). At a larger size, most molecules are too deep inside to be affected by surface heating, energetic photons or particles (solar X or UV radiation, solar-wind particles and cosmic rays). Desorption processes and chemical reactions in the bulk of the ices, or on the probably large internal surface of this highly porous material, are limited, due to the very low temperature (a few tens of K to 150K at most). Occasionally, collisions occurring during the accretion process may heat locally the cometesimals. The accretion of particles to form comets (or icy planetesimals) has been thoroughly studied by Weidenschilling (1997); his simulations show the formation of comet-size bodies from micrometre-size grains up to bodies 80km in diameter in 2.5×10^5 yr.

8.4.4 Are Today's Comets Like Comets in the Early Solar System?

Were early comets similar to present ones? A given cometary nucleus is thought to have negligibly evolved since its formation, due to its low temperature. Exceptions may be a thin surface layer (due to particle and photon processing in the Oort cloud and the Kuiper Belt, and a few possible passages close to the Sun, see Mumma et al., 1993), and a slow volume loss of very volatile species (rare gases, CO). Occasional collisions may also have occurred in the Kuiper Belt and the Oort Cloud.

May chemistry inside the nucleus have altered the pristine composition of comets since their accretion? Navarro-Gonzalez et al., (1992) and Navarro-Gonzalez and Romero (1996) have studied theoretically the effect of ionizing radiation (cosmic rays and embedded radionuclides) on the cometary material and conclude that pristine organic compounds should not be altered except in the external layers of the comet. It is also predicted that an original enantiomeric excess of alanine would not be destroyed by racemisation during the decay of radionuclides. At the very most it should be attenuated, but comets could have contributed to the origin of chirality on Earth. The limitation of this work is that the kinetic data used in the calculations are for the liquid phase only, since no solid phase values are available; this may distort the result to some extent. The thermal racemization is a priori expected to be negligible at the comet low temperatures, but here also more theoretical and experimental work is required.

As stated before, the largest icy bodies (> 500km) in the Kuiper Belt might have for a limited time reached internally at some place conditions for melting to occur. This is, of course, a cause of chemical transformation.

If comets themselves are thought to have kept their original composition, their reservoirs have undergone at least a slow evolution in number and orbital parameters (e.g. Morbidelli et al., 2000). This affects directly the possibilities of delivery to the Earth.

8.5 Delivery to the Earth

8.5.1 Shooting Stars (Meteors)

When a comet passes close to the Sun, the gases that are produced by the sublimation of the ice drag along the dust particles and release them into the interplanetary medium. Comets are thus one of the two principal sources of interplanetary dust (interplanetary dust particles, IDPs, also called “meteoroids”). The other source of IDPs is the collisions between rocky objects: asteroids or asteroid fragments. The largest cometary dust particles remain confined in the vicinity of the comet orbit and spread progressively along this orbit, forming a ring-like swarm of particles. In fact, planetary perturbations deform the orbits, which are no longer closed but transform into a tightly packed set of successive turns. Due to small differences in ejection conditions, individual particles follow different orbits, which, however, are close one to another and form a long ribbon through the Solar System. When the Earth crosses such a swarm, we experience a shower of shooting stars: during the entry into the Earth’s atmosphere, particles larger than a size of about 1 mm produce, through heating, combustion and ionization of the air, a trail visible to the naked eye.

8.5.2 Overall Picture of Matter Delivery to the Earth

Several kinds of objects of the Solar System are likely to bring matter to the Earth: large-size bodies (asteroids or comets) responsible for more or less devastating impacts, small-size bodies (smaller than 10 m) called meteoroids in general, and interplanetary dust for the smallest; if a fragment of these bodies reaches the ground, it is called a meteorite (or micrometeorite). This delivered material will affect the land, the oceans, the atmosphere and the terrestrial biosphere.

In Fig. 8.16 we present an overview of the different kinds of matter delivered to the Earth, displayed according to size. Around 0.1 micrometres are particles that are probably grains coming directly from the local interstellar medium surrounding the Sun. Above 10 micrometres the range of interplanetary particles starts. The smallest ones, around 10 micrometres, are decelerated and stopped in the stratosphere, where they can be collected by airplanes: these are the “stratospheric IDPs” previously mentioned. The slightly larger particles reach the ground and are thus called micrometeorites. If one considers the delivered mass (Fig. 8.17) and not the number of particles, the distribution presents a peak towards 100 micrometres. In the size range 10–100 micrometres these particles produce in the atmosphere ion trails detectable by radar echoes; when the size exceeds about 100 micrometres (the value depending on the velocity of the particle) they appear in the visible as “shooting stars”. With even larger particles, ranging from centimetre to decametre, one enters the field of the traditional meteorites. A few tens of metres is roughly

Fig. 8.16. Overview of particles delivered to Earth, displayed according to their size

the size of the bolide presumed to be responsible for the Tunguska explosion, which occurred in Siberia in June 1908, and blew down the forest over 2000 km²; the nature of the object is still debated, see Shuvalov and Artemieva 2002, Jopek et al., 2002 for recent discussions. At around ten kilometres diameter lies the object (comet or asteroid – e.g. Jeffers et al., 2001 – recent data favours the latter hypothesis, e.g. Kyte 1998) which would have been responsible, 65 Myr ago, for producing the K-T sedimentary layer that marks in many places the boundary of the Cretaceous and the Tertiary geological periods, and of inducing massive species extinction, most notably that of dinosaurs (e.g. Frankel 1999; but the debate is still active, e.g. Stankel 2001, Facett et al., 2001, Le Loeuff and Laurent 2001). Such an impact occurs roughly every 100 Myr.

Fig. 8.17. Distribution in mass of the contributions to the Earth. The actual mean influx from the very largest objects is very uncertain. Rates are for present, and are believed to have been much higher in the first few 100 Myr of Earth's history (Steel 1996)

The micrometeorites represent a major contribution to the delivery of matter and especially of organic compounds and volatiles to the Earth; they may even be considered as a small prebiotic chemical reactor, as they contain many significant prebiotic compounds, including clays (catalyst), and insuring a natural confinement avoiding the dilution of the reactants (Maurette 1998, Maurette et al., 2000). The extrapolation of the micrometeoritic delivery in the past is highly uncertain, and ranges from conservative factors of 100 times the present rate to a high of 10^6 times.

8.5.3 Delivery of elements and Water

According to different estimations, extraterrestrial delivery to Earth over 4.5 billion years ranges from 10^{21} to 7×10^{23} kg. The lower limit of this amount that can be attributed to comets has been estimated to be 10% by Chyba et al., (1990).

• H_2O

It has been suggested that most of the water of the Earth oceans (1.4×10^9 km³, roughly 10^6 times comet Halley mass) could have been imported by comet impacts during a period of heavy bombardment (e.g. Delsemme 2000). Recent dynamical models of the early Solar System (Morbidelli et al., 2000), and recent measurements of the D/H in cometary water (to be compared with D/H in the oceans (SMOW)) (Dauphas et al., 2000) both lead to a maximum of $\sim 10\%$ of

water of cometary origin; the latter argument assumes that the D/H ratio measured in 3 comets is typical of all comets. Petit and Morbidelli discuss further the delivery of water in their chapter. An even lower limit (1%) on cometary H₂O in ocean water has been recently presented, from indirect arguments on rare gases and metals (Dauphas and Marty 2002).

- *Carbon*

Carbon in comets is roughly 18% by mass. Chyba et al., (1990) estimated that the contribution of comets to the terrestrial carbon inventory ranges from 2×10^{19} to 10^{22} kg; while the total budget of carbon on Earth is about 9×10^{19} kg. Even if uncertainties linked to the total amount of comets impacting the Earth since its formation are not lifted, those estimations show that they brought a significant amount of carbonaceous material. The extent to which organic molecules can survive cometary impact is discussed in Sect. 8.5.5.

- *Other Elements*

The other elements required for a protocell formation are also present on comets. Phosphorus, which is involved in the synthesis of sugars, has been detected by mass spectroscopy ($m/e = 31$) in grains of comet Halley by the PUMA mass spectrometer on board Vega 1. But its abundance is very low and detection may have been affected by interference from ions such CH₂OH⁺ (Kissel and Krueger 1987). However, analysis by laser probe mass spectroscopy of interplanetary dust particles (IDPs), whose cometary origin is probable, has led to the detection of PO₂ and PO₃ anions (Radicati-Di-Brozolo et al 1986). Ni and Fe have been detected in comet Ikeya-Seki and Halley.

8.5.4 Prebiotic Molecules from Comets?

Five families of compounds are considered to be the key prebiotic monomers required before starting a chemical evolution from which life would arise. These are amino acids (whose combinations lead to proteins), *purine bases* (adenine and guanine), *pyrimidines bases* (cytosine, uracil and thymine), *sugars* (whose association lead to RNA and DNA molecules), and *fatty acids* (cell walls). It is very interesting to note that, even if these compounds have not been detected in comets (maybe because of limitations in the sensitivity of telescopes, but also essentially because the synthesis of most of them requires liquid water), all but thymine can be easily produced in an early Earth environment from cometary precursors such as HCN, HC₃N, H₂CO and CO that have been firmly detected in cometary comae (Table 8.6).

Nevertheless, complex compounds of exobiological interest may also be present in comets. The only detection of adenine is a very tentative interpretation of PUMA's mass spectra of comet Halley's dust (Kissel and Krueger 1987). Such a molecule could be synthesized by HCN condensation without any

Table 8.6. Prebiotic syntheses from cometary molecules, from (Oró and Cosmovici 1997)

liquid water (Oro and Cosmovici 1997, Wakamutsu et al., 1966). Moreover, as already seen in this chapter, when ices relevant to the composition of interplanetary dust particles or comets are irradiated, complex molecules are formed, and among them, the simplest amino acid, glycine (Briggs et al., 1992). After an acid hydrolysis in water other amino acids, such as alanine, valine, proline and others, have also been identified (Bernstein et al., 2002; Kobayashi et al., 1995; Muñoz Caro et al., 2002).

8.5.5 Do Molecules Survive From Comets to the Earth?

Thus, comets may have imported prebiotic elements to early Earth, which, when mixed with liquid water, may have allowed the synthesis of all molecules thought to be necessary for the origin of life. To date, it is not clear as to whether the importation of such key compounds occurs at the simple stage of HCN, HC₃N, HCHO..., or more elaborate species such as amino acids, puric and pyrimidic acids and others. But before seeding the oceans, those compounds have to survive:

- if brought by small dust particles, they are subject in the interplanetary medium to the action of solar UV radiation, solar-wind particles and galactic cosmic rays; while the comet particle is slowed down and warmed up by the Earth's atmosphere, they must resist pyrolysis (destruction at very high temperature), and chemical reactions in the atmosphere. If they reach the ground, they should also survive the ensuing impact.
- alternatively, if the nucleus impacts directly the Earth, can the molecule survive the dramatic energy release?

Experiments conducted in space have shown that amino acids are quite unstable to solar UVs, but also that when somehow shielded in minerals, such as meteoritic powder, they can survive in space, and undergo no racemization (Barbier et al., 2002; Boillot et al., 2002).

The case of impacts of large bodies has been theoretically treated by Chyba et al (1990). It appears that organic compounds (even amino acids, if present) contained in cometary impactors of 100 to 200m in size could survive a collision with Earth in a 10-bar CO₂ atmosphere thanks to an efficient aerobreaking. Comparisons with Venus and Mars lead us to think that it is the most probable composition of the primitive atmosphere. The authors note in their conclusion that “*It is intriguing that it is exactly these dense CO₂ atmospheres, where photochemical production of organic molecules should be the most difficult, in which intact cometary organics would be delivered in large amounts*”. Indeed, organic syntheses are efficient in reduced atmospheres, and even in weakly reduced atmospheres such as that of Titan (N₂, CH₄), whereas they are very difficult in the oxidized environment that must have been the early Earth’s atmosphere.

On the experimental scene, Blank et al (2001) conducted a series of shock experiments to assess the feasibility of the delivery of amino acids to the Earth via cometary impacts. It appears that a large fraction of the amino acids do survive impacts. It has also been shown that some chemistry occurs, which leads to the formation of peptide bonds and new compounds including amino-acid dimers.

8.5.6 Comparison of Comets with Other Likely Sources of Prebiotic Molecules

Figure 8.17 displays the total mass delivered to the Earth for each mass interval (note that these intervals are logarithmic). Two main contributions show up, which are very different in nature: while the small particles could more or less softly deliver molecules to the Earth atmosphere and surface, large-size impactors bring also large quantities of matter but of course in a very different – discontinuous and catastrophic – mode. The very high temperatures reached by gases allow the synthesis of some compounds, as well as leading to their destruction as discussed in the previous section.

In the so-called intermediate atmospheres (in which the main gases are e.g. CO₂, H₂O, N₂ instead of NH₃ and CH₄) extraterrestrial delivery plays a major role in the total budget of prebiotic molecules (Chyba and Sagan 1996, Jenniskens et al., 2000). Table 8.7 gives in kg/yr the quantity of these molecules brought by various processes in the case of reducing and neutral (or moderately oxidizing) atmospheres. The large difference between these two types of atmosphere is noticeable, in particular for the synthesis of molecules by the shock waves induced by impacts. It should be noted that if many experiments have been undertaken in the laboratory on the chemical syntheses induced by electric discharges or energetic photons, the experimental studies relevant to the entry of particles in the atmosphere are very difficult and are still in a much less elaborate stage. The direct observation of molecules deposited by the meteors in the

Table 8.7. Major sources of prebiotic organics for two candidate early Earth atmospheres. The intermediate atmosphere corresponds here to a ratio $\text{H}_2/\text{CO}_2 = 0.1$. Note the considerably larger synthesis efficiency in the case of reducing atmospheres, which are those used by Urey and Miller in their experiments. In the more probable case of an intermediate atmosphere, external delivery is a major source of organics, as 30% come from IDPs. After Chyba and Sagan (1996) for the atmospheric processes, and Ehrenfreund et al., (2002) for the hydrothermal vents and comet impact delivery estimations

Source	Reducing atmosphere (kg/yr)	Intermediate atmosphere (kg/yr)
UV photolysis	1×10^{12}	3×10^8
Electric discharge	3×10^9	3×10^7
IDPs	2×10^8	2×10^8
Shocks from impacts	2×10^{10}	4×10^2
Shocks from meteors	4×10^9	8×10^1
K/T extrapolation	2×10^8	2×10^8
<i>Total (atmosphere)</i>	1×10^{12}	7×10^8
Hydrothermal vents	1×10^8	1×10^8
Comet impact delivery	1×10^{11}	1×10^{11}

atmosphere has been attempted during the recent Leonid shower (CN: Rairden et al., 2000, HCN: Despois et al., 2000).

8.5.7 Chiral Molecules: from the Interstellar Medium to the Early Earth?

Among the most intriguing questions related to the origin of life on Earth is the origin of the chirality for some key molecules: amino acids (configuration L) and sugars (configuration D).

Even if the cometary contribution were modest in mass, it might still have played a remarkable role, allowing via cometary dust particles or impact to directly forward to the early Earth some interstellar molecules, which could have played an important part in the apparition of homochirality (e.g. Bonner et al., 1999 and references therein). Indeed, an enantiomeric excess has been measured for some nonbiological amino acids in meteorites (see Cronin and Reisse Chapt. 3, Part II). Therefore, it is conceivable that an excess was also present for the biological amino acids (for which analysis is much more difficult due to the risk of contamination by terrestrial biomolecules). Such an excess could have been transmitted to the early Earth, and constitute an initial asymmetry later amplified by prebiotic chemistry (see Commeyras et al., 2004). The possible importance of this scenario is the fact that abiotic mechanisms able to produce nonracemic mixtures are very rare.

Which physical or chemical mechanism could then have led to a non-racemic mixture in the meteorites? Bailey and collaborators highlighted conditions favourable for the buildup of chiral asymmetry in the interstellar medium, and more especially in regions of star formation (Bailey et al., 1998, Bailey 2001). They detected the presence of circularly polarized infrared radiation in vast regions, which could easily include a whole Solar System in formation. This suggests the possible existence in these same regions of circularly polarized ultraviolet radiation, which still has to be detected. This circularly polarized ultraviolet radiation could lead to a differential synthesis or destruction of one enantiomer with respect to the other. If conditions similar to those in Orion prevailed at the time of formation of our Solar System, and if these interstellar molecules could actually be preserved till their integration into the matter of the protosolar nebula, this could be a plausible and relatively natural scenario for L/D symmetry breaking between enantiomers. This scenario seems at least as probable as the assumption of a fortuitous encounter of the protosolar nebula with a neutron star (a pulsar), also suggested as a likely source of polarized light. In comets, the search for non-racemic mixtures will require in situ chemical analysis or laboratory analysis of returned samples.

8.6 Ground-based and Space Exploration of Comets: New Developments

In the Solar System, several major space missions relate to comets. ESA is preparing the ROSETTA probe that will reach comet 69P/Churyumov-Gerasimenko (the previous target, P/Wirtanen, had to be abandoned as the launch was delayed); after a ten-year cruise, it will meet the comet and follow it for almost two years, during which a lander will be deposited on the surface. On the lander, the COSAC experiment (e.g. Rosenbauer et al., 1999) will perform a chemical analysis of cometary volatiles by gas chromatography of samples taken after drilling down to 20cm below the surface. With a detection limit of 10^{-5} – 10^{-6} with respect to water, more than 100 cometary species might be detected (Szopa et al., (2003) and Crovisier (2004)). The use of chiral columns will allow the measurement of enantiomeric excess.

A US mission, STARDUST, aims to collect thousand of cometary grains and bring them back to Earth. Another probe, CONTOUR, intended to tour 3 cometary nuclei, seems unfortunately to have been definitively lost. Table 8.8 summarizes all the space efforts directed towards comets in the next few years. As for ground-based observers, they have to wait for a new bright comet, like the recent comets Hyakutake and Hale–Bopp. In the near future, large ground-based telescopes, like the Atacama Large Millimeter Array (64 antennas, 12m in diameter, operating as an interferometer in a very good high altitude astronomical site in Chile), the Large Millimeter Telescope (50-m antenna), the Green Bank

Table 8.8. Recent, in progress and planned cometary missions (Nov. 2003)

Missions to comets	Launch	Dates	Events	Comet	Goal
DEEP SPACE 1 (NASA)	Oct. 24, 1998	Sept. 22, 2001	Flyby	P/Borrelly	Nucleus imaging, plasma
STARDUST (NASA)	Feb. 7, 1999	Jan. 2, 2004 Jan. 15, 2006	Flyby Return	P/Wild 2	Comet dust sample return
ROSETTA (ESA) (1)	Feb. 26, 2004	4/2014 11/2014 8/2015	Comet orbit Landing Perihelion	67P/Churyumov-Gerasimenko	Orbiter + lander Ice and dust in situ analysis
DEEP IMPACT (NASA)	Dec. 30, 2004	Jul. 4, 2005	Flyby + impact	P/Temple 1	500 kg projectile
CSSR (NASA) (2)	Aug. 2009	5/2017 3/2018 12/2018	Rendez-vous Comet depart Earth return	46P/Wirtanen	Comet surface sample return
Other Missions of interest	Launch	Results	Comet-related science		
SIRTf (NASA)	Aug. 2003	2003 →	Interplanetary dust disks (Exozodi)		
COROT (CNES)	June 2006	2006 →	Exocomets		
HERSCHEL (ESA)	Feb. 2007	2007 →	D/H in a variety of comets		
NEW HORIZONS (NASA)	Jan. 2006	2015/2016 2017/2023	Pluto flyby KBO flyby	Pluto + Kuiper belt object imaging	

(1) Rosetta Launch, foreseen 2003, has been rescheduled; previous target was 46 P/Wirtanen
(2) Project stage, not yet accepted; dates are indicative only.

Telescope (100m antenna) will bring higher sensitivity and space resolution. Out of the Solar System, the Corot mission should make it possible to detect comets around other stars (Lecavelier des Etangs et al. 1999).

8.7 Conclusion

Comets can bring down to the Earth elements like carbon, as well as water (in an amount that remains to be determined). Moreover, they contain simple organic molecules, and it is probable that they contain more complex ones. Thus comets are likely candidates for early Earth enrichment in prebiotic molecules, either through the dust particles they release – some of which end up encountering the Earth atmosphere – or through the atmospheric chemical syntheses – and possibly also through direct delivery – taking place when cometary nuclei impact the Earth. The same impacts may also strongly affect the later development of life, either locally, or on the scale of the planet.

Many questions are central to the current debates, which we hope will find a response in coming years, and for which space missions can bring important results:

- Where and when were formed the cometary matter, and then the comets?
- How close is cometary matter to interstellar matter?
- Do comets contain amino acids and other bricks of life?
- Do these molecules present an enantiomeric excess, or are they in racemic mixture?
- What is the precise budget of the cometary contributions to the Earth (fraction of the water of the oceans; fraction of carbon; fraction of prebiotic molecules)?
 - What is the global effect of comets on life, its appearance and its development?

Out of the Solar System, is the presence of an Oort cloud or a Kuiper Belt an exceptional characteristic of our Solar System or a banal fact among main sequence stars? Given the crucial part potentially played by comets in the origin and the evolution of life on Earth, it appears fundamental to know the probability for a star with habitable planets to be also surrounded by comets. New research topics thus develop on these *exocomets* (comets orbiting around other stars). The properties of the spectra of a close star, β Pictoris – one of the rare main sequence stars around which a disc has been detected – are currently convincingly interpreted as due to a constant infall of “evaporating bodies” on this star (Lagrange et al., 2000, Karmann et al., 2001, 2003). Much is then to be expected from ambitious space experiments under development, like the Corot mission (Baglin 2003), which should make it possible to detect directly comets, as well as Earth-size planets around a wide range of other stars (Lecavelier des Etangs et al., 1999, Bordé et al., 2003).

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