Chapter 2
Raw Materials

Abstract A presolar (molecular) cloud supplied dust and gas to the solar nebula ancestral to our solar system. The dust originated in different varieties of star including low mass stars at the end of their evolution and exploding supernovae. They include silicates and graphite. The gas is predominantly molecular hydrogen (H_2). Calcium-aluminium-rich inclusions (CAIs) and chondrules are found in meteorites which yield some of the oldest ages for the solar system. Polycyclic aromatic hydrocarbons (PAHs) are widespread; at low temperatures they may be transformed into more complex organic molecules by UV radiation.

The composition of the giant molecular cloud that was ancestral to our solar nebula is inferred from the residual nebula itself, from analogy with 'stellar nurseries' in other parts of the Milky Way and other galaxies, and from computer models. As with research on human origins when founded on genetic data, these procedures yield probabilities and not certainties; and, of course, the search is two-way: finding ancestors requires a sound grasp of the genotype (or its equivalent) of the descendants, in this case our particular ancestral planetary nursery, and of environmental change during the period at issue.

In the earliest phase of star formation, dense and cold cores of molecular clouds are supported against gravitational collapse by magnetic and turbulent as well as thermal effects. Magnetic fields within the cloud are enhanced by shearing caused by turbulence (Fig. 2.1). Theories that hinge on turbulence and on magnetic fields broadly agree in indicating that molecular clouds collapse on the way to forming stars on a time scale of ~10 Myr [26]. That molecular clouds form and fade in less than ~10 Myr is also suggested by evidence that the carbon monoxide (CO) in our galaxy is found mainly in its spiral arms, as this is the time required for cloud material to pass through the arms [35].

The collapse into a nebula is thought to take place once a core has attracted a critical mass of dust and gas from the parent cloud. Examples can be seen as the red clumps in the image of the Orion Molecular Cloud Complex (Fig. 2.1). The most prominent, to the lower left of centre, is the Orion Nebula, also known as M42 according to the 1774 catalogue of nebulae and star clusters by Charles

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C. Vita-Finzi, *A History of the Solar System*, DOI 10.1007/978-3-319-33850-7_2

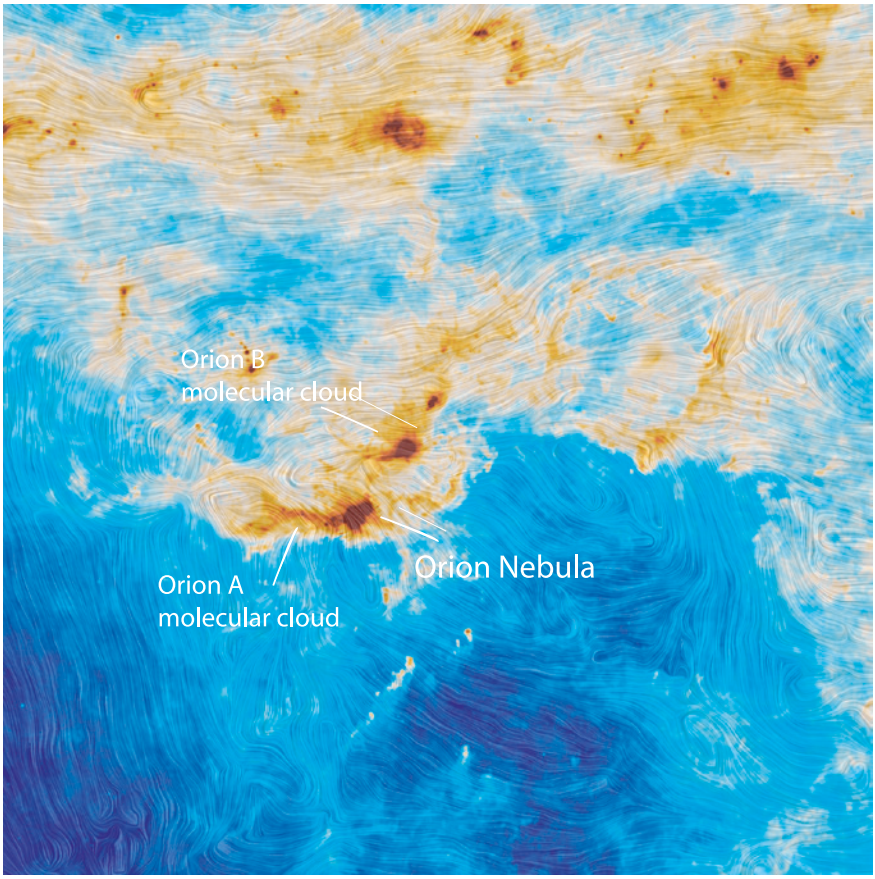


Fig. 2.1 Location of the Orion Nebula and of two molecular clouds. Image based on data from ESA's Planck satellite. Magnetic field orientation is shown by the texture, as in the upper part of the picture where the field is arranged roughly parallel to the Galactic plane. *Yellow* and *red areas* reflect denser and mostly hotter clouds containing larger amounts of dust and gas. Image roughly 40° across, Courtesy of ESA and the Planck Collaboration

Messier; at 1340 light years it is the nearest large star-forming region. The nebulae in turn generate protostellar discs each surrounding a protostar. Hubble has revealed 42 such protoplanetary discs or proplyds in the Orion area (Fig. 3.1). (The term protoplanetary nebula is confusingly also used for the penultimate stage in the evolution of an intermediate-mass star.)

Gas

Molecular clouds are dense and large enough to allow molecules—usually H_2—to form. They have temperatures in the region of 10 K (that is, a mere 10 degrees above absolute zero) and diameters of 20–200 parsecs (a parsec or pc corresponds

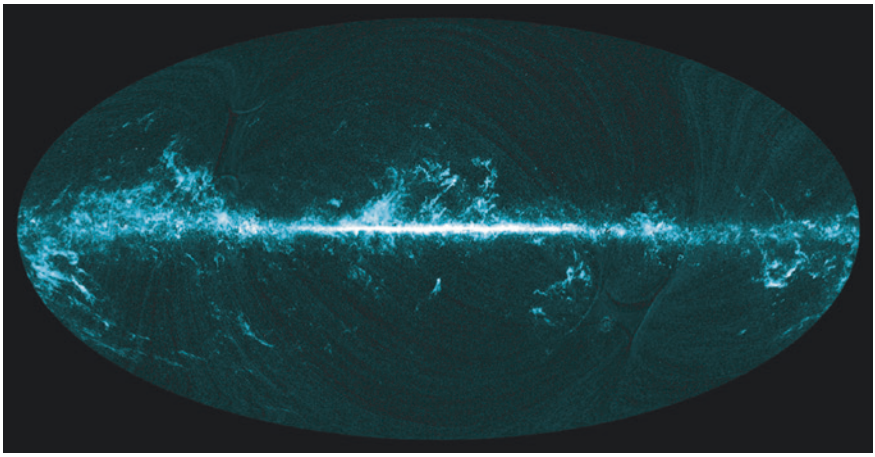


Fig. 2.2 Column density of molecular hydrogen in entire sky based on carbon monoxide probed by Planck's High Frequency Instrument (HFI). Courtesy of ESA/Planck Collaboration

to ~3.3 light years) and they measure up to 1 million solar masses. The discovery of molecular clouds in our galaxy has greatly progressed [23] to the point where chemical and physical composition, temperature and active processes may be observed in several examples. We are talking about features many light years distant, but the range of specimens—some 6000 in the Milky Way—is such that a composite history can be constructed, to the benefit of our parochial concerns, by relying on the principle (sometimes called ergodic) by which past states in one system are inferred and ordered from the present condition of several other analogous systems.

As cold H_2 does not emit much radiation we use other molecules for inspecting the clouds. CO has been found useful in this connexion as it emits several emission lines within the range of the frequency detectors on the Planck satellite (Fig. 2.2). Planck was launched by the European Space Agency in 2007 primarily to detect variations in the Cosmic Microwave Background radiation (CMB) in order to identify, among other things, changes in the wavelength of the CMB as a measure of expansion of the Universe. The CMB has been described as a snapshot of the oldest light in our Universe when it was just 380,000 years old. Molecular clouds are in the way of the CMB; their imaging was a byproduct of their analytical removal ('foreground subtraction'), not unlike the identification of individuals removed from images in successive Soviet encyclopedias.

A molecular cloud also shows up at infrared (IR) wavelengths because its molecular hydrogen is well mixed with about 1 % of dust consisting of silicates and graphites. Like interplanetary dust particles (IDPs) in general, those found in molecular clouds were formerly ignored, dismissed as a nuisance to observers, or appreciated for their collective delineation of the Horsehead Nebula (Fig. 2.3), but IDPs are now ascribed an important role in the evolution of galaxies, stars and planetary systems and in the synthesis of organic molecules.

By analogy with the Orion and other nebulae and their ancestral molecular clouds the Sun, like other stars, inherited its chemical composition from a nebula which was



Fig. 2.3 The Horsehead Nebula, part of the Orion Molecular Cloud complex, a dark cloud of gas and dust silhouetted against the bright nebula IC 434. *Credit and Copyright* Jean-Charles Cuillandre and Hawaiian Starlight (Canada-France-Hawaii Telescope in Hawaii) and NASA

itself derived from a molecular cloud. Hydrogen, helium-3 and helium-4, deuterium and lithium were produced by the nucleosynthesis associated with the Big Bang, whereas the metals (a term used by astronomers for elements heavier than helium and hydrogen) were created by stellar nucleosynthesis in stars which, on completing their stellar evolution, returned their material to the interstellar medium. Since the Sun formed, some of the helium and metals have settled under gravity from its photosphere (or visible surface); the protostellar Sun's composition, to judge from that of primordial (C1 chondrite) meteorites, had a higher metal content than today's 1.49 % [22].

Dust

IDPs may thus include grains whose origin antedates our solar system. These presolar grains generally consist of silicates and graphites emitted into interstellar space by stars within which they been generated by nucleosynthesis, that is to say the production of novel chemical elements by nuclear fusion, a process which sometimes imprinted the grains with a distinctive isotopic signature.

The isotopic analyses that reveal their history are made on grains as small as 1 μm, that is to say a thousandth of a millimetre, but they reveal a wide range

of distinctive sources. They include Asymptotic Giant Branch (AGB) type stars, which are at a late stage of their evolution and emit substantial winds from which grains condense, and supernovae, which are explosions of a white dwarf in a binary star system or of a massive star which has exhausted its nuclear fuel [4]. In this way laboratory studies have added an important dimension to astrophysical observation and greatly extended the range of solar system history.

The silicates, which include crystals of two minerals commonly encountered on Earth, enstatite ($MgSiO_3$) and forsterite (Mg_2SiO_4), are viewed as a fundamental building block of solar systems. They have in fact been detected around both young and old stars by the Infrared Space Observatory (ISO) [8] as well as in chondritic meteorites and comets. Silicate dust absorbs UV and visible light that is emitted by stars in the vicinity, and emits it as IR radiation. The two indices are linked, as the extremely low temperatures that prevail in the cloud may favour the precipitation of CO on the dust grains.

As regards the graphite component, analysis of IDPs coupled with chemical modelling and astrophysical considerations show it was contributed by outflow from AGB stars of about 1.1–5 solar masses ($M_\odot$) [5]. In other wornebula and then trapped in clathratesds we now have an idea of the dimensions as well as the evolutionary stage of the source stars, an integral part of attempts to trace 'the timing and tempo of the transformation of the disk of gas and dust to the solids that formed the planets' in our solar system and by extension in other solar systems [11] and the extent to which stellar material is recycled from earlier generations.

The IR emission that betrays the presence of dust also reflects any heating by ultraviolet (UV) radiation and cosmic rays, and hence the level of resistance by the cloud to gravity. Gravitational potential energy was invoked in the 19th century, notably by Lord Kelvin and Hermann von Helmholtz, to power the Sun (leading to a maximum age for it of 31 Myr). In the present context the concept enters into the Jeans length (λJ), a measure of the relative strength of the gravitational force and the resisting gas pressure.

Many molecules besides H_2, carbon and silicates are found in nebulae. They range from simple molecules such as ammonia (NH_3) and CO to complex organic molecules. A spectral line survey of Orion nebular clouds by the Far Infrared (HIFI) instrument on ESA's Herschel satellite (launched in 2009) revealed (Fig. 7.1) water and sulphur dioxide (SO_2), and several organic compounds, among them formaldehyde (CH_2O), methanol (CH_3OH), dimethyl ether (CH_3OCH_3) and hydrogen cyanide (HCN). Polycyclic aromatic hydrocarbons (PAHs) have also been detected. The organic molecules have been described as 'potential life-enabling organic molecules'; the processes that might have fulfilled this promise to the ultimate benefit of terrestrial life are discussed in Chap. 7.

Ices

Ices are thought to make over half of the material which condensed in the solar nebula at about 4 AU from the Sun, notably the ices of water (Fig. 2.4), carbon dioxide, ammonia and methane [12]. As we have seen, dust and gas have been

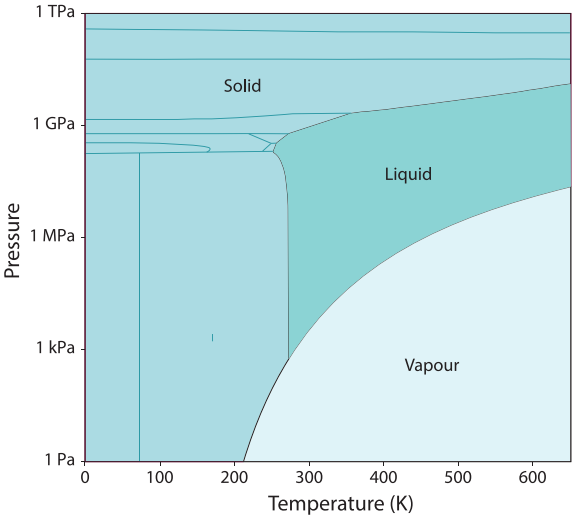


Fig. 2.4 Phase diagram of water to illustrate how minor changes in temperature or pressure may produce major changes in behaviour, most familiarly at the triple point in the lower centre but more subtly with the 18 known ices. Phase transitions have to be taken into account when considering such matters as the role of convection on the larger icy moons. Courtesy of various sources

intimately associated from earliest times; gas-phase molecules froze out on dust particles to form ices as interstellar material evolved into molecular clouds.

The term snowline defines the point beyond which water ices could exist in a protostellar disk around a star. For the young Sun it would have been at ~2.7 AU.

Methane is thought to have formed in the interstellar medium before it was incorporated in the nebula and then trapped in clathrates ($CH_4 \cdot 7H_2O$) as the disk cooled, and embodied in comets, icy bodies and giant planets. Titan too may hold primeval methane clathrate whereas on Earth it is mainly biological in origin and on Mars it may derive from hydrothermal reactions with olivine-rich material [17, 29].

Two important present-day reservoirs for ices are the disk-shaped Kuiper-Edgeworth Belt, just beyond the orbit of Neptune at 30–1000 AU, and the Oort Cloud, a spherical shell which surrounds the Solar system and extends from 20,000 to 50,000–200,000 AU from the Sun (Frontispiece). The former hosts 10^8–10^9 or so short-period comets, including Jupiter-Family comets (orbital period (p) < 20 year) and Halley-type comets (p 20–200 year), as well as the dwarf planets Pluto, Haumea and Makemake. The Oort cloud holds perhaps as many as 3–5.10^{12} predominantly icy bodies and is the source of long-period comets (p > 200 year) such as Hale-Bopp.

The dimensions of the Oort Cloud and to a lesser degree the Kuiper Belt are debated: both are hypothetical zones for which evidence has been understandably slow to accumulate. The original formulation for the eponymous cloud by J.H. Oort (following E. Öpik) in 1950 depended on orbital data for 19 comets, a database expanded by 1978 to 300 [7]. The Kuiper Belt was first substantiated in 1992–3 when two bodies were detected at 50 AU [6]. That figure now stands at over 1000 Kuiper Belt Objects.

Although the nuclei of comets are widely thought to contain ‘the most pristine material’ in the solar system it is not certain whether this protosolar interstellar dust has remained totally unmodified rather than being evaporated before

incorporation in comets [21]. But there is little doubt that Oort bodies represent icy planetesimals which formed among the giant planets in the outer part of the protoplanetary disk, that is they consist of reworked primeval material.

In order to clarify the sequence of events that led to the ubiquity of water in the solar system—in oceans, icy moons, the giant planets and cometary ice—we must turn to the D/H ratio (^{2}H or deuterium relative to H or protium), a value that combines ancestry with upbringing as it reflects environmental changes and also points to plausible evolutionary sequences.

Deuterium is a product of Big Bang nucleosynthesis, with the primordial ratio with hydrogen-1 (D/H) estimated on the basis of theoretical models as 2.61×10^{-5} (0.0000261) [33]. Modelling suggests that the conditions that prevail in protostellar disks are not conducive to the production of high levels of 'deuterated' water, as the ionization or levels that are derived from galactic cosmic rays are inadequate, and a major source must therefore be presolar, that is to say derived from interstellar sources via the molecular cloud [10]. This line of argument boils down to stating that a source of water must have been available to all candidate solar systems.

The search for a source of the Earth's water inevitably considered comets as a possible option and this became credible when astronomers were able to quantify the incidence of cometary infall from space imagery, but the isotopic composition (D/H or H_2/H) of four comets including Halley's (1P/Halley) seemed to conflict with this suggestion [2] as it is very different from the mean value for the Earth's oceans (Figs. 2.5 and 2.6). The organic load of Halley's comet [9] would

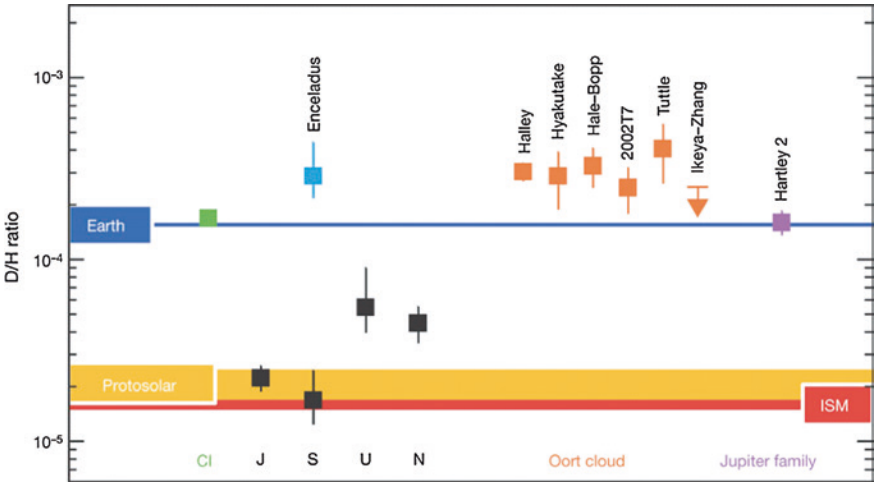


Fig. 2.5 D/H values for Oort-cloud comets (orange squares, the atmosphere of the giant planets Jupiter (J), Saturn (S), Uranus (U) and Neptune (N) (*black symbols*), water in the plume of Saturn's moon Enceladus and in CI carbonaceous chondrites (*light blue* and *green symbols*, respectively). Earth's ocean (*blue line*), protosolar value, local interstellar medium (ISM). Error bars 1σ. After Hartogh et al [15] with permission

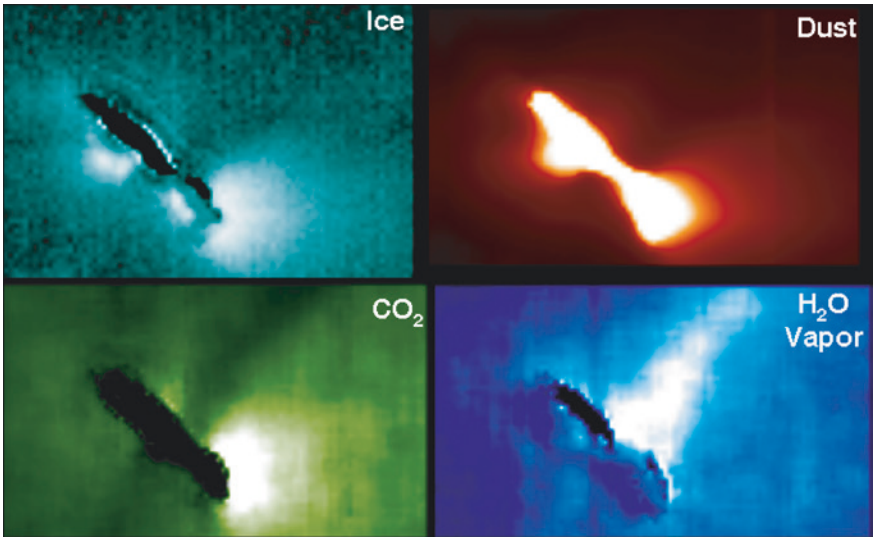


Fig. 2.6 Infrared scans of Comet 103P/Hartley 2 by NASA's EPOXI mission spacecraft show CO_2, dust and ice being ejected from one location and water vapour from another. 4 November 2010. Courtesy of NASA/JPL-Caltech/UMD

consequently be a poor guide to the likely cometary contribution to an extraterrestrial origin of life on Earth.

However, Herschel measurements on the Jupiter-family comet 103P/Hartley 2 show a D/H ratio similar to that of the Earth's oceans [2]. This complicates the issue of the provenance of Jupiter-family comets in the disk but revives the case for a cometary origin of the Earth's water rather than meteorites originating in protoplanets in the outer asteroid belt [28].

Moreover, samples from the Kuiper Belt comet 81P/Wild 2 that were returned to Earth in 2006 by the Stardust mission include some grains from other stars, but the bulk of the solids are solar system materials which formed over an extended time period at both the highest and the lowest temperatures in the early solar system, perhaps originating the hot inner regions before being transported beyond the orbit of Neptune. They include fragments of CAIs and also tungsten, molybdenum, ruthenium, and other refractory materials.

CAIs and Chondrules

Calcium-aluminium-rich inclusions (CAIs) are found in chondritic meteorites—that is to say primitive meteorites characterised by the spherical bodies known as chondrules (Fig. 2.7)—which yield some of the oldest ages for the solar system. Chondrites are a mixture of presolar and solar nebula materials and also asteroidal debris, as chondrules continued to form after early planetesials had formed and collided [32].

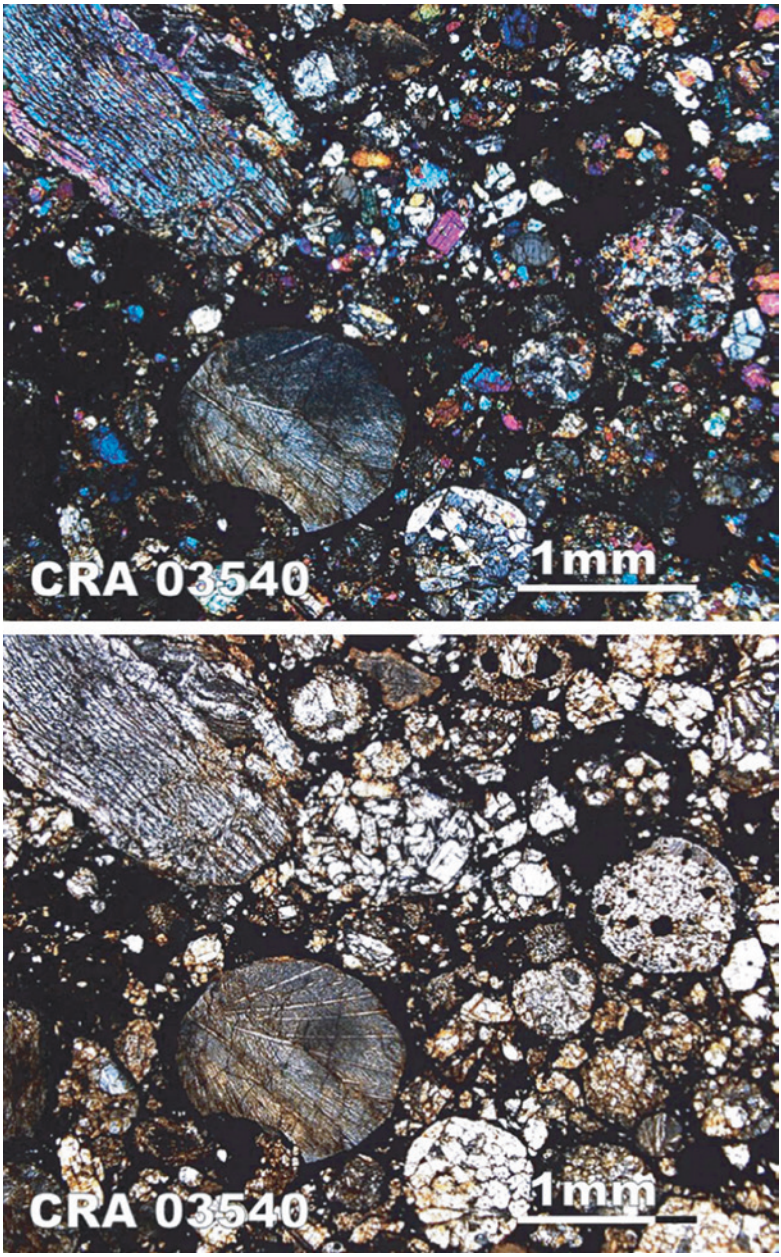


Fig. 2.7 Thin section under cross-polarised light (*upper*) and plane-polarised light (*lower*) **of the L3 chondrite** CRA 03540 **showing distinctive chondrule textures:** barred olivine type (*upper left corner*), radial pyroxene type (*lower centre*), **and** porphyritic type (near the *scale bar*). Courtesy of NASA

CAIs are not restricted to the CV chondrites where they were first reported and the basis for the original studies, the Allende meteorite, is now known to have undergone substantial postaccretion reprocessing [27]. Isotopic studies suggest that CAIs formed near the young Sun and were latter scattered to different accretion sites. They solidified from partly to completely molten material, perhaps more than once, interacted with gases or liquids, and were reheated by shock events.

Chondrules are spherical bodies typically measuring several microns (μm) and composed of olivine or pyroxene or both. They are thought to have formed from molten or partly molten material 1–3 Myr after the CAIs although their ages overlap [14]. The melting was accomplished by flash heating followed by cooling slow enough to favour crystal growth. Suggestions for the process include solar nebula lightning, sudden exposure to sunlight, collision between asteroids, shocks resulting from gravitational instability within the nebula and planetesimal bow shocks.

On balance the thermal histories indicated by the chondrules favour melting driven by gravitational instability associated with spiral arms in the solar nebula [13]. Even if the collisional mechanism prevailed and involved several generations of planetesimals primary chondrule formation it would have lasted a mere 2 Myr whereas CAI formation could have lasted several 10^5 years [24].

Some of the larger (>2 μm) dust fragments in Comet 81P/Wild 2 resemble chondrules in their mineralogy, which accords with the claim that they formed in the inner solar system; the finer material has a more complicated signature and could include dust from the outer nebula or diverse conditions in the inner nebula [30]. The comet has been in orbit beyond Neptune since it formed and, unlike some asteroids whose composition has been 'compromised' by heating and wetting, apparently retains a faithful record of early solar system conditions.

Chondrites of the CI group contain up to 20 % of water and minerals that have been altered in the presence of water (Fig. 2.8) such as hydrous phyllosilicates similar to terrestrial clays, oxidized iron in the form of magnetite, and sparsely distributed crystals of olivine scattered throughout the black matrix. In addition,

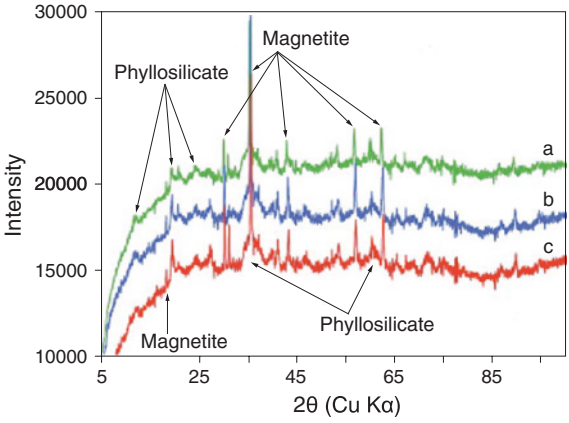


Fig. 2.8 PSD-XRD patterns for the CI chondrites Alais (*green*), Orgueil (*blue*) and Ivuna (*red*), showing the main identified phases. Alais and Ivuna are offset on the Y-axis for clarity. After King et al [20] with permission

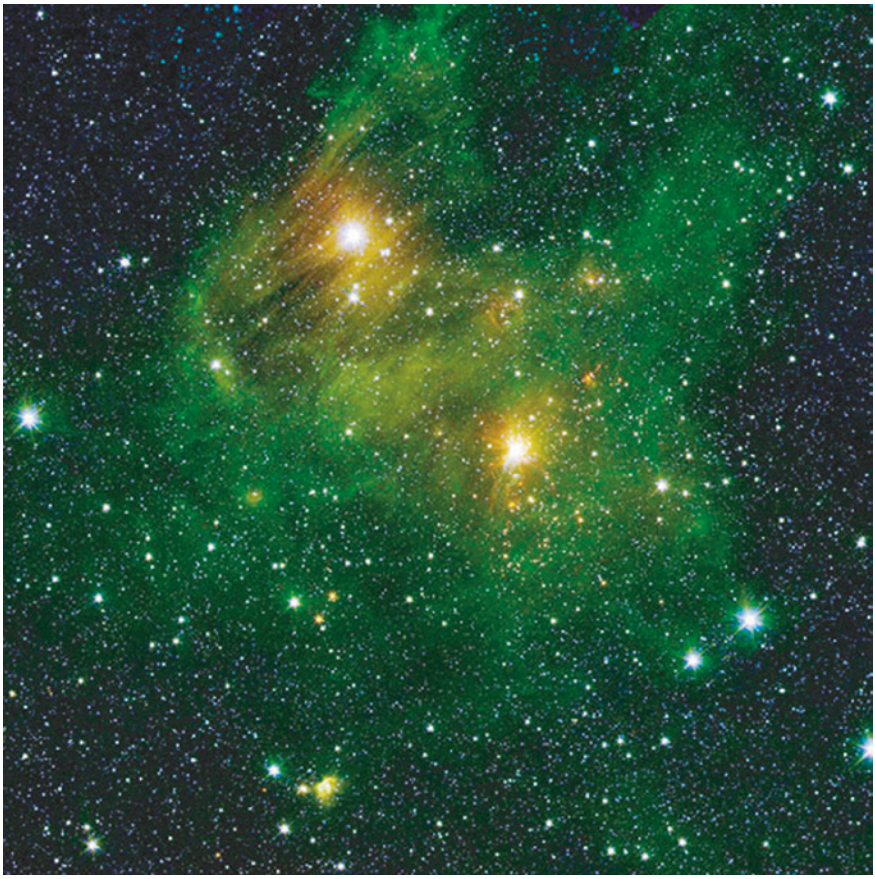


Fig. 2.9 Two bright stars illuminate a mist of PAHs in this image, a combination of data from Spitzer and the Two Micron All Sky Survey (2MASS). Courtesy of NASA/JPL-Caltech/2MASS/SSI/University of Wisconsin-Spitzer

they contain certain amounts of organic matter like amino acids, which are of course the building blocks of life on earth.

The D/H value for water locked in carbonaceous chondrites reflects an origin in the inner early solar system [18] but, as the chondrules of CI chondrites were never heated above 50 °C during their formation, there must have been an active interplay between outward turbulent diffusion and inward advection of the water within the disk. Low values would have prevailed in the hot inner disk and higher values in the outer disk but, especially in the early stages of disk evolution, D/H values rose again in the outermost disk as water that was incorporated early in the disk's evolution was pushed out. Thus Oort cloud comets that formed early would have D/H values similar to those of the giant planets. In short, the early solar nebula was not fixed in composition, as it received fresh contributions from the molecular cloud as well as undergoing internal reorganisation [36].

PAHs

Polycyclic aromatic hydrocarbons (PAHs) appear to be abundant in the universe. For some years a mysterious set of emissions in the infrared was detected around many celestial objects in our galaxy and in other galaxies. In 1985 they were tentatively identified, at least in part, with large PAHs [2], ubiquitous component of organic matter in space (Fig. 2.9), having been identified in interstellar graphite grains, protoplanetary nebulae, circumstellar disks, IDPs comets and meteorites [34] as well as in planetary settings including the upper atmosphere of Titan. Abundant PAHs were detected on fresh fracture surfaces in Martian meteorite ALH84001, which was found in Antarctica in 1984 and displays carbonate globules and a number of isotopic and morphological features which are deemed organic in origin [25] (see Chap. 7). Cosmic ray exposure data suggest ALH84001 was in space about 16 Myr before landing 13,000 years ago, but the PAHs in ALH84001 were at concentrations 10^3–10^5 times greater than in Greenland ice dating from the last 400 year and show every indication of being 'indigenous' to the meteorite. PAHs may form when complex organic substances are exposed to high temperatures or pressures; they consist of as many as 6 fused benzene rings containing only carbon and hydrogen [3].

From being suspected of contributing to infrared emission spectra, PAHs have emerged as playing a key role in photoelectric heating of interstellar gas. And there is general acceptance that they contained ~10 % of the carbon in the interstellar medium (~40 % being in the form of dust) when the protoplanetary disk began to collapse [12] and that they first formed as early as two billion years after the Big Bang.

Laboratory studies suggest that interstellar conditions can transform PAHs into more complex organic molecules [15] by hydrogenation and oxygenation at temperatures as low as 5 K when subjected to UV radiation. This may account for the lack of PAH signatures in interstellar ice.

More important, the UV flux in protoplanetary or circumstellar environments is far higher than in dense molecular clouds. A possible route to greater complexity is via pyrimidine, also carbon-rich, which is suspected of condensing on the surfaces of cold icy grains in dense molecular clouds. If subjected to UV (see Fig 4.1) radiation in the laboratory, pyrimidine in ice rich in H_2O (as well as methane, ammonia or methanol) may yield uracil, cytosine and thymine, 'informational subunits of DNA and RNA' [31]. Nucleobases are of course found in several meteorites including the carbonaceous chondrites Murchison and Orgueil. The debate over the timing and setting of the origin of life [19] refuses to focus down.

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http://www.springer.com/978-3-319-33848-4

A History of the Solar System

Vita-Finzi, C.

2016, XII, 100 p. 54 illus., 43 illus. in color., Softcover
ISBN: 978-3-319-33848-4