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Introduction

1.1 The Molecular Universe

Over the last 20 years, we have discovered that we live in a molecular Universe: a Universe with a rich and varied organic inventory; a Universe where molecules are abundant and widespread; a Universe where molecules play a central role in key processes that dominate the structure and evolution of galaxies; a Universe where molecules provide convenient thermometers and barometers to probe local physical conditions. Understanding the origin and evolution of interstellar and circumstellar molecules and their role in space is therefore key to understanding the Universe around us and our place in it and has become a fundamental goal of modern astrophysics.

After the discovery of the first diatomic molecules some 100 years ago, the preeminent astrophysicist of his time, Sir Arthur Eddington, lamented that “atoms are physics, but molecules are chemistry.” Ever since, astrophysicists rued the moment that simple physical formulas had to give way to complex chemical solutions in a molecular Universe. To molecular astrophysicists, though, interstellar molecules provide a tool to probe macroscopic aspects of the Universe, whereas the harsh environment of space offers unique insight in microscopic processes controlling excitation and relaxation of isolated molecules. The chapters in this textbook introduce the reader to both aspects of molecular astrophysics.

The field is heavily driven by new observational tools that have become available over the last twenty years; in particular, space-based missions that have opened up the IR and submillimeter window at an ever accelerating pace. Furthermore, our progress in understanding the molecular Universe is greatly aided by close collaborations between astronomers, molecular physicists, astrochemists, spectroscopists, and physical chemists who work together in loosely organized networks. Together these groups provide the molecular data that is required to turn astronomers’ pretty pictures into a quantitative understanding of the Universe around us. One focus is of course on understanding the unique and complex organic inventory of regions of star and planet formation that may well represent the prebiotic roots to life. A second focus is to appreciate the role of molecules in the evolution of the Universe. The third area to consider is the use of molecules to study the characteristics of the Universe, including physical conditions and the dynamics of, in particular, regions of star and planet formation but also stellar outflows and explosions, the interstellar medium of galaxies, and toroids around active galactic nuclei. In this chapter, we will introduce these three aspects in order to highlight the many uses of molecular astrophysics in astronomy. This will start with an overview of the rapid developments in astrobiology and the prebiotic origin of life, continue with examples of the use of molecules to study the Universe, and conclude with a bird's eye view of astrochemistry.

1.2 Astrobiology

1.2.1 Exoplanetary Science

Some 25 years ago, only nine planets were known and they were all part of the solar system. While some people have in the mean time mislaid one of those, at the moment of writing a variety of techniques have led to the discovery of some 3,800 additional planets (and counting) around distant stars. The field of exoplanetary studies was opened up by radial velocity studies in the mid 1990s that detected the presence of planets based on their small gravitational "tug" on the line position in the spectrum of the host star. The NASA Kepler mission revolutionized the field with the transit method that infers the presence of planets from small dips in brightness of the host star when planets pass in front of it. A number of other techniques, including direct imaging, have added a handful of planets. As a result, we now know that essentially every star has a planetary system. There are some hundred billion stars in the Milky Way and there are some hundred billion galaxies in the Universe accessible to us. That makes for a truly staggering number of ten thousand quintillion planetary systems. While the architectures of these planetary systems are not well known – as this is fraught with systematic issues – many of the detected planets are "hot-Jupiters": gas giants close to their host star that are quite inhospitable. We are, of course, particularly interested in planets like the Earth. The Kepler mission has taught us that one in every six stars like the Sun has a planet like the Earth at a distance where water would be liquid. That means that there are more than seven billion Earth-like planets in the habitable zone of their star and about one billion in the habitable zone around stars like the Sun. It is clear that the Universe provides ample opportunity for life to form.

1.2.2 Microbiology

While in the past we thought that life required very benign conditions, we have now discovered that life can thrive in a wide range of conditions. Indeed, extremophiles – organisms that thrive under extreme physical or chemical conditions – are very much part of the Earth's biosphere. Cyanobacteria give the Grand Prismatic Pool in Yellowstone National Park its much photographed color palette. These bacteria have no issue living in the scalding temperatures of this environment – or so we thought – yet they do. Likewise, the subglacial lakes in the Antarctic are home to a rich ecosystem. Bacterial colonies have built stromatolites reminiscent of billion-year-old fossils of early life on Earth.

These bacteria derive their energy not from the sun but from geothermally released chemicals. In the 1970s, tubeworm colonies were discovered living on and around hydrothermal vents on the deep ocean floor where mineral-rich, hot water is released through "chimneys." Life is made possible here by microbes that use chemosynthesis to convert chemical energy available in the disolved minerals to nutrients, and in the end this feeds the whole ecosystem. Life has also been discovered deeply buried in the driest spot on Earth, the Atacama desert in Chile. Here, bacteria have been discovered attached to hygroscopic salt pellets, a few meters deep in the ground. While it is not clear that these organisms developed here, for sure, they adapted well to these extreme conditions. Our definition of the habitable zone may well have been guided too much by the disclaimer "life as we know it."

1.2.3 Paleobiology

Some 4.567 billion years ago, dust particles coagulated in the early solar nebula and these aggregates were subsequently processed by energetic events to form the calcium-aluminum inclusions (CAI): one of the constituents of carbonaceous meteorites. These are the oldest objects known in the solar system: fossils of preplanet-forming events in the solar nebula. These CAIs were incorporated into planetesimals within a million years of their formation. The Earth (and other terrestrial planets) was put together through collisions of such planetesimals and larger embryonic bodies over a period of $\simeq$10 million years. During this assemblage process, the Earth was covered by a magma ocean. In this Hadean period, some 25–30 million years after the Earth was formed, the moon was created in a glancing collision of a Mars-sized impactor: the last one of these giant impacts. This resulted in very high temperatures, enduring magma oceans, and a silicate cloud cover. The runaway greenhouse effect lasted until the CO_2 in the atmosphere was subducted, perhaps some 100 million years later. Small (10's of microns) zircon crystals recovered from the Jack Hills in Australia are the oldest known crust and date back to 3.9–4.2 billion years ago. With the formation of a crust, a hydrosphere could develop and evidence for oceans dates back to this same period. Hence, life could start to take hold of the planet very early. The late heavy bombardment – when the solar system's architecture was rearranged due to a resonance between Jupiter and Saturn and a "flood" of planetesimals impacted the terrestrial planets – occurred 3.7–3.9 billion years ago, some 700 million years after the first rocks formed in the solar system. If life existed, the resulting impacts may well have "sterilized" the Earth.

Searches for the oldest fossils are highly contentious. Fossilized stromatolites discovered in Western Australia and dating back to $\simeq$3.5 billion years ago are widely accepted as genuine and attest to flourishing microbial life at that time. There are more controversial claims of "biological" activities preserved as structures in even older ($\simeq$3.7 billion years) rocks, which would have biology take off almost immediately after the end of the late heavy bombardment. But even $\simeq$200 million years is the equivalent of a blink of an eye in terms of starting life. It seems that as soon as conditions on the early Earth were conducive, life just took hold.

1.2.4 A New Paradigm

Thus, each of these fields – astronomy with the presence of countless planets like the Earth; microbiology with extremophiles everywhere; paleobiolology with fossiled life dating back to as far as we can trace – has undergone a revolution turning preconceived notions upside down. In essence, this is the logical conclusion of the Copernican and Darwinian revolutions and, together, they have changed our perception of the Universe and our place therein. The new paradigm is that the Universe teems with life. This has given rise to the new field of astrobiology where astronomy, planetary sciences, molecular physics, spectroscopy, chemical physics, geochemistry, geology, atmospheric sciences, biochemistry, and biology meet and mate.

1.3 The Prebiotic Origin of Life

1.3.1 The Earth's Volatile and Organic Inventory

From a molecular astrophysics point of view, one key aspect of astrobiology is the study of the inventory of volatiles such as water and organics available to newly formed terrestrial planets and our moons. This is a very active area of research and our insights are in a state of constant flux. Even the total water content of the Earth is controversial with estimates ranging from 0.5 to 2.5 times the water in the oceans. Presently, there is an active water cycle between the Earth's mantle and the surface where water is released by volcanic activity from the mantle and subducted in the form of hydrated sediments with a cycling timescale of $\sim 10^9$ yr. The carbon content of the Earth is equally uncertain with some researchers placing much of the Earth's inventory of carbon in the iron core. That carbon is of course not accessible and plays no further role in biochemistry. However, this does affect discussions on the carbon budget of the Earth and the processes that played a role in its origin. From the accessible carbon, some 90% may be stored in the mantle – as carbonates or graphite/diamond/carbides rather than dissolved in minerals – and cycles on a similar timescale as water.

Taking the solar system as our measure, the Earth could have derived its volatiles and organics from multiple sources. First, the last stages of the build up of the earth from smaller bodies are characterized by collisions of moon-sized bodies – embryos – and are highly stochastic in nature where "feeding" occurs over a wide range of initial radii (Figure 1.3). Hence, while, following the strong temperature gradient, embryos in the planetary disk may have started with a clear gradient in volatility and organic content, the "feeding-zone" of terrestrial planets in the habitable zone will include volatile- and organic-rich embryos. The heat released during this collisional formation process would have produced a steam atmosphere. Much of the water would dissolve in the magma ocean, only to be outgassed when the crust – mainly anhydrous minerals such as olivine and pyroxene – formed. For the Earth, this initial stage ended with the giant, moon-forming collision, which could have sheared off much of the initial water atmosphere but have left much water dissolved in the magma ocean.

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Second, while this discussion has focused on planetesimal accretion as the main driver of planet formation, pebble accretion may provide a relevant alternative. Observations show that protoplanetary disks contain a large reservoir of millimeter- to centimeter-sized grains. Such pebbles may be the natural outcome of the dust coagulation process that is limited by bouncing or fragmentation. Observations show that pebble disks extend to some 100 AU and, as these pebbles will drift inward, they can provide a source of volatile- and organic-rich material for growing planets in the inner regions (Figure 1.4).

Third, the late heavy bombardment provides another scenario for the delivery of volatile and organic rich material to the inner terrrestrial planets. The mean-motion resonance between Jupiter and Saturn rearranged the solar system, flipping Neptune and Uranus around and dislodging the cometary bodies in the outer solar system, some of which impacted the Earth–moon system, producing, among others, the prominent lunar basins and delivering volatiles to the Earth (Figure 1.5). This so-called late veneer delivered some 0.5% of the Earth's mass in the form of cometary bodies and much of this in the form of water ice and organics.

Hence, the volatile and organic inventory of the Earth has a diverse origin, where materials derived from a diverse set of locations were delivered by a variety of methods to the Earth (Figure 1.1). All may have contributed at some level. As will be discussed elsewhere in this book, the temporal evolution of a system may leave its imprint in the isotopic composition, reflecting, for example, a difference in zero-point energy that dominates the chemical exchange between different reservoirs in a kinetic (low temperature) setting. Alternatively, selective photodissociation may play an important role in the isotopic composition. These aspects have been used to assess the role of these different volatile/organic reservoirs for the Earth, and the isotopic composition of, e.g., H and N suggests that asteroidal delivery was a major contributor for the Earth (Figure 1.2) but this issue is not fully settled as we do not have a comprehensive inventory of the isotopic signature of relevant bodies.

1.3.2 Exogenous versus Endogenous Prebiotic Chemistry

Meteorites impacting the earth derive from collisional processes in the asteroid belt and hence their study may teach us much about the composition of their parent bodies. Of particular importance are CM and CI carbonaceous meteorites, which contain, by weight, some 5–20% of water and some 1–5 % of C mainly in the form of insoluble, poorly characterized, macromolecular material but also as well-defined chemical compounds. Hence, asteroidal bodies may have contributed to the volatile and organic inventory of the terrestrial planets. Sensitive analytical tools – originally developed for the analysis of moon rocks – have allowed detailed investigations of the composition of meteorites at the parts per million level. One spectacular result from this effort has been the identification and quantification of a very rich organic inventory, containing among others amino acids, carboxylic acids, purines and pyrimidines, and aliphatic and aromatic hydrocarbons (Table 1.1). While less well characterized, comets have a similar, diverse molecular composition. These rich and

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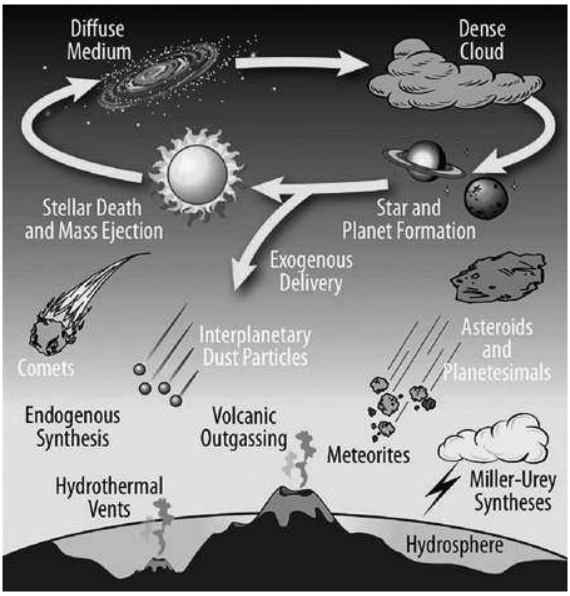

Figure 1.1 The cosmic history of prebiotic species will have left an imprint on the volatile and organic inventory of newly formed planets, including the Earth. As matter is injected by old stars and cycles between diffuse and dense star-forming clouds, a large number of processes contribute to a rich inventory of organic species in the interstellar medium. Some of this material may be incorporated into pebbles, cometesimals, and planetesimals where it can be further processed. These are the building blocks of planets and their organic inventory will be an amalgam of these sources and the processes involved. Further processing on the planetary surface, in its oceans, and in its atmospheres will drive further chemical complexity, leading possibly to the start of life. Figure kindly provided by J. Dworkin and adapted from [4]

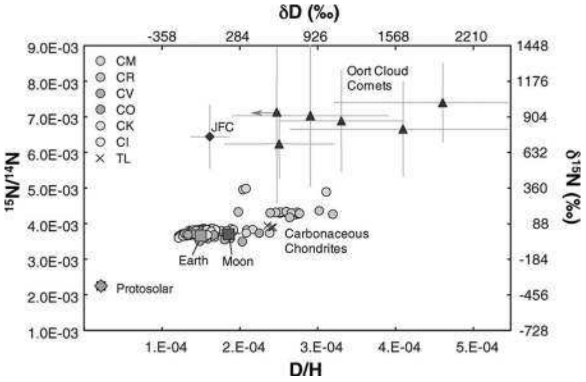

Figure 1.2 Isotopes are commonly used as tracers of the origin of molecular compounds. Here, the H and N isotopic composition of the Earth–Moon system is compared to that of different classes of meteorites and comets. JFC represents measurements for some Jupiter Family Comets. Note that N-isotopes derive from HCN/CN measurements which may not be representative of the nitrogen reservoir of comets. Figure taken from [24]

Table 1.1 *Organic compounds in meteorites*

Compound	Abundance[a] [ppm]	Compound	Abundance[a] [ppm]
CO_2	106	Monocarboxylic acids	332
CO	0.06	Dicarboxylic acids	25.7
CH_4	0.14	$\alpha-$Hydroxycarboxylic acids	14.6
NH_3	19	Amino acids	60
Alcohols	11	Diamino acids	0.04
Aldehydes	11	Sulphonic acids	67
Ketones	16	Phosphonic acids	1.5
Amines	8	Aliphatic hydrocarbons	12–35
$CO(NH_2)_2$	25	Aromatic hydrocarbons	15–28
Sugar-related compounds	~ 24	Basic N-heterocycles[b]	0.05–0.5
		Pyrimidines[c]	0.06
		Purines	1.2

Data taken from [31]. [a] Abundances in Murchison in parts per million. [b] Pyridines & quinolines. [c] Uracil and thymine

diverse inventories, and in particular the presence of a rich array of amino acids, have driven the point home that the organics delivered to the early Earth may well have prebiotic implications. This has brought the questions "has exogenous delivery given life a jump start on the early Earth and could it do so on exoplanets?" into focus in astrobiology. Some 5×10^{10} g/yr of organic carbon may have been delivered to the early Earth, including 3×10^6 g/yr of amino acids and 5×10^4 g/yr of nucleobases. Perhaps more relevant, taking Murchison as a model, a single meteorite could deliver 10 g of amino acids and 0.1 g of nucleobases and if trapped in a single warm pond could well be of importance. These amino acids are generally attributed to aqueous alteration on the meteoritic parent body and, specifically, the Strecker synthesis process where, for example, formaldehyde, ammonia, and hydrogen cyanide react to form aminoacetonitrile (NH_2CH_2CN). With water, this species reacts then on to glycine (NH_2CH_2COOH).

The alternative to exogenous delivery is endogenous synthesis. This is a logical consequence of Darwinian evolution and the idea can be traced back to a letter in 1871 from Charles Darwin to Joseph Hooker: "But if (and oh what a big if) we could conceive in some warm little pond with all sorts of ammonia and phosphoric salts, light, heat, electricity etcetera present, that a protein compound was chemically formed, ready to undergo still more complex changes." The best known example of endogenous synthesis is the Urey–Miller experiment where a gas mixture – simulating the early Earth's atmosphere – was subjected to electric discharges – representing lightning on the early Earth – and the products were collected. After many, many cycles of this process, the resulting mixture was analyzed and the presence of, among others, amino acids was demonstrated. The starting gas mixtures were very reducing, consisting of H_2O, NH_3, CH_4, and H_2.

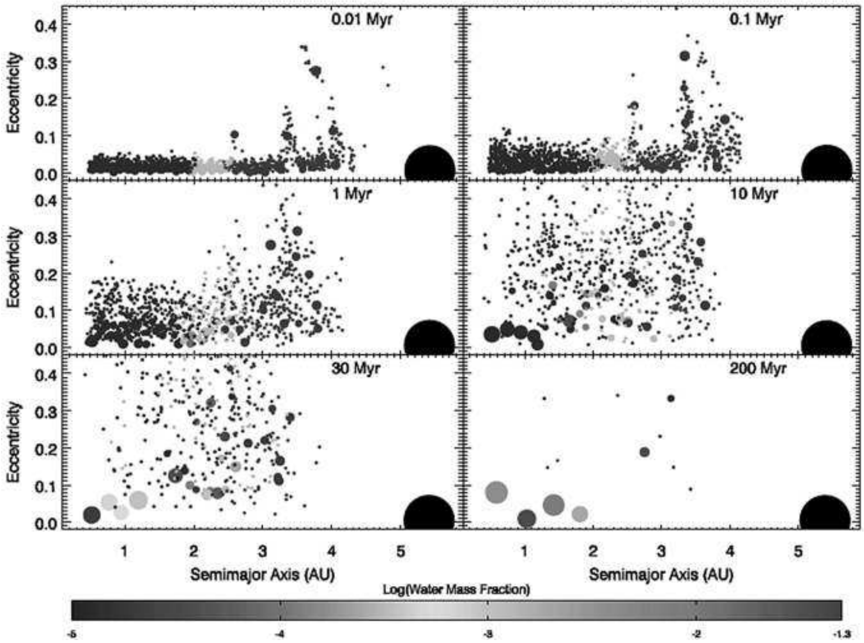

Figure 1.3 Snapshots in the evolution of disks of embryos from a simulation where Jupiter and Saturn are in the 3:2 mean motion resonance. The size of each body is proportional to its mass (but is not to scale on the x-axis). The interaction with Jupiter pumps up the eccentricity of the orbits of the embryos and they start to collide and grow, eventually leading to the formation of terrestrial planets. The temperature gradient in the protoplanetary disk has led to a compositional gradients in the embryos formed at different positions. The color of each body corresponds to its water content by mass (bottom scale, ranging from dry to 5% water). Jupiter is shown as the large black dot. Saturn is not shown. Figure taken from [21] (A black and white version of this figure will appear in some formats. For the color version, please refer to the plate section.)

In an aqueous setting, methane and ammonia are converted to formaldehyde and hydrogen cyanide. Strecker synthesis can then (again) take over to build amino acids. The Urey–Miller experiment has been repeated with many variations changing the composition of the initial mixture and/or the energy source. The conclusion is that, with the addition of energy, simple compounds can be converted into organic building blocks of proteins and other macromolecules in a reducing environment. In an oxidizing environment, on the other hand, this process is not very efficient.

1.3.3 Composition of the Early Earth's Atmosphere

The importance of the exogenous delivery versus endogenous synthesis debate hinges on the reducing versus oxidizing condition of the early Earth's atmosphere. This atmosphere resulted from outgassing and, taking current volcanic outgassing as a guide, would have

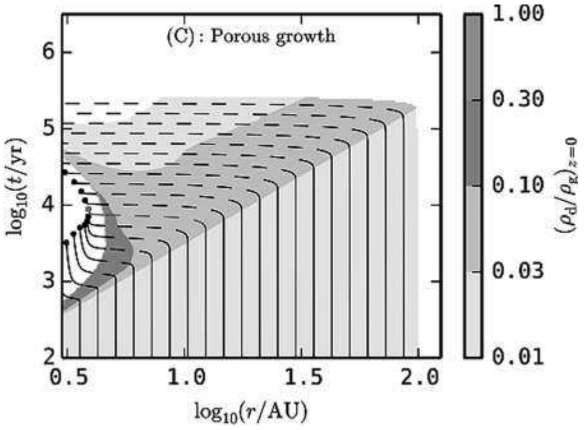

Figure 1.4 Growth from dust to pebbles to planetesimals in a protoplanetary disk. An initial phase of rapid coagulation and pebble formation (solid lines) is followed by a phase in which these pebbles decouple from the gas and drift inward (dashed lines). Pebbles formed in the inner disk will continue to grow and this growth is more rapid than the drift, culminating in the formation of a planetesimal (indicated by the black dot). The surface density in the outer disk is too low to allow planetesimal formation and the pebbles will drift inward where they can be "caught" by planets that have already formed. The gray scale indicates the dust-to-gas density in the mid plane. The details of these growth processes depend very much on the evolution of the porosity of the resulting aggregates. In this particular calculation, porosity is maintained to large sizes. Figure taken from [11]

been highly oxidized. However, as discussed in Section 1.3.1, outgassing is part of a cycle that balances with subduction, and on the early Earth this might have been different. If, on the early Earth, the O_2 fugacity of the magma was some two orders of magnitude lower, then ammonia and methane would be more important than carbon dioxide and molecular nitrogen. There is, however, little direct information on the mantle's fugacity. The composition of zircons seem to indicate that some 200 million years after the Earth's formation, the atmosphere was oxidizing in nature.

In a different approach, we can calculate the composition of an exoplanet's atmosphere resulting from outgassing. In thermodynamic equilibrium, the composition of the early Earth's atmosphere is a function of temperature, pressure, and (elemental) composition. The results reveal a strong dependence on the initial composition. Figure 1.6 shows exemplary calculation resulting in very reducing and very oxidizing atmospheres depending on whether H chondritic or CI chondritic compositions are adopted. H chondrites are thought to derive from S-type asteroids formed in the inner part of the asteroid belt (∼2.2–3 AU). CI chondrites are thought to derive from asteroids in the outer ($\gtrsim$4 AU) asteroid belt. We do not really know the relative importance of these two potential sources for the early Earth let alone for exoplanetary systems. These results are only meant to illustrate the dependence on elemental composition. Real atmospheres are much more complex where, for example, penetrating UV radiation, cloud formation and settling, as well as

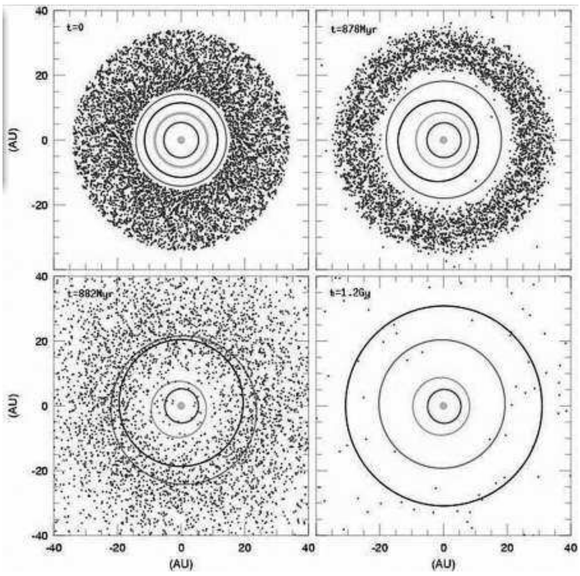

Figure 1.5 Four snapshots in the Nice simulation. The four giant planets were initially on nearly circular, co-planar orbits with semimajor axes of 5.45 (Jupiter), 8.18 (Saturn), 11.5 (Neptune), and 14.2 (Uranus) AU, indicated by the four circles. The outer cloud of dots indicates the cometary belt. The dynamically cold planetesimal disk was 35 $M_\oplus$, with an inner edge at 15.5 AU and an outer edge at 34 AU. The panels represent the state of the planetary system at four different epochs: (a) beginning of planetary migration (100 Myr); (b) just before the beginning of Late Heavy Bombardment (LHB; 879 Myr); (c) just after the LHB has started (882 Myr); (d) 200 Myr later, when only 3% of the initial mass of the disk is left and the planets have achieved their final orbits. The orbits of the planets evolve slowly through interaction of cometesimals with Jupiter, where the cometesimal is ejected and Jupiter's orbit shrinks. LHB is initiated by resonance between Jupiter and Saturn. As a result, Neptune leapfrogs over Uranus, creating havoc in the planetesimal disk. Most of the cometesimals are ejected but some are thrown into the inner solar system. Figure taken from [9]

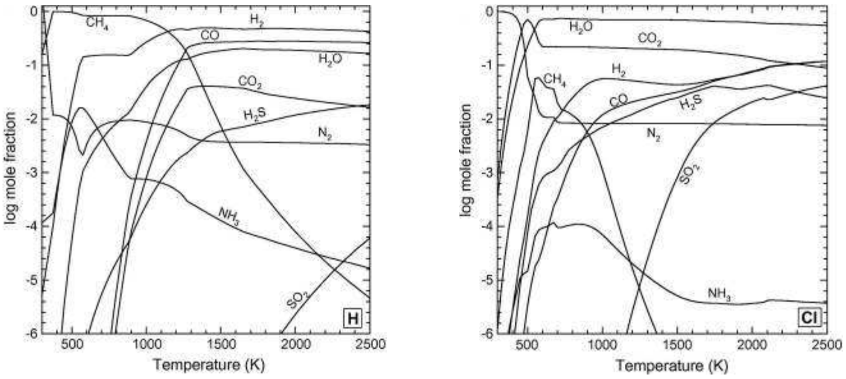

Figure 1.6 Atmospheric composition produced by outgassing calculated in thermodynamic equilibrium. The two panels are calculated for different elemental compositions corresponding to those of H chondrites (left) and CI chondrites (right). Calculations are performed at a pressure of 100 bars. Figure taken from [26]