REVIEW ARTICLE

# **Our astrochemical heritage**

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**Abstract** Our Sun and planetary system were born about 4.5 billion years ago. How did this happen, and what is the nature of our heritage from these early times? This review tries to address these questions from an astrochemical point of view. On the one hand, we have some crucial information from meteorites, comets and other small bodies of the Solar System. On the other hand, we have the results of studies on the formation process of Sun-like stars in our Galaxy. These results tell us that Sunlike stars form in dense regions of molecular clouds and that three major steps are involved before the planet-formation period. They are represented by the prestellar core, protostellar envelope and protoplanetary disk phases. Simultaneously with the evolution from one phase to the other, the chemical composition gains increasing complexity.

In this review, we first present the information on the chemical composition of meteorites, comets and other small bodies of the Solar System, which is potentially linked to the first phases of the Solar System's formation. Then we describe the observed chemical composition in the prestellar core, protostellar envelope and protoplanetary-disk phases, including the processes that lead to them. Finally, we draw together pieces from the different objects and phases to understand whether and how much we inherited chemically from the time of the Sun's birth.

**Keywords** Astrochemistry · ISM: clouds · Stars: formation · Protoplanetary disks · Comets: general · Meteorites, meteors, meteoroids

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# **1 Introduction**

Once upon a time, there was a small cold cloud of gas and dust in an interstellar medium broken into several clumps and filaments of different masses and dimensions. Then, about 4.5 billion years ago, the small cloud became the Solar System. What happened to that primordial cloud? When, why and how did it happen? Did the Earth receive a heritage from those old eons? Can this heritage help us to understand our origins?

The answers to these questions can only come from putting together many pieces of a giant puzzle that covers different research fields: from what the Earth is made of to its evolution, from what are the most pristine meteorites from outer space that have fallen on Earth to their present composition, from which other small bodies of the Solar System, comets and asteroids, have the imprint of the first composition of the solar nebula to their origin and evolution. Last but not least, the study of other small clouds and young Sun-like stars in our Galaxy gives a wide range of possible outcomes of star and planet formation, and we would like to understand why the Solar System and the Earth chose one of them.

Each single piece of the puzzle brings precise and precious information. The problem is that sometimes the information is hidden in a scrambled code whose key is unknown. Take meteorites as an example. As explained to us by an expert colleague, assessing the composition of the Solar Nebula from the study of the meteorites is like trying to assess Napoleon's army structure looking at the few survivors of the Russian war. How representative are those survivors? Although, evidently, they still provide very precious information, extracting the whole information from them is far from obvious. The example is to say that every single piece of the puzzle is important, even the pieces that seem to be redundant. Actually, the redundant ones are likely the most important, as they may allow to distinguish and disentangle all the various intervening effects. In this context, the study of the objects similar to the Solar System progenitor takes a particular relevance, because it can provide us with plenty of pieces to compare with the other pieces from the present Solar System. The hope is that they will provide us with the keys of the scrambled codes.

In this review, we will focus on just a subset of these pieces, those coming from the study of the chemical composition during the birth of stars and planetary systems like our Solar System. In Sect. [2,](#page-2-0) we will first give a very general overview of how we think the Solar System and stars of similar mass have formed and how this process influences the chemistry. This is based on the ensemble of observations and studies on star-forming regions and Solar System objects. Then, in Sect. [3,](#page-3-0) we will describe in detail some pieces of the puzzle which potentially connect what we observe in the objects of the Solar System nowadays and what we know about star formation in our Galaxy. The next sections will discuss star- and planet-formation studies. We will describe how the evolution of the matter from a cold cloud (Sect. [4\)](#page-12-0) to a protostellar envelope (Sect. [5\)](#page-20-0) and a protoplanetary disk (Sect. [6](#page-31-0)) corresponds to an increase of the molecular complexity. Section [7](#page-39-0) will provide specific examples on the link between the present Solar System small bodies with the pre- and protostellar phase. A final section will try to draw some conclusions.

<span id="page-2-0"></span>We emphasize that the present review is complementary to several reviews recently appeared in the literature on different aspects just touched upon by us and that will be cited in the appropriate sections.

# **2 Solar-type star formation and chemical complexity**

The formation of a Sun-like star and molecular complexity proceed hand in hand. As the primordial cloud evolves into a protostellar envelope, protoplanetary disk and planetary system, the chemical composition of the gas becomes increasingly more complex. The five major phases of the process that we think have formed the Earth are sketched in Fig. [1](#page-2-1) and here listed.

- Phase 1: *Pre-stellar cores.* These are the "small cold clouds" mentioned above. During this phase, matter slowly accumulates toward the center of the nebula. As a result, the density at the center increases while the temperature decreases. Atoms and molecules in the gas-phase freeze-out onto the cold surfaces of the sub-micron dust grains, forming the so-called icy grain mantles. Thanks to the mobility of the H atoms on the grain surfaces, hydrogenation of atoms and CO (the most abundant molecule, after  $H_2$ , in cold molecular gas) takes place, forming molecules such as water  $(H_2O)$ , formaldehyde  $(H<sub>2</sub>CO)$ , methanol (CH<sub>3</sub>OH) and other hydrogenated species.
- Phase 2: *Protostellar envelopes.* The collapse proceeds, gravitational energy is converted into radiation and the envelope around the central object, the future star, warms up. The molecules frozen in grain mantles during the previous phase acquire mobility and likely form new, more complex species.

# **FROM A DIFFUSE CLOUD TO A SUN + PLANETARY SYSTEM FROM ATOMS & SIMPLE MOLECULES TO LIFE**



<span id="page-2-1"></span>**Fig. 1** Star formation and chemical complexity. The formation of a star and a planetary system, like the Solar System, passes through five fundamental phases, marked in the sketch

When the temperature reaches the mantle sublimation temperature, in the so-called hot corinos, the molecules in the mantles sublimate back in the gas phase, where they react and form new, more complex, molecules. Simultaneously to the collapse, a fraction of matter is violently ejected outward in the form of highly supersonic collimated jets and molecular outflows. When the outflowing material encounters the quiescent gas of the envelope and the molecular cloud, it creates shocks, where the grain mantles and refractory grains are (partially) sputtered and vaporized. Once in the gas phase, molecules can be observed via their rotational lines.

- Phase 3: *Protoplanetary disks.* The envelope dissipates with time and eventually only a circumstellar disk remains, also called protoplanetary disk. In the hot regions, close to the central object, new complex molecules are synthesized by reactions between the species formed in the protostellar phase. In the cold regions of the disk, where the vast majority of matter resides, the molecules formed in the protostellar phase freeze-out again onto the grain mantles, where part of the ice from the prestellar phase may still be present. The process of "conservation and heritage" begins.
- Phase 4: *Planetesimal formation.* The sub-micron dust grains coagulate into larger rocks, called planetesimals, the seeds of the future planets, comets and asteroids. Some of the icy grain mantles are likely preserved while the grains glue together. At least part of the previous chemical history may be conserved in the building blocks of the Solar System rocky bodies.
- Phase 5: *Planet formation.* This is the last phase of rocky planet formation, with the embryos giant impact period and the formation of the Moon and Earth. The leftovers of the process, comets and asteroids, copiously "rain" on the primitive Earth, forming the oceans and the Earth second atmosphere. The heritage conserved in the ices trapped in the planetesimals and rocks is released onto the Earth. Life emerges sometime around 2 billion years after the Earth and Moon formation.<sup>[1](#page-3-1)</sup>

<span id="page-3-0"></span>Sections [4](#page-12-0) to [6](#page-31-0) will review and discuss in detail the chemistry in the first three phases of the process, those where the heritage is likely accumulated. Box [1](#page-4-0) briefly explains the data and tools needed to interpret the observations and Table [1](#page-5-0) summarizes some key proprieties of the phase 1 to phase 3 objects.

#### <span id="page-3-1"></span>**3 Pieces of the puzzle from the Solar System**

A variety of information on the formation process of the Solar System is provided to us by the small bodies believed to be the most pristine objects of the Solar System: Kuiper Belt Objects (KBOs), comets, meteorites and particularly carbonaceous

<sup>&</sup>lt;sup>1</sup>The famous fossils of cyanobacteria of Australia and for long considered as the first traces of life dated 3.5 Myr (Schopf et al. [2002\)](#page-63-0), are interpreted as inorganic condensations (Skrzypczak et al. [2003;](#page-63-1) García et al. [2002\)](#page-52-0) and still source of intense debate (Marshall et al. [2011](#page-58-0)). Conversely, there is consensus on the rise of life about 2 Gyr after the Earth formation, as testified by the rise in the  $O_2$  abundance in the atmosphere (Czaja [2010](#page-50-0)).

### <span id="page-4-0"></span>**Box 1** Data needed to interpret the astronomical observations

In order to derive the chemical composition of a celestial body from line observations one needs to identify correctly the lines as due to a specific molecule and to convert the observed line intensity into the species abundance. Then, to understand what these abundances mean one needs to compare the observed with model predicted abundances. The process, sketched in Fig. [2](#page-5-1) requires, therefore, data from different communities: (i) spectroscopic data, to identify the lines; (ii) collisional coefficients, to convert them into abundances; (iii) chemical reactions to build up astrochemical models. The three sets of data necessitate specific skills and enormous laboratory and computational efforts. The available information is centralized in the following databases:

– Spectroscopic databases:

+ JPL Molecular spectroscopy database (Pickett et al. [1998\)](#page-61-0):

<http://spec.jpl.nasa.gov/home.html>

+ Cologne Database for Molecular Spectroscopy database (CDMS, Müller et al. [2005\)](#page-59-0):

<http://www.astro.uni-koeln.de/cdms/>

+ Splatalogue database for astronomical spectroscopy (SPLATALOGUE): <http://splatalogue.net/>

– Collisional excitation databases:

+ Ro-vibrational collisional excitation database (BASECOL, Dubernet et al. [2004\)](#page-51-0):

<http://basecol.obspm.fr/index.php?page=pages/generalPages/home> + Leiden Atomic and Molecular Database (LAMDA, Schöier et al. [2005\)](#page-63-2): <http://home.strw.leidenuniv.nl/~moldata/>

– Chemical reaction databases:

+ The KInetic Database for Astrochemistry (KIDA, Wakelam et al. [2012\)](#page-65-0): [http://kida.obs.u-bordeaux1.fr/](http://kida.obs.u-bordeaux1.fr/ )

+ The Ohio State University (OSU) gas-phase and gas-grain chemical models (e.g., Garrod et al. [2008\)](#page-52-1):

<http://www.physics.ohio-state.edu/~eric/research.html>

+ The UMIST database for astrochemistry (UDFA, Woodall et al. [2007\)](#page-66-0): <http://www.udfa.net/>

We emphasize that the databases just collect the data which are provided by several colleagues from all over the world. We would like here to pay our tribute to Pierre Valiron and Fredrik Schoier, who enormously contributed to the collisional excitation coefficients and to the set up of the LAMDA database, respectively, and who prematurely passed away.

chondrites, and interplanetary dust particles (IDPs). Here we will review some properties of these objects that can shed light on the formation process when compared with what we know about other solar-type forming stars in the Galaxy. We emphasize

Phase & Object		Age $(yr)$	Radius (AU)	Temp. $(K)$	Density $\rm (cm^{-3})$	Chemical processes
1	Pre-stellar core	$\sim 10^5$	$\sim 10^4$	$7 - 15$	$10^4 - 10^6$	Ice formation & molecular deuteration
2	Protostellar envelope:	$10^4 - 10^5$	$\sim 10^4$			
	Cold envelope		$100 - 104$	< 100	$10^5 - 10^7$	Ice formation & molecular deuteration
	Hot corinos		< 100	>100	>10'	Complex molecules formation
3	Protoplanetary disk:	$\sim 10^6$	$\sim$ 200			
	Outer midplane		$20 - 200$	$100 - 10$	$10^8 - 10^6$	Ice formation & molecular deuteration
	Inner midplane		$20$	>100	$\geq 10^8$	Complex molecules formation

<span id="page-5-0"></span>**Table 1** Summary of the proprieties of the objects in the first three phases of the solar-type star-formation process, before planet formation



<span id="page-5-1"></span>**Fig. 2** The four steps required to measure the chemical structure of an astrophysical object, as described in Box [1,](#page-4-0) including the tools needed to complete each step: (1) observations at the telescope, (2) identification of the lines and species, (3) derivation of the physical and chemical structure using radiative transfer codes, which require accurate collisional coefficients, and (4) chemical models

<span id="page-6-0"></span>that this summary is far from being exhaustive and the reader is invited to look at the reviews cited in the following subsections.

# 3.1 Where does the terrestrial water come from?

We all know how fundamental water is for the terrestrial life. It is the best solvent, allowing chemical reactions to form large biotic molecules and to break down ATP (Adenosine TriPhosphate), a process at the very base of the energy metabolism of living cells. Water had a fundamental role also on planet Earth, its history, evolution and equilibrium, for example allowing the magma to be viscous enough for tectonics to take place.

Sometimes the most obvious questions, like the one on the origin of water or why the night sky is dark, do not have obvious answers. The explanation of the dark night sky had to wait for the discovery of the expansion of the Universe, while the explanation of why Earth is so abundant in water is still hotly debated. But what are the facts? Two main facts are fundamental pieces of this puzzle. The first one is the quantity of terrestrial water, the second is its isotopic composition.

Regarding the amount of water on Earth, we can easily measure it in the Earth's crust where it is  $\sim$ 3 × 10<sup>-4</sup> the Earth mass (Lécuyer et al. [2000\)](#page-56-0). It is much less obvious to measure it in the mantle and core, where the vast majority of the Earth's mass resides and where it is impossible to directly measure the volatile components. Measurements of Earth's mantle water content are in fact based on indirect evidence, mostly using noble gases as proxies for the volatile hydrogen (Fisher [1982](#page-51-1); Allegre et al. [1983\)](#page-45-0), which implies assuming that the solar abundance ratios are maintained in the Earth mantle. The most recent estimates give a total amount of  $\sim$ 2 × 10<sup>-3</sup> Earth masses (Marty [2012](#page-58-1)), namely almost ten times more than in the crust. It has to be noted, though, that Earth in the Archaean was most likely more volatile-rich than in our days (e.g., Kawamoto [1996\)](#page-55-0).

The second fundamental piece of the puzzle is the HDO/H<sub>2</sub>O ratio,  $1.5 \times 10^{-4}$  in the terrestrial oceans, namely about ten times larger than the elemental D/H ratio in the Solar Nebula (Geiss and Gloeckler [1998](#page-52-2)). Direct measurements of the HDO/H<sub>2</sub>O ratio in the Earth mantle are impossible, but indirect ones seem to suggest a slightly lower value than that of the oceans (Marty [2012\)](#page-58-1).

The problem on the origin of the terrestrial water comes from the fact that the planetesimals that built up the Earth, if they were located at the same place where Earth is today, must have been dry. Therefore, either water came later, when Earth was mostly formed, or the planetesimals that formed the Earth were from a zone more distant than 1 AU. The first theory, also called "late veneer", was first proposed by Delsemme [\(1992](#page-50-1)) and Owen and Bar-Nun [\(1995](#page-60-0)) and postulates that water is mostly delivered to Earth from comets, especially during the Late Heavy Bombardment (Dauphas et al. [2000;](#page-50-2) Gomes et al. [2005](#page-53-0)). For almost a decade, the theory had the problem, though, that the HDO*/*H2O abundance ratio in the six comets where it had been measured is about a factor of two too high (Jehin et al. [2009\)](#page-54-0); see Sect. [3.4](#page-9-0) and Fig. [4.](#page-9-1) However, new Herschel measurements are changing the situation. The measure on the 103P/Hartley2 comet gives exactly the terrestrial value (Hartogh et al. [2011](#page-53-1)), whereas measurements toward C/2009 P1

give again a larger HDO*/*H2O value, 2 × 10−<sup>4</sup> (Bockelée-Morvan et al. [2012\)](#page-47-0). The other possibility is that Earth was partly built from water-rich planetesimals from the outer zone (Morbidelli et al. [2000\)](#page-59-1). Two arguments are in favour of this theory. First, the HDO*/*H2O ratio of carbonaceous chondrites is very similar to the terrestrial one  $(1.3-1.8 \times 10^{-4}$ , Robert [2003;](#page-62-0) see Sect. [3.4](#page-9-0) and Fig. [4\)](#page-9-1). Second, numerical simulations of the young Solar System from several authors predict that up to 10 % of the Earth may have been formed by planetesimals from the outer asteroid belt, providing enough water to Earth (e.g., Morbidelli et al. [2000;](#page-59-1) Raymond et al. [2009](#page-61-1)). The same simulations tend to exclude the cometary delivery as a major contribution. However, as any model, the predictions are subject to a number of uncertainties, a major one being how much water is in the outer asteroid belt planetesimals (Licandro et al. [2012](#page-57-0)).

Finally, the question on the origin of Earth's water is somewhat linked to the question on the origin of the Earth's atmosphere. Even though the methods are different, also for the Earth's atmosphere it is discussed a cometary delivery versus a meteoritic origin. Likely, in this case, both sources are necessary (e.g., Dauphas [2003\)](#page-50-3).

<span id="page-7-0"></span>We emphasize the key role played, in both theories, by the  $HDO/H<sub>2</sub>O$  ratio in the terrestrial water, comets and asteroids. In the following sections of this review, we will see why, when and how water becomes enriched of deuterium.

# 3.2 Molecular species in comets and KBOs

Several molecular species have been detected in comets since decades and in KBOs since the last decade. Here we briefly summarise which species have been detected and recommend to the interested reader the reviews by Mumma and Charnley [\(2011](#page-59-2)) and Bockelée-Morvan [\(2011](#page-47-1)), and Brown [\(2012](#page-48-0)) on the comets and KBOs, respectively.

*Comets* Two dozens of molecular species have been identified in various comets by several authors (e.g., Biver et al. [2002;](#page-46-0) Crovisier et al. [2009](#page-50-4)). More specifically:

- (i)  $H_2O$ , CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>OH, H<sub>2</sub>CO, NH<sub>3</sub>, HCN, HNC, CH<sub>3</sub>CN and  $H_2S$  have been detected in more than 10 comets;
- (ii) HCOOH, HNCO, HC<sub>3</sub>N, OCS and  $S_2$  have been detected in more than one comet;
- (iii) HOCH<sub>2</sub>CH<sub>2</sub>OH, HCOOCH<sub>3</sub>, CH<sub>3</sub>CHO, NH<sub>2</sub>CHO, SO<sub>2</sub>, H<sub>2</sub>CS have been observed in one comet, Hale–Bopp.

Not all species are considered primary species, namely species present in the sublimated ices. Some, like HNC, are product species, namely they are the products of chemical reactions involving the primary species once ejected in the gas. Other species, like  $H_2CO$  and  $CO$ , have contributions from both primary and product species. The measured abundances are summarised in Fig. [3](#page-8-0). To this list one has to add the recent detection of glycine, the simplest of amino acids, in the 81P/Wild2 comet by the mission STARDUST (Elsila et al. [2009\)](#page-51-2).

<span id="page-8-0"></span>

*KBOs* KBOs are the objects beyond Neptune's orbit, at an heliocentric distance between 30 and 50 AU, and are thought to hold precious information on the pristine chemical composition of the Solar Nebula at those distances. Being relatively small objects, they are difficult to study. However, in the last decade, important progress has been made. Briefly, the six large KBOs where spectroscopic observations could be obtained showed the presence in their atmosphere of  $H_2O$ ,  $CH_4$ ,  $N_2$ , and CO, even though with different proportions from object to object (e.g., Barucci et al. [2005;](#page-46-1) Schaller and Brown [2007](#page-62-1); Brown et al. [2012](#page-48-1)). In addition, ethane  $(C_2H_6)$ , believed to be the result of CH4 photolysis processes caused by the solar wind and cosmic rays, has been detected in Makemake (Bennett et al. [2006](#page-46-2)). In other smaller KBOs, spectroscopic observations showed the presence of water, ammonia and likely methanol ices (Barucci et al. [2011](#page-46-3); Brown et al. [2012\)](#page-48-1).

From Fig. [3](#page-8-0), it is clear that the most abundant species in comets  $(H_2O, CO, CO_2$ ,  $CH_4$ , NH<sub>3</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>6</sub>) are observed also in KBOs and, in turn, the species observed in KBOs are the most abundant species in comets. Formaldehyde and hydrogen sulfide have abundances in comets comparable to  $CH<sub>4</sub>$  and  $NH<sub>3</sub>$ . Their non detection in KBOs may, however, be due to observational effects only.

#### 3.3 Organics in meteorites and IDPs

Carbonaceous chondrites are rich in carbon, which constitutes about  $1-4$  % of this kind of meteorites. Organic carbon is present in two forms, following the methods to extract the organic material: insoluble organic matter (IOM) and soluble organic matter (SOM).

IOM is mainly  $(\geq 70\%)$  constituted of organic compounds with a relatively complex structure (nanoglobules, venatures, . . . ). The compounds are made of small aromatic units (with up to six rings) linked by branched aliphatic linkages shorter than seven carbon atoms (e.g., Remusat et al. [2005;](#page-62-2) Le Guillou et al. [2012](#page-56-1)). Similarly, IDPs contain about 10–12 % carbon, mostly in organic material, including aromatic and aliphatic compounds (Thomas et al. [1993;](#page-64-0) Keller et al. [2004\)](#page-55-1).

<span id="page-9-1"></span>

<span id="page-9-0"></span>SOM is principally made of carboxylic acids, aliphatic and aromatic hydrocarbons, and amino acids (e.g., Pizzarello et al. [2001\)](#page-61-2). In the Murchison meteorite, they represent ∼50 %, ∼25 % and ∼10 %, respectively, of the organic soluble matter. Of particular interest, amino acids with no known terrestrial distribution have been found in meteorites. In addition, a sub-group of amino acids shows a small but significant L-enantiomeric excesses (e.g., Pizzarello et al. [2003](#page-61-3)), namely one of the two chiral forms is more abundant than the other, a characteristic of chiral biomolecules in terrestrial life.

#### 3.4 The hydrogen and nitrogen isotopic anomalies

One direct evidence of the link between pristine small Solar System bodies like carbonaceous chondrite, IDPs and comets, and the first phases of the Sun formation (phases 1 to 3 in Fig. [1\)](#page-2-1) comes from the presence of the so-called isotopic anomalies. Among the five most abundant elements in the Universe (H, He, O, C and N), three present large anomalies, namely they have isotopic values more than twice different from in the Solar Nebula: hydrogen, oxygen and nitrogen (while carbon also shows different values but to a lesser extent). Each of them brings different information. Here, we briefly review the information provided by the hydrogen and nitrogen isotopes. Oxygen isotopic anomalies are discussed in Sect. [3.5.](#page-11-0)

*Deuterium in comets* The first and most important isotopic anomaly, the deuterium enrichment of terrestrial water, has been already discussed in Sect. [3.1](#page-6-0). We also briefly mentioned that comets show a D enrichment one to two times the one of the terrestrial oceans (Fig. [4\)](#page-9-1). Regardless whether comets substantially contributed or not to the terrestrial water, the relatively high abundance of deuterated water can help us to understand when and where comets formed and, consequently, how the Solar System formed. So far, the HDO/H<sub>2</sub>O ratio has been observed in seven comets from the Oort Cloud, the most recent being the C/2009 P1 comet, and in one, 103P/Hartley2, from the Jupiter-family comets. In the first six comets, HDO/H<sub>2</sub>O has been measured to be  $\sim$ 3 × 10<sup>-4</sup> (Muñoz Caro et al. [2002;](#page-59-3)

Bockelee-Morvan et al. [1998\)](#page-47-2), in C/2009 P1 it is  $2 \times 10^{-4}$  (Bockelée-Morvan et al. [2012\)](#page-47-0), and in 103P/Hartley2 it is  $1.5 \times 10^{-4}$  (Hartogh et al. [2011](#page-53-1)). If, on the one hand, this last measurement has brought back to life the debated late veneer theory (Sect. [3.1](#page-6-0)), it has also challenged the present view of where these comets are formed. In fact, according to the widely accepted theory, comets from the Oort Cloud and the Jupiter family were likely formed in the Uranus-Neptune zone (Dones et al. [2004](#page-51-3)), even though the Oort Cloud comets may also originate from the Jupiter–Saturn region (Brasser [2008\)](#page-48-2). The HDO/H<sub>2</sub>O ratio is an almost direct measure of the temperature where the comet is formed and larger heliocentric distances are expected to correspond to colder regions. Therefore, one would expect that comets in the Oort Cloud present a similar or lower HDO*/*H2O ratio than the Jupiter-family comets, contrary to what is measured. Dedicated models sup-port this simple intuitive argument (e.g., Horner et al. [2007;](#page-54-1) Kavelaars et al. [2011;](#page-55-2) Petit et al. [2012\)](#page-60-1). Therefore, either comet formation theory is not correct in this aspect (for example a new theory postulates that Oort Cloud comets are captured from nearby stars; (Levison et al. [2010\)](#page-57-1)), or the temperature in the Solar Nebula was not monotonically decreasing with increasing heliocentric distance. This is in principle possible during the accreting disk phase where viscosity may have created warm regions (e.g., Yang and Ciesla [2012\)](#page-67-0). This will be further discussed in Sect. [7.](#page-39-0) So far for water, but deuterium enrichment is also observed in HCN, in one comet (Meier et al. [1998\)](#page-58-2), and it is about 10 times larger than the water D enrichment. This difference is not necessarily a problem as it may just outline the different chemical formation pathway of these two species, as explained in Sect. [4.2.1.](#page-17-0)

*Deuterium in carbonaceous chondrites and IDPs* The bulk of carbonaceous chondrites contains hydrated silicates and hydrous carbon with a D/H ratio  $= 1.2 2.2 \times 10^{-4}$  (e.g., Robert [2003](#page-62-0)), very similar to that of the terrestrial oceans. However, D enrichment, similar to that measured in comets and even higher, has also been found in the so-called "hot spots", namely micrometer-scale regions with positive isotope anomalies, in the IOM of chondrites and IDPs. These hot spots are in fact so named because of the enrichment of D and  $^{15}N$ , and are systematically found in small regions of organic material. The D enrichment in carbonaceous chondrites and IDPs is very variable, with regions having D/H  $\sim$ 8 × 10<sup>-5</sup> close to the Solar Nebula value, and others having D/H up to  $\sim 10^{-2}$  (Alexander et al. [2007;](#page-45-1) Remusat et al. [2009\)](#page-62-3). High spatial resolution measurements suggest that the largest D enrichment is associated with organic radicals (Remusat et al. [2009](#page-62-3)). Similarly, molecules in the soluble organic matter component show enhanced abundances of D species with respect to H species, at a level of D/H up to almost  $10^{-2}$  (Pizzarello and Huang [2005\)](#page-61-4).

<sup>15</sup>N *in comets* Several measurements of the bulk of the  $\frac{14N}{^{15}N}$  in the Solar Nebula, from observations of  $NH_3$  in Jupiter (Owen et al. [2001;](#page-60-2) Fouchet et al. [2004](#page-52-3)) and the solar wind (Marty et al. [2010](#page-58-3)) give a value of ∼440, consistent with standard stellar nucleosynthesis models. In comets, though, the 14N*/*15N ratio measured in CN and HCN species is more than a factor 2 lower, around 150 (Arpigny et al. [2003;](#page-46-4) Manfroid et al.  $2009$ ). The origin of this  $15N$  enrichment in comets has puzzled astrochemists for years. One possibility is that this is a direct heritage of the prestellar

core phase (Sect. [4\)](#page-12-0) or protoplanetary-disk phase (Sect. [6\)](#page-31-0). Finally, it is also possible that  $15N$  has been injected in the material forming the Solar System by the explosion of a nearby supernova (Sect. [3.5](#page-11-0)).

<sup>15</sup>N *in chondrites and IDPs* The <sup>14</sup>N/<sup>15</sup>N as measured in TiN in a pristine condensate Ca-Al-rich inclusion of a carbonaceous chondrites is very similar to the Solar Nebula value ∼440 (Meibom et al. [2007](#page-58-4)). However, the <sup>14</sup>N/<sup>15</sup>N in the IOM material of carbonaceous chondrites and IDPs is low, up to ∼50 (Bonal et al. [2009,](#page-47-3) [2010;](#page-47-4) Matrajt et al. [2012\)](#page-58-5), as low as in comets and significantly lower than in the Solar Nebula and the interstellar medium. Similar  ${}^{15}N$  enrichment has been reported in two amino acids (Pizzarello and Holmes [2009](#page-61-5)). Therefore, the same question on the origin of the 15N enrichment in comets applies to the organic material in carbonaceous chondrites and IDPs.

<span id="page-11-0"></span>*A common origin for the D and* 15N *enrichment in comets and the organic material in carbonaceous chondrites and IDPs?* Since comets and the organic material in chondrites and IDPs are enriched in both D and  $^{15}N$ , the question whether the enrichment has a common origin is a natural one (e.g., Busemann et al. [2006;](#page-48-3) Aléon [2010](#page-45-2)). Against this hypothesis is that D-enriched spots in chondrites and IDPs do not coincide spatially with <sup>15</sup>N-enriched ones (Busemann et al. [2006](#page-48-3); Aléon [2010;](#page-45-2) Robert and Derenne [2006](#page-62-4)). Similarly, while the D enrichment differs by a factor two in 103P/Hartley2 and the other six comets, the  $15N$  enrichment is practically the same in all comets (Fig. [4\)](#page-9-1). Therefore, very likely D and <sup>15</sup>N enrichments do not have a common origin (see also Wirström et al. [2012\)](#page-66-1).

# 3.5 A violent start in a crowded violent environment

Short-lived nuclides<sup>[2](#page-11-1)</sup> present at the formation of the Solar System and now disappeared, and isotopic oxygen anomalies in meteorites tell us that the Solar System had a violent start in a violent environment. First, the young Sun irradiated the forming planetary system with a strong wind of energetic particles. Second, the Sun was likely born in a large cluster of stars where one or more massive stars exploded. All this is based on anomalies with respect to the "normal" values of the abundances of these elements, which can only be firmly known by assessing what is the normality in other forming stars and, therefore, it is an important piece of the puzzle to mention here.

<span id="page-11-1"></span>*A violent start* It is now well-known that young solar-type stars are bright X-rays emitters, about  $10<sup>3</sup>$  times brighter than the present day Sun (Feigelson and Mont-merle [1999](#page-51-4); Preibisch and Feigelson [2005\)](#page-61-6). It is very likely that, together with X-rays, H and He nuclei with energies larger than 10 MeV are also emitted in large quantities in the early stages of star formation (e.g., Lee et al. [1998\)](#page-56-2). The Sun likely passed through a similar violent phase and irradiated the forming planetary system with energetic particles (sometimes also referred as "early solar cosmic rays"). Extinct shortlived nuclides bring traces of this violent past. Specifically, the enhanced abundances

<sup>&</sup>lt;sup>2</sup>Short-lived nuclides are the radionuclides with half-lives shorter than about 10 Myr.

of <sup>10</sup>Be, <sup>7</sup>Li and <sup>21</sup>Ne (McKeegan et al. [2000](#page-58-6); Chaussidon and Srinivasan [2012\)](#page-49-0) can only be explained by spallation reactions of solar energetic particles with O and C atoms of the Solar Nebula. Similarly, other short-lived nuclides,  ${}^{36}Cl$ ,  ${}^{53}Mg$  and  ${}^{41}Ca$ , are now explained in terms of irradiation from the early Sun (e.g., Marhas et al. [2002;](#page-58-7) Gounelle and Meibom [2008\)](#page-53-2).

*A crowded violent environment* Several lines of evidence converge toward a picture where the Sun was born in a cluster of at least 1000 stars (see the review by Adams [2010\)](#page-45-3). Likely, within this cluster, some were massive stars and some exploded a little before or during the formation of the Solar System. Since its discovery in meteorites, <sup>26</sup>Al (Kita et al. [2000](#page-56-3); Villeneuve et al. [2009\)](#page-65-1) became one of the proofs, indeed highly debated for decades, that the Solar System was polluted with material ejected from a nearby type II supernova, whose progenitor mass is  $\sim$ 25 M<sub> $\odot$ </sub> (Cameron and Truran [1977](#page-48-4); Gounelle and Meibom [2008\)](#page-53-2). Support to this hypothesis was added by the discovery of  ${}^{60}Fe$  (Kita et al. [1998\)](#page-56-4), but the value of the  ${}^{60}Fe$  excess with respect to the Galactic one has been revised since and nowadays it is believed to be close to zero (Moynier et al.  $2011$ ). As a consequence, theories based on <sup>60</sup>Fe have to be taken with a grain of salt (see the review by Dauphas and Chaussidon [2011](#page-50-5)). Recently, the anomalous  $^{18}O/^{17}O$  in meteorites,  $5.2 \pm 0.2$  (see the compilation in Young et al. [2011\)](#page-67-1), with respect to the Galactic one,  $4.1 \pm 0.1$  (Wouterloot et al. [2008\)](#page-67-2) has also been taken as a proof of the injection of material from a type II supernova exploded just before the birth of the Solar System.

#### <span id="page-12-0"></span>**4 The calm before the storm: pre-stellar cores**

Stars like our Sun form in slowly rotating and collapsing magnetized dense cloud cores (e.g., Goodman et al. [1993](#page-53-3); Troland and Crutcher [2008\)](#page-64-1). Dense cores not associated with stars are called "starless cores" and they represent the initial conditions in the process of star formation (Shu et al. [1987\)](#page-63-3). They are the starting point of our journey. These objects have average volume densities at least one order of magnitude larger than the surrounding medium, have typical kinetic and dust temperatures of 10 K and their internal energy is dominated by thermal motions (see review by Bergin and Tafalla [2007\)](#page-46-5). Not all starless cores give birth to stars, though. Some of them reach configurations close to hydrostatic equilibrium and display kinematic features consistent with oscillations (Lada et al. [2003](#page-56-5)). Others show expanding motions (Tafalla et al. [2004\)](#page-63-4). This class of starless cores typically displays a relatively flat density distribution, with central densities below  $10^5$  H<sub>2</sub> molecules cm<sup>-3</sup>. This is the critical density for gas cooling by gas-dust collisions (Goldsmith [2001](#page-53-4)) and it represents the "dividing line" for dynamical stability. Starless cores with central densities below this critical density are thermally subcritical (Keto and Caselli [2008](#page-55-3)) and they may disperse back into the interstellar medium. When the central densities of H<sub>2</sub> molecules overcome  $\simeq 10^5$  cm<sup>-3</sup>, starless cores become thermally supercritical and gravitational forces take over. These are the so-called *prestellar cores*, first identified by Ward-Thompson et al. ([1994](#page-66-2)) in the sub-millimeter continuum and then chemically and kinematically labelled by Crapsi et al. [\(2005](#page-50-6)) using millimeter spectroscopy. It is within prestellar cores that future star and planetary systems will form.



<span id="page-13-1"></span><span id="page-13-0"></span>**Fig. 5** The chemical zones of the prototypical prestellar core L1544, embedded in the Taurus Molecular Cloud Complex, at a distance of 140 pc. The background color image is the 1.3 mm dust continuum emission map obtained with the IRAM-30m antenna (Ward-Thompson et al. [1999\)](#page-66-3). *The cyan contours* show the different chemical zones, with the corresponding main chemical processes listed in *the right panel*. *Blue labels* indicate reaction partners

#### 4.1 Freeze-out, deuterium fractionation and the ionization fraction

Pre-stellar cores span a range of number densities which goes from a few times 10<sup>3</sup> cm−<sup>3</sup> toward the outer edges, where they merge with the surrounding molecular cloud, to about  $10^7 \text{ cm}^{-3}$  within the central 1,000 AU (e.g., Evans et al. [2001;](#page-51-5) Keto and Caselli [2010\)](#page-55-4), where the gas and dust temperature drops to 6–7 K (Crapsi et al. [2007;](#page-50-7) Pagani et al. [2007\)](#page-60-3). These gradients in physical properties affect the chemical structure. Figure [5](#page-13-0) schematically shows the main chemical processes in the twozones of the prototypical prestellar core L1544, embedded in the Taurus molecular cloud. In the outer part of the core (between about 7,000 and 15,000 AU), the gas density is  $\approx 10^4$  cm<sup>-3</sup> and the temperature  $\approx 10$  K. "Classical" dark-cloud chemistry is at work, with ion-molecule reactions (Herbst and Klemperer [1973](#page-54-2)) dominating the carbon chemistry, and neutral-neutral reactions which start the transformation of nitrogen atoms into  $N_2$  (e.g., Hily-Blant et al. [2010\)](#page-54-3). These reactions form the "popular" species CO,  $N_2H^+$  and  $NH_3$ , which are widely used to study cloud structures and kinematics.

*Freeze-out* Within the central 7,000 AU, the density increases above  $10^5$  cm<sup>-3</sup>, the temperature drops below 10 K and species heavier than He tend to disappear from the gas phase due to the process of freeze-out (the adsorption of species onto dust grain surfaces). CO freeze-out has been measured in starless and prestellar cores at a 80–90 % level (Willacy et al. [1998](#page-66-4); Caselli et al. [1999;](#page-48-5) Bacmann et al. [2002;](#page-46-6) Redman et al. [2002\)](#page-61-7). Nitrogen-bearing species have also been found to deplete from the gas phase, although not as much as CO (e.g., Bergin et al. [2002](#page-46-7); Tafalla et al. [2006;](#page-63-5) Friesen et al. [2010\)](#page-52-4). The reason for this differential freeze-out has to be found in the fact that N-bearing species, such as  $N_2H^+$  and  $NH_3$ , experience larger production rates when neutral species (in particular CO) start to disappear from the gas phase.

The freeze-out is a natural consequence of the quiescent nature of prestellar cores: once species land on a grain surfaces, they cannot thermally evaporate (because dust temperatures are  $T_{\text{dust}} \le 10 \text{ K}$ , typical binding energies are  $E_B \ge 1000 \text{ K}$  and the thermal evaporation rate is  $\propto \exp[-E_B/(k T_{\text{dust}})]$  and they cannot photodesorb as interstellar photons cannot penetrate within prestellar cores (whose central regions have visual extinctions larger than 50 mag). Only a small fraction of the adsorbed species can return in the gas phase via non-thermal desorption mechanisms mainly driven by cosmic rays, such as dust impulsive heating due to cosmic-ray bombardment (e.g., Leger et al. [1985\)](#page-57-3) and photodesorption due to the Far-UV (FUV) field produced by cosmic-ray impacts with  $H_2$  molecules (Prasad and Tarafdar [1983;](#page-61-8) Gredel et al. [1989;](#page-53-5) Shen et al. [2004\)](#page-63-6), although molecular hydrogen formation (Willacy and Millar [1998;](#page-66-5) Roberts et al. [2007\)](#page-62-5) and surface reactions involving radicals (D'Hendecourt et al. [1982\)](#page-50-8) may also play a role. Desorption of mantle species by FUV photons has been included in the chemical-dynamical models of L1544, to explain the recent Herschel detection of water vapor in the center of this prototypical prestellar core (Caselli et al. [2012\)](#page-48-6). Freeze-out time scales ( $t_{\text{freeze-out}} \propto 10^9/n_H$  yr, where  $n_H$  is the total number density of hydrogen nuclei (Jones and Williams [1985](#page-55-5))) are significantly shorter than the dynamical (free-fall) time scale ( $t_{\text{free-fall}} \propto 4 \times 10^7 / \sqrt{n_{\text{H}}}$ , Spitzer [1978](#page-63-7)), so dust grains are expected to build thick icy mantles during the prestellar phase of the starformation process (Sect. [4.2\)](#page-15-0).

*Deuterium fractionation* In the cold environments of prestellar cores, another important process takes place: deuterium fractionation. The starting point is the exothermic reaction between  $H_3^+$  and HD, which produces  $H_2D^+$  and  $H_2$  ( $H_3^+$  + HD  $\rightarrow$  $H_2D^+ + H_2 + 230$  K, Watson [1974\)](#page-66-6). This reaction cannot proceed from right to left when the kinetic temperature is below  $\approx$  20 K and if a large fraction of H<sub>2</sub> molecules is in para form, as expected in cold and dense cores (Flower et al. [2006;](#page-52-5) Pagani et al. [2009;](#page-60-4) Troscompt et al. [2009](#page-64-2)). Therefore, the  $H_2D^+/H_3^+$  abundance ratio becomes significantly larger than the D elemental abundance with respect to H. When the freezeout of neutral species (especially CO and O, which are the main destruction partners of  $H_2D^+$ ) becomes important, deuterium fractionation is further enhanced (Dalgarno and Lepp [1984](#page-50-9)). In fact, the deuteration zone of Fig. [5](#page-13-0) is the region where the bright-est line of ortho-H<sub>2</sub>D<sup>+</sup> has ever been detected (Caselli et al. [2003](#page-48-7)). This deuteration "jump" allows multiply deuterated forms of  $H_3^+$  to thrive (Vastel et al. [2004;](#page-65-2) Parise et al. [2011\)](#page-60-5) and their dissociative recombinations with electrons liberate D atoms, locally increasing the D/H ratio to values larger than 0.1 (Roberts et al. [2003\)](#page-62-6). The large D/H ratio in the gas phase implies efficient deuteration of surface species (in particular CO), with the consequent production of deuterated and doubly deuterated formaldehyde as well as singly, triply and doubly deuterated methanol (e.g., Tielens [1983;](#page-64-3) Charnley et al. [1997;](#page-49-1) Caselli et al. [2002a](#page-48-8); Taquet et al. [2012a,](#page-63-8) [2012d\)](#page-63-9). HDCO, D<sub>2</sub>CO and CH<sub>2</sub>DOH have been detected in prestellar cores (Bacmann et al. [2003;](#page-46-8) Bergman et al. [2011\)](#page-46-9), while doubly and triply deuterated methanol have been detected in the envelope of young stellar objects (Parise et al. [2002](#page-60-6), [2004](#page-60-7)), see Sect. [5.](#page-20-0)

*The ionization fraction* Deuterated species are the main probes of the central regions of prestellar cores, the future stellar cradles. Their observation allows us to trace the kinematics (e.g., van der Tak et al. [2005](#page-64-4); Crapsi et al. [2007](#page-50-7)) and, together with the non-deuterated isotopologue, to measure the elusive electron number density  $n(e^-)$ , which plays a crucial role in the dynamical evolution of the cloud. In fact, electrons and ions gyrate around magnetic field lines which permeate the clouds, and decouple from the bulk motions. During the gravitational collapse, neutral species slip through magnetic field lines and collide with molecular ions in a process called ambipolar diffusion (Mouschovias [1979;](#page-59-5) Shu et al. [1987\)](#page-63-3). Depending on the fraction of ions present in the gas phase, neutral-ion collisions can significantly slow down the collapse compared to free-fall. How do we measure the ionization degree? Using simple steady-state chemistry of (easy-to-observe) molecular ions, such as HCO<sup>+</sup> and DCO<sup>+</sup>, which form from the reaction of CO with  $H_3^+$ and  $H_2D^+$  and are destroyed by electrons, it is easy to arrive at analytic expressions relating the observed DCO<sup>+</sup>/HCO<sup>+</sup> abundance ratio to  $n(e^-)$  (Guelin et al. [1977;](#page-53-6) Wootten et al. [1979\)](#page-67-3). Using time dependent chemical codes (Caselli et al. [1998](#page-48-9)) and (Bergin et al. [1999\)](#page-46-10) obtained values of  $x(e^-)$  ( $\equiv n(e^-)/n(H_2)$ ) between 10<sup>-8</sup> and 10<sup>−6</sup>. Given that the time scale for ambipolar diffusion is  $t_{AD} \approx 2.5 \times 10^{13} x(e^-)$  yr (Spitzer [1978](#page-63-7)), the above measurements imply values of  $t_{AD} \simeq 2.5 \times 10^5$  and  $2.5 \times 10^7$  yr, factors of 2–200 larger than *t*<sub>free-fall</sub> for prestellar cores with an average  $n_{\rm H} = 10^5 \text{ cm}^{-3}$ .

<sup>15</sup>N *fractionation* On the one hand, no significant <sup>15</sup>N fractionation (compared to the Solar Nebula value of ~440, see Sect. [3.4\)](#page-9-0) has been found in NH<sub>3</sub> (<sup>14</sup>N/<sup>15</sup>N ≃ 350–850, Gerin et al.  $2009$ ;  $334 \pm 50$ , Lis et al.  $2010$ ) toward prestellar cores and protostellar envelopes, and in  $N_2H^+$  (<sup>14</sup>N/<sup>15</sup>N = 446 $\pm$ 71, Bizzocchi et al. [2010\)](#page-46-11) toward the prototypical prestellar core L1544. On the other hand, (Milam and Charnley [2012](#page-58-8)) and Hily-Blant et al. (submitted) found significant <sup>15</sup>N enrichment in HCN toward prestellar cores (between 70 and 380). Similar values have been found by Adande and Ziurys [\(2012](#page-45-4)) in HNC observations of star-forming regions across the Galaxy. It is interesting to point out here that the  $15N$  fractionation observed in comets (Sect. [3.4](#page-9-0)) has been measured for CN and HCN (<sup>14</sup>N/<sup>15</sup>N ~ 130–170, Bockelée-Morvan et al.  $2008$ ). This differential <sup>15</sup>N fractionation for amines and nitriles has been recently reproduced in chemical models of dense clouds by Wirström et al. [\(2012](#page-66-1)), who suggest that the processes able to reproduce the observed differentiation could be at the origin of the poor correlation between D and  $15N$  fractionation observed in some primitive material in our Solar System (Sect. [3.4](#page-9-0)). Thus, a further link between prestellar core chemistry and the Solar System composition has been found (see Sect. [7\)](#page-39-0).

# <span id="page-15-0"></span>4.2 Ice formation and evolution

Interstellar dust grains are crucial for the chemical and physical evolution of interstellar clouds and for our astrochemical origins. First of all, hydrogen atoms can quickly scan their surfaces, meet and form volatile  $H_2$  molecules at rates large enough to defeat H<sub>2</sub> photodissociation due to the interstellar radiation field (Hollenbach and Salpeter [1971;](#page-54-4) Pirronello et al. [1999](#page-61-9); Cazaux and Tielens [2002;](#page-48-10) Cuppen and Herbst [2005\)](#page-50-10). Thus, dust grains are responsible for the transition of interstellar gas in our Galaxy (as well as in external galaxies) from atomic to molecular the first step toward chemical complexity. Secondly, they are efficient absorbers of the FUV photons, so that they act as "UV-filters", protecting molecules within clouds from the UV destructive action. Thirdly, they catalyze the formation of important species, in particular H<sub>2</sub>O, with such high efficiency that more than 30 % of oxygen atoms are locked into water ice as soon as the visual extinction reaches values ≥3 mag (e.g., Murakawa et al. [2000](#page-59-6); Hollenbach et al. [2009;](#page-54-5) Whittet [2010;](#page-66-7) Chiar et al. [2011\)](#page-49-2). Finally, they become the main gas coolants in the central regions of prestellar cores, where the densities are above  $\approx 10^5$  cm<sup>-3</sup>, the temperatures fall below 10 K and species heavier than He (including important coolants such as CO) are mostly frozen onto their surfaces. In such conditions, the freeze-out rate will become even more extreme and dust grains should develop thick ice mantles. How thick? A simple estimate can be made considering that levels of CO freeze-out of about 90 % are seen within the central prestellar core regions (see Sect. [4.1\)](#page-13-1). Assuming that all species heavier than helium are affected by a similar amount of freeze-out (including nitrogen, Hily-Blant et al. [2010\)](#page-54-3), then in clouds with total hydrogen density of 2 × 10<sup>6</sup> cm<sup>-3</sup>, the total number density of heavy species frozen onto dust grains is about  $1.3 \times 10^3$  cm<sup>-3</sup>. Further assuming that they are combined in molecules with two heavy elements on average (e.g. CO, CH<sub>3</sub>OH, CO<sub>2</sub>, H<sub>2</sub>O), the total number of solid species will be about 660 cm<sup>-3</sup>. Now, we just need to divide this number by the total number of sites on an average grain with radius 0.1  $\mu$ m ( $\approx$ 10<sup>6</sup>; Hasegawa et al. [1992\)](#page-53-8) to have the number of monolayers ( $\simeq$ 250). Considering a monolayer thickness of about 1 Å, the total mantle thickness is then  $2.5 \times 10^{-6}$  cm, or about a quarter of the grain radius. Such thick mantles boost dust coagulation (Ossenkopf and Henning [1994\)](#page-60-8).

What are the main chemical processes on the surface of dust grains? Our understanding is based on (i) observations of absorption features along the line of sight of stars located behind molecular clouds or protostars embedded in dense cores (e.g., Whittet et al. [2011](#page-66-8) and references therein), and on (ii) laboratory work (e.g., Watanabe and Kouchi [2002](#page-66-9); Hiraoka et al. [2002](#page-54-6); Miyauchi et al. [2008;](#page-58-9) Ioppolo et al. [2008;](#page-54-7) Fuchs et al. [2009](#page-52-6); Dulieu et al. [2010](#page-51-6)). From these studies, we now know that surface reactions are mainly association reaction: oxygen is transformed into water via successive association reactions with hydrogen (e.g. O  $+ H \rightarrow OH$ ; OH  $+ H \rightarrow H_2O$ , but see Sect. [4.2.1](#page-17-0) for more pathways to water ice); similarly, CO is transformed first into formaldehyde,  $H_2CO$ , and then into methanol, CH<sub>3</sub>OH, via two and four association reactions, respectively; atomic nitrogen saturates into ammonia, NH3. Other important processes are photoprocesses and cosmic-ray bombardments. Photoprocesses are experimentally found to promote the formation of organic species more complex than CH3OH (Gerakines et al. [1996;](#page-52-7) Bennett and Kaiser [2007;](#page-46-12) Öberg et al. [2009a,](#page-59-7) [2010b](#page-59-8)) up to amino acids (e.g., Bernstein et al. [2002](#page-46-13); Muñoz Caro et al. [2002](#page-59-3), [2004\)](#page-59-9) and allow solid species to return into the gas phase (Öberg et al. [2009b,](#page-59-10) [2009c\)](#page-59-11). Cosmic rays, unlike UV photons, traverse dense cores relatively unhampered, although their flux may be reduced by a factor of a few by the mirroring effect of magnetic fields (Padovani and Galli [2011](#page-60-9)). When colliding with dust grains, they can alter mantle compositions (e.g., Palumbo et al. [2000](#page-60-10); Ioppolo et al. [2009;](#page-54-8) Modica and Palumbo [2010;](#page-58-10) Sicilia et al. [2012](#page-63-10); Boduch et al. [2012;](#page-47-6) Pilling et al. [2012\)](#page-61-10). Cosmic rays also play a crucial role in molecular desorption, as mentioned in the previous section. Surface chemistry is one of the most challenging disciplines in astrochemistry, but



<span id="page-17-1"></span>**Fig. 6** Ice mantle evolution within a prestellar core, from the outer-edge, where the core merges with the surrounding molecular cloud, to the dark-cloud zone and deuteration zone as depicted in Fig. [5](#page-13-0). Ice mantles become thicker and richer in complex organic molecules moving toward the center of a prestellar core, where star- and planet-formation takes place

in the recent years several models have been successful in reproducing the ob-served abundance of some simple and complex species (e.g., Aikawa et al. [2008;](#page-45-5) Garrod et al. [2009;](#page-52-8) Hollenbach et al. [2009;](#page-54-5) Cuppen et al. [2009;](#page-50-11) Cazaux et al. [2011;](#page-49-3) Taquet et al. [2012a](#page-63-8), [2012b](#page-63-11)).

The picture that has emerged from the combination of observations, laboratory work and modeling is sketched in Fig. [6,](#page-17-1) which shows the evolution of a dust grain mantle from the outer-edge to the central regions of a prestellar core embedded in a molecular cloud bathed by the interstellar radiation field (with reference to Fig. [5](#page-13-0) to locate the various zones). At the outer edge of the prestellar core, photoprocesses are important and the ice mantles are just beginning to form. Here, oxygen atoms are transformed into water, carbon (still not locked in CO) into methane (CH4) and nitrogen into ammonia. Water dominates the mantle composition (probably reflecting the larger cosmic abundance of oxygen relative to C and N). Moving toward the dark-cloud zone (where the prestellar core merges with the molecular cloud within which it is embedded), UV photons are absorbed by dust grains, CO becomes the second most abundance molecule (after  $H_2$ ) and the mantle starts to accumulate CO.  $CO<sub>2</sub>$  also starts to form, either via cosmic-ray bombardment (Ioppolo et al.  $2009$ )) and/or via the CO+OH reaction (Oba et al. [2010;](#page-59-12) Ioppolo et al. [2011;](#page-54-9) Noble et al. [2011;](#page-59-13) Garrod and Pauly [2011\)](#page-52-9). Here, the limited amount of CO freeze-out limits the degree of deuteration to levels of  $\leq$  a few % (as measured from the observed DCO<sup>+</sup>/HCO<sup>+</sup> abundance ratio; e.g., Caselli et al. [2002b](#page-48-11)). Deeper into the prestellar core, CO molecules are mostly in solid form, deuteration processes are dominant and the D/H ratio reaches values above 0.1 (see Sect. [4.1\)](#page-13-1). When freeze-out is dominant, the main reactive species landing on dust grain surfaces are atomic H and D. Thus, CO is not only hydrogenated into formaldehyde and methanol, but also deuterated. Large amounts of deuterated and multiply deuterated  $H_2CO$  and  $CH_3OH$  are produced (see Sect. [4.1](#page-13-1)).

# <span id="page-17-0"></span>*4.2.1 The origin of water*

Extra attention is given here to the production of water, because of its dominant presence in interstellar ices and its crucial role in our astrochemical origins. Recent measurements of water vapor toward a prestellar core with the Herschel Space Observatory and the use of chemical/dynamical/radiative transfer models, allowed (Caselli et al. [2012](#page-48-6)) to measure a total mass of water vapor of 0.5 Earth masses within the central 10,000 AU and predicted about 2.6 Jupiter masses of water ice (thus, plenty of ice to boost dust coagulation and the formation of giant planets via core accretion models, e.g., Pollack et al. [1996\)](#page-61-11). From observations of water ices in molecular clouds (e.g., Whittet et al. [2011,](#page-66-8) and references therein), it is now well established that water ice forms on the surface of dust grains in regions of molecular clouds where the visual extinction is at least 3 mag (when the impinging radiation field is close to the average Galactic value, called the Habing field; larger extinctions are needed for stronger fields). For lower extinction values, the interstellar UV field does not allow dust grain surfaces to accumulate a significant amount of water molecules, as they are efficiently photodesorbed (Öberg et al. [2009b\)](#page-59-10). Laboratory work shows that  $H_2O$  can form via hydrogenation of atomic oxygen (Hiraoka et al. [1998;](#page-54-10) Dulieu et al. [2010](#page-51-6); Jing et al. [2011](#page-55-6)), molecular oxygen (Ioppolo et al. [2008;](#page-54-7) Miyauchi et al. [2008\)](#page-58-9), ozone (Mokrane et al. [2009;](#page-59-14) Romanzin et al. [2011](#page-62-7)) and via  $OH + H<sub>2</sub>$  at 10 K (Oba et al. [2012](#page-59-15)). As the abundance of water ice in molecular clouds, within which prestellar cores form, is already large (close to  $10^{-4}$  w.r.t. H<sub>2</sub> molecules; e.g., Whittet and Duley [1991\)](#page-66-10), we now generally believe that the main production of water happens *before* the formation of a prestellar core, as also found by chemical models (e.g., Aikawa et al. [2008;](#page-45-5) Hollenbach et al. [2009;](#page-54-5) Cazaux et al. [2010;](#page-49-4) Taquet et al. [2012b](#page-63-11)). This suggests that also the production of heavy water must be regulated by the molecular cloud characteristics. This is an important point, as the HDO*/*H2O ratio is well measured on Earth, comets and asteroids (Sect. [3.1](#page-6-0)), as well as in star-forming regions (Sect. [5.4](#page-27-0)). Therefore, one could use our current understanding of surface chemistry and the observed HDO*/*H2O abundance ratios in starforming regions to find the link between interstellar chemistry and the Solar System.

Cazaux et al.  $(2011)$  $(2011)$  predict that significant variations in the HDO/H<sub>2</sub>O ratio can be attributed to small variations of the dust temperature at the time of ice formation. In particular, if the dust temperature is lower than  $\simeq$  15 K, the HDO/H<sub>2</sub>O ratio is predicted to be  $\leq 0.01$  %, because, in these conditions, a large fraction of the dust surface is covered by  $H_2$  molecules, allowing the reaction of  $H_2 + O$  to proceed despite the large barrier of 3000 K (Oba et al. [2012\)](#page-59-15) did not find evidence in the laboratory that this reaction is indeed proceeding, but more laboratory work is ongoing to assess this). The HDO/H<sub>2</sub>O ratio in these conditions simply reflects the HD/H<sub>2</sub> ratio, always close to the interstellar D/H value ( $\approx$ 1.5 × 10<sup>-5</sup>, Oliveira et al. [2003\)](#page-60-11). For dust temperatures above  $\simeq$  15 K, H<sub>2</sub> molecules do not stay on the dust surface for long (as their evaporation rate becomes an increasingly large fraction of their accretion rate) and water formation will mostly happen via the reaction of oxygen with atomic hydrogen. As the gas-phase D/H ratio sharply increases above the cosmic deuterium abundance when ice formation takes place (see Fig. 1 of Cazaux et al. [2011\)](#page-49-3), then the HDO*/*H2O ratio can be as large as a few %. In this scenario, our Solar System formed in a prestellar core embedded in a molecular cloud with dust temperature slightly above 15 K. Taquet et al. [\(2012b](#page-63-11)), using a multilayered formation mechanism of ice mantles (Taquet et al. [2012b\)](#page-63-11), find that water is formed first on dust surfaces and that the HDO*/*H2O ratio depends on the (poorly constrained) ortho:para ratio of  $H_2$ , on the cloud volume density and, to a lesser extent, on the dust temperature and visual extinction. However, water deuteration can also occur in the gas phase: Thi et al. [\(2010b](#page-64-5)) found that significant deuteration levels ([HDO]/[H<sub>2</sub>O]  $\approx$ 10<sup>-3</sup>–10<sup>-2</sup>) can be produced without surface reactions and at high temperature ( $T > 100$  K), in the inner regions of protoplanetary disks (Sect. [6.2](#page-34-0)). The fractionation occurs because of the difference in activation energy between deuteration enrichment and the back reactions.

#### 4.3 Complex organic molecules

In the freezing cold of dark clouds and prestellar cores, active gas-phase and surface chemistry produce complex organic molecules (COMs). Since the '80s, organic molecules have been discovered in the TMC-1 dark cloud, part of the Taurus Molecular Cloud complex: methyl cyanide ( $CH<sub>3</sub>CN$ , Matthews and Sears [1983\)](#page-58-11), methylcyanoacetylene (CH<sub>3</sub>C<sub>3</sub>N, Broten et al. [1984](#page-48-12)), acetaldehyde (CH<sub>3</sub>CHO Matthews et al. [1985\)](#page-58-12), ketene (CH<sub>2</sub>CO; Irvine et al. [1989](#page-54-11)), methanol (CH<sub>3</sub>OH Friberg et al. [1988\)](#page-52-10), methylcyanodiacetylene (CH3C5N Snyder et al. [2006](#page-63-12)), methyl-triacetylene (CH<sub>3</sub>C<sub>6</sub>H Remijan et al. [2006](#page-61-12)), propylene (CH<sub>2</sub>CHCH<sub>3</sub> Marcelino et al. [2007\)](#page-58-13), methyldiacetylene (CH<sub>3</sub>C<sub>4</sub>H), cyanopolyynes (HC<sub>2n+1</sub>N,  $n = 0, 1, \ldots, 5$ ) and  $C_{2n+1}$ N radicals (Walmsley et al. [1984;](#page-66-11) Hirahara et al. [1992](#page-54-12); Ohishi and Kaifu [1998;](#page-60-12) Kaifu et al. [2004](#page-55-7)) and the negative ions  $C_6H^-$ ,  $C_8H^-$  (McCarthy et al. [2006;](#page-58-14) Brünken et al. [2007\)](#page-48-13). Complex organics have also been found in two prestellar cores: L183 (CH<sub>3</sub>CHO, Matthews et al. [1985](#page-58-12); HCOOH, Requena-Torres et al. [2007\)](#page-62-8) and L1689B (CH<sub>3</sub>CHO, HCOOCH<sub>3</sub>, CH<sub>3</sub>OCHO, CH<sub>2</sub>CO, Bacmann et al. [2012\)](#page-46-14). The chemistry of C-bearing species such as cyanopolyynes and  $CH<sub>3</sub>C<sub>5</sub>N$  can be understood if the gas phase is carbon-rich (C/O  $\approx$  1.2 Wakelam et al. [2006](#page-65-3)) or if polycyclic aromatic hydrocarbons (PAHs) are included in the chemistry (with a standard C/O abundance ratio of  $\simeq 0.4$ , Wakelam and Herbst [2008\)](#page-65-4). More problematic is the explanation of complex O-bearing species, such as methanol, which require surface chemistry. Garrod et al. ([2007\)](#page-52-11) assumed that the energy released during the formation process could be at least partially used for the surface species to desorb upon formation, reconciling observations with theory for CH3OH and propylene (if the desorption of this species is efficient). Oxygen-bearing species more complex than methanol can also be formed on the surface of low temperature dust grains if a source of UV photons is present (Sect. [4.2](#page-15-0)). For example, in the laboratory experiments of Öberg et al.  $(2009a)$  $(2009a)$ , it has been shown that the photodissociation of CH<sub>3</sub>OH produces radicals such as  $CH_3$  and  $CH_3O$  (recently discovered in a dark cloud by Cernicharo et al., in press), which can then recombine to form CH3OCH3 or react with CHO (probably produced by the photodissociation of solid  $CH_4$  and  $H_2O$ , see below) to form CH3CHO and HCOOCH3, respectively. Interstellar UV photons are expected to be important up to values of visual extinction of  $\simeq$  3 mag (e.g., Hollenbach et al. [2009\)](#page-54-5), where CO is not yet significantly frozen onto dust grains (see Fig. [5](#page-13-0)). Deeper into prestellar cores, a significantly more tenuous field of UV photons can be produced by the collisions of cosmic-rays with  $H_2$  molecules (Prasad and Tarafdar [1983;](#page-61-8) Gredel et al. [1989\)](#page-53-5). It is not yet clear if this cosmic-ray induced field is able (i) to produce enough radicals, (ii) to furnish them enough energy to move on the surface,

recombine and form complex molecules, and (iii) to release them into the gas phase where they are observed (see also the discussion in Taquet et al. [2012b\)](#page-63-11). Consequently, it is not yet clear whether models are able to reproduce the abundances of complex molecules observed by Bacmann et al. [\(2012](#page-46-14)).

In summary, possible first steps toward the formation of COMs in the ice (before the switch-on of the protostar) are as follows.

(1) *Production and storage of radicals.* In the molecular cloud within which the prestellar core forms, at  $A_V \approx 3$  mag, interstellar UV photons can still partially dissociate important ice components  $(H<sub>2</sub>O$  and  $CH<sub>4</sub>)$  and some of the products can be trapped within the ice, which already contains significant fractions of water (e.g., Chiar et al. [2011](#page-49-2)). Alternatively, because of the multilayered nature of icy mantles, radicals can be stored in the inner layers during mantle formation (Taquet et al. [2012b\)](#page-63-11).

(2) *Radical-radical reactions.* As the density increases and CO starts to freeze-out onto the first water-dominated ice layers, the CO is transformed into  $CH<sub>3</sub>OH$  more and more with increasing freeze-out (given that with the freeze-out of CO and O, the H/O and H/CO abundance ratios in the gas-phase increase, as the number density of H atoms is kept about constant to  $1 \text{ cm}^{-3}$  by the cosmic-ray dissociation and surface reformation of H2 molecules). The energy released during the formation of methanol is partially used by methanol itself to evaporate and partially released as heat on the icy surface, allowing some of the previously trapped radicals to move. The new radicals produced in the dissociation of  $CH<sub>3</sub>OH$  by cosmic-ray-induced UV photons (and probably some of the intermediate compounds produced during the  $CO \rightarrow CH_3OH$ conversion) will then participate in the formation of the observed complex organic molecules (e.g., Öberg et al. [2009a](#page-59-7)). As for the case of methanol, the energy released in the process of formation of these COMs can be partially used to return in the gas phase. The impulsive heating of dust grains due to the impact of heavy cosmic rays (Leger et al. [1985\)](#page-57-3) may also temporarily enhance the mobility of the stored radicals, allowing complex molecule formation.

<span id="page-20-0"></span>We emphasize that the above steps remain highly speculative and more experimental and theoretical work is necessary to better understand the grain-surface chemistry processes. Given that the observed COMs are building blocks of biologically important species, this once again underlines the importance of prestellar cores for the first steps toward our astrochemical origins.

#### **5 The cocoon phase: protostars**

Once the collapse starts, the gravitational energy released at the center of the infalling envelope is converted into radiation. During the first phases of star formation, this is the main source of the protostar luminosity  $L_*$  and it is given by  $L_* = G M_* \dot{M} / R_*$ , where  $M_*$  and  $R_*$  are the mass and radius of the central object, and  $\dot{M}$  is the mass accretion rate. The approximate structure of the envelope, as derived by observations of the continuum and line emission (e.g. Ceccarelli et al. [2000a;](#page-49-5) Jørgensen et al. [2002;](#page-55-8) Robitaille et al. [2006\)](#page-62-9) is reported in Fig. [7.](#page-21-0) Both the density and temperature increase toward the center. Similarly, the velocity of the infalling gas increases with decreasing distance from the center with an *r*−1*/*<sup>2</sup> power law, although part of the envelope

<span id="page-21-0"></span>

<span id="page-21-2"></span>may not be collapsing yet. The infall motion has proved difficult to disentangle from the outflow motions, but high spatial and spectral resolution observations recently obtained with  $ALMA<sup>3</sup>$  $ALMA<sup>3</sup>$  $ALMA<sup>3</sup>$  have succeeded to probe it unmistakably toward IRAS16293-2422 (Pineda et al. [2012](#page-61-13)). Finally, new Herschel observations provide a much more complicated picture where, at least in some sources, the cavity created by the outflowing gas is illuminated and heated by the UV photons of the central star, making the interpretation of the observed lines not straightforward (Visser et al. [2012](#page-65-5)).

5.1 The chemical composition of protostellar envelopes: a powerful tool to understand the present and the past

Chemistry has been recognised to be a powerful diagnostic tool in several fields of astrophysics to understand the present and the past of the studied object. For example, at large scale, the chemical enrichment in stars throughout the Milky Way tells us about different star populations and ages, and, consequently, how the Milky Way formed (e.g., Gratton et al. [2012\)](#page-53-9). Similarly, at much smaller scales, the chemical composition in protostellar envelopes tell us about their present status and past history.

<span id="page-21-1"></span>Figure [7](#page-21-0) shows the approximate and very simplified density and temperature profiles of a typical protostellar envelope. To a scale of  $\geq$ 100 AU, a roughly spherical envelope heated by the internal new born star this is probably a correct description. However, at smaller scales, the envelope is not spherical, because of the presence of a circumstellar disk (Sect. [6\)](#page-31-0) and the presence of multiple sources, as in the case of IRAS16293-2422 and NGC1333-IRAS4 (e.g., Wootten [1989\)](#page-67-4), among the two most studied examples of solar-type protostars. Nonetheless, from a chemical point of view, four major zones can be identified (Fig. [7\)](#page-21-0): (i) an outer zone, with the

<sup>&</sup>lt;sup>3</sup>The Atacama Large Millimeter/sub-millimeter Array.

same chemical composition as that of the placental molecular cloud; (ii) a CO depleted zone, usually called cold envelope, with the chemistry is very similar to that of prestellar cores (Sect. [4](#page-12-0)); (iii) a  $CH_4$  ice sublimation region, where the chemistry is dominated by the warm carbon chain chemistry, called WCCC, triggered by sublimation of the methane from the grain mantles; (iv) the hot corino zone, where the chemistry is dominated by the water-matrix grain mantle sublimation and hot gas chemistry. The transition between zones (ii) to (iv) is determined by the dust temperature, which governs the sublimation of the icy mantles, whereas the CO depleted region depends on the density and age of the protostellar envelope. In the following we summarise the characteristics of the four zones.

- Zone (i) The chemical composition in this zone is similar to typical molecular clouds, with no particularly important freeze-out of species. Whether this zone is present or not in a protostellar envelope depends on the envelope density and age, which determines the existence of zone (ii).
- Zone (ii) As described in Sect. [4](#page-12-0), if the density and age of the envelope are high enough, molecules freeze-out onto dust surfaces. Important for the various reasons again described in Sect. [4](#page-12-0) is the region where CO freezes out, defined by a dust temperature lower than about 22 K. Jørgensen et al. [\(2005](#page-55-9)) found that a large fraction of Class 0 and Class I protostars have COdepleted regions in their envelopes, typically where the density is larger than  $\sim$ 10<sup>5</sup> cm<sup>-3</sup>. Models of the chemistry in young protostellar envelopes provide a theoretical interpretation to these observations (e.g., Lee et al. [2005\)](#page-56-6).
- Zone (iii) When the dust temperature exceeds the methane sublimation temperature,  $~\sim$ 25 K, the chemistry is governed by the injection of methane in the gas phase, if the CH<sub>4</sub> abundance is larger than  $\sim 10^{-7}$ . In this case, CH<sub>4</sub> becomes a major destruction partner for  $C^+$ , starting the efficient formation of C-chain molecules in the relatively warm (30–60 K) gas (Aikawa et al. [2008;](#page-45-5) Hassel et al. [2008](#page-53-10), [2011\)](#page-53-11). So far, only a few protostellar envelopes with very abundant C-chain molecules have been discovered. L1527 is the prototype of this class of sources, called Warm-Carbon-Chain-Chemistry (WCCC) sources (Sakai et al. [2008,](#page-62-10) [2010a,](#page-62-11) [2010b](#page-62-12)). Note that the abundance of methane has been indirectly inferred in those sources by modeling the observed C-chain molecules, as gaseous CH4 does not have observable rotational transitions.
- Zone (iv) When the dust temperature exceeds about 100 K, the grain mantles evaporate and all species trapped in them are released in the gas phase, giving rise to a rich chemistry, first discovered in high-mass protostellar envelopes and called hot core chemistry (e.g., Blake et al. [1987\)](#page-47-7), and successively unveiled in low-mass protostellar envelopes (Cazaux et al. [2003\)](#page-48-14). However, as will be discussed in detail in Sect. [5.2](#page-24-0), the chemical composition of low- and high- mass cores is not identical.

The transition zones in Fig. [7](#page-21-0) are, of course, approximate, as laboratory experiments show that ice sublimation is a complex process where molecules are released into the gas through several steps at different dust temperatures (e.g., Viti et al. [2004\)](#page-65-6).

Also, the outflows emanating from the central objects open up cavities which are directly illuminated by the UV photons of the new born star (e.g., van Kempen et al. [2009;](#page-65-7) Yıldız et al. [2012;](#page-67-5) Visser et al. [2012\)](#page-65-5). In these cases, large Photon-Dominated-Regions (PDRs) may dominate and mask the molecular emission from the various zones, depending on the extent of the cavity.

As already mentioned, the presence of the WCCC zone (zone iii) depends on the abundance of methane in the dust mantles. Methane is formed, as the vast majority of the grain mantles, during the prestellar phase (Sect. [4](#page-12-0)). Specifically, it is believed to form by hydrogenation of neutral carbon. However, in typical molecular clouds, neutral carbon is a rare species because of the efficient formation of CO. Therefore, to have a large quantity of iced CH4, one needs particular conditions, namely a relatively high abundance of neutral carbon in the gas phase. This occurs when the transition from the diffuse cloud to molecular cloud is very fast, and a substantial fraction of carbon atoms freeze-out into the grain mantles before the CO formation is achieved (e.g., Hassel et al. [2011\)](#page-53-11). Therefore, the presence of a WCCC zone may be a signature of fast collapse (Sakai et al. [2008](#page-62-10)), for example triggered by a shock from a nearby forming star or two encountering diffuse clouds. Alternatively, if the prestellar core is embedded in a relatively tenuous cloud, CO photodissociation could still play a role and led to a large amount of methane ice. Unfortunately, the limited number of observations do not allow us to go much further in the interpretation of this peculiar chemistry, and more studies are needed to fully exploit it. In the same vein, the chemical composition in the hot corino zone, as well as the observed molecular deuteration, are all largely influenced by the prestellar phase. These cases will be discussed in detail in the following paragraphs.

Last, a potentially powerful diagnostic is provided by the relative abundances of isomers of the same generic formula. Since the interstellar chemistry is dominated by kinetics, different isomers have in principle the imprint of the different chemical formation routes. Therefore, the isomer relative abundances help understanding the reactions at work and, consequently, how well we understand the interstellar chemistry. A puzzling and interesting example is provided by the isocyanic acid (HNCO) and its isomers fulminic acid (HCNO) and cyanic acid (HOCN), which have zero energies, respectively, 71 and 25 kcal/mol above HNCO. In cold gas, the HNCO/HCNO and HNCO/HOCN abundance ratios are about 50, whereas in warm gas HNCO/HCNO is about 50 and HNCO/HOCN more than 5 times larger (Marcelino et al. [2010\)](#page-58-15). The difference of abundances between the different isomers is thought to be due to the different chemical routes of formation and destructions (Quan et al. [2010](#page-61-14)). However, the available gas-phase and gas-grain+gas-phase models have some difficulties in reproducing the observations and the results very much depend on the assumption made on the  $CH_2 + NO$  reaction rate coefficient. Even more puzzling, these models do not explain the observed difference in the HCNO/HOCN ratio between cold and warm sources. Marcelino et al. [\(2010](#page-58-15)) speculate the presence of a mechanism that converts HCNO into HOCN, despite the large energy barrier necessary for the isomerisation. On the other hand, Lattelais et al. [\(2009](#page-56-7)) already noted that a pseudo-isomerisation seems to occur to the majority of species where different isomers have been detected. They studied 14 species and 32 isomers and found that the larger the energy difference, the larger the abundance ratio between the most stable species and its isomer,

with a few exceptions. They called it the "minimum energy principle" and its origin is still unclear, as the isomerisation barriers are generally very large and different isomers are formed from different "mother" species.

<span id="page-24-0"></span>Similar arguments on the diagnostic value applies for the isotopologues of a species. Nice examples are provided by the CCS and CCH studies by Sakai and collaborators (e.g., Sakai et al. [2007](#page-62-13), [2010a](#page-62-11)). Studying the abundance ratio of <sup>13</sup>CCS/C<sup>13</sup>CS and <sup>13</sup>CCH/C<sup>13</sup>CH, they constrained the formation routes of CCS and CCH and demonstrated that the  ${}^{12}C/{}^{13}C$  depends on the position of the carbon in the chain.

#### 5.2 The chemical complexity in hot corinos

In the 90s, several abundant complex organic molecules (COMs) were discovered in an unbiased spectral survey of the prototype massive star-forming region, the Orion Molecular Cloud (Blake et al. [1987](#page-47-7)). Soon after, a similar rich chemistry was observed in several other massive protostellar envelopes. The proprieties of the line emission indicate that these COMs reside in compact ( $\leq 0.01$  pc), dense ( $\geq 10^7$  cm<sup>-3</sup>) and hot  $(\geq 100 \text{ K})$  regions, soon called "hot cores". A simple and obvious interpretation is that the observed rich chemistry is due to the sublimation of some species from the grain mantles, called "mother" or "primary" species, and the synthesis of others, called "daughter" or "secondary" species, thanks to the high gas temperature (e.g., Charnley et al. [1992\)](#page-49-6). Almost two decades later, similar results were obtained toward the envelope of the prototype low-mass protostar IRAS16293-2422 (Ceccarelli et al. [2000b;](#page-49-7) Cazaux et al. [2003\)](#page-48-14), where several COMs were detected. Since then, more low-mass hot cores have been discovered and, to distinguish them from the high-mass hot cores, they were called hot corinos (Bottinelli et al. [2004a](#page-47-8), [2004b,](#page-47-9) [2007;](#page-47-10) Lahuis et al. [2006;](#page-56-8) Jørgensen et al. [2012\)](#page-55-10); see also the review by Herbst and van Dishoeck [\(2009](#page-54-13)). Hot corinos differ from hot cores not only for the smaller sizes, lower temperatures and densities, but also chemically. In fact, when normalized to methanol or formaldehyde, hot corinos have typically one order of magnitude more abundant COMs (such as HCOOCH<sub>3</sub> or CH<sub>3</sub>OCH<sub>3</sub>) than hot cores (Ceccarelli et al. [2007;](#page-49-8) Bottinelli et al. [2007;](#page-47-10) Herbst and van Dishoeck [2009](#page-54-13); Öberg et al. [2011c](#page-60-13); Cordiner et al. [2012\)](#page-50-13). The difference in the richness and COMs abundances between hot cores and hot corinos is likely due to various factors. Among them, two certainly play a major role: (i) the gas temperature, which governs the neutral-neutral reactions that often possess large activation energy barriers; (ii) the composition of the sublimated ices, governed by the past prestellar history (Sect. [4](#page-12-0)).

In addition to being weak line emitters and small objects, the study of hot corinos is also complicated by the fact that low-mass protostars are often binary or multiple systems (as in the case of high-mass protostars). The hot corino prototype IRAS16293-2422 is in fact a binary system and the two objects composing it, called A and B in the literature, show definitively a different chemistry (see for example the recent articles by Caux et al. [\(2011](#page-48-15)) and Jørgensen et al. ([2011\)](#page-55-11), and reference therein). To illustrate this aspect, Fig. [8](#page-25-0) shows a sketch of the chemical composition of IRAS16293-2422, based on the analysis of the single-dish unbiased spectral millimeter and sub-millimeter survey carried out by Caux et al. ([2011\)](#page-48-15) and confirmed by

<span id="page-25-0"></span>

the sub-millimeter interferometric unbiased survey of Jørgensen et al. ([2011\)](#page-55-11). Four groups of species are identified:

- *Group I:* Millimeter lines from simple molecules, like CN and HCO<sup>+</sup>, are dominated by the cold envelope. Also, emission from simple carbon-chains are associated with the cold envelope (see the discussion of their chemistry in Sect. [5.1\)](#page-21-2).
- *Group II:* Source A is rich in N- and S-bearing molecules.
- *Group III:* Source B is rich in O-bearing COMs.
- *Group IV:* Molecules like CH<sub>3</sub>OH, H<sub>2</sub>CO, CH<sub>3</sub>CCH and OCS emit low-lying lines in the cold envelope and high-lying lines in the two sources A and B.

The obvious question is: why are source A and B so chemically different? They must have had a similar composition of the sublimated ices, as they belong to the same core, so that the difference is probably originating from the different evolutionary status caused by the difference in mass of the two objects (Bottinelli et al. [2004b;](#page-47-9) Caux et al. [2011;](#page-48-15) Pineda et al. [2012](#page-61-13); Jørgensen et al. [2012](#page-55-10)). However, so far no attempt has appeared in the literature to theoretically model the two sources to understand what exactly causes the observed chemical differences.

Finally, as mentioned in Sect. [4,](#page-12-0) COMs are predicted to be formed on grain surfaces. Four fundamental steps are involved: (i) freeze-out of atoms and simple molecules (such as O and CO) on the grain surface; (ii) successive additions of H atoms to form hydrogenated species (such as  $CH<sub>3</sub>OH$ ); (iii) formation and trapping of radicals, such as  $CH_3$ , on the grain surfaces; (iv) combination of radicals to form COMs in the warm-up period. While laboratory experiments and quantum chemistry calculations have tested and quantified the second step, the third step is still a matter of debate. Garrod and Herbst ([2006\)](#page-52-12) and subsequent work from the same authors assume that the radicals are formed from the secondary UV photons emitted by the interaction of cosmic rays with  $H_2$  molecules. Specifically, it is assumed that UV photons break iced species like  $CH<sub>3</sub>OH$  into radicals like  $CH<sub>3</sub>$  and that the broken pieces remain frozen on the grains, which may not be necessarily the case. On the

<span id="page-26-0"></span>

other hand, Taquet et al. ([2012b\)](#page-63-11) showed that radicals can indeed be trapped in the grain mantles without the intervention of UV photons, just because of the intrinsic layered structure of the forming mantle.

<span id="page-26-1"></span>However, it is important to emphasize that, whatever is the possible origin of the radicals, models still fail to reproduce the observed amount of COMs. For example, Fig. [9](#page-26-0) shows the comparison between the observed and predicted methyl formate abundance normalized to the methanol one. Published models are off by at least one order of magnitude. Considering that COMs are also observed in prestellar cores (see Sect. [4](#page-12-0)) and outflows (Sect. [5.3\)](#page-26-1), something basic on how COMs are formed in the ISM must still escape our understanding.

#### 5.3 The chemical complexity in molecular outflows

The birth of a star is accompanied by a violent and substantial ejection of material simultaneous to the accretion toward the central object. The process has an enormous importance in the star-formation process because (i) it allows the infalling matter to lose angular momentum and accrete onto the central object, and (ii) the ejected material interacts with the surroundings, deeply modifying it and completely destroying, in some cases, the parental cloud (e.g., Lefloch et al. [1998;](#page-56-10) Shimajiri et al. [2008;](#page-63-13) Arce et al. [2011](#page-45-6); López-Sepulcre et al. [submitted\)](#page-57-5). The ejected material creates shocks at the interface between the outflowing jet and the quiescent material. Those shocks are chemically rich sites, showing a chemical composition very similar to hot cores/corinos. In fact, in the shocks, dust grains are sputtered and vaporized releasing the mantle components and part of their refractory material into the gas phase. Moreover, shocked regions become hot enough to allow neutral-neutral reactions to take over and produce complex molecules. In the following, we will only review the studies on the chemical composition of the outflow shocks, leaving out the many and important questions on the physical structure of the shock and the acceleration mechanisms of the jet.

Although several molecular outflows have been observed and mapped in the past three decades, the study of their molecular complexity started much later. Bachiller and Perez Gutierrez [\(1997](#page-46-16)) were the first to show the chemical structure of L1157-B1,

considered nowadays a prototype for the studies of molecular complexity in molecular outflows. Toward this source, not only relatively simple complex molecules, like methanol, have been detected (Codella et al. [2010\)](#page-49-9), but also molecules considered hot cores/corinos tracers, like methyl formate (HCOOCH<sub>3</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), formic acid (HCOOH) and methyl cyanide ( $CH<sub>3</sub>CN$ ) (Arce et al. [2008](#page-45-7)). High spatial resolution observations show that emission of these species is concentrated in a small region associated with the violent shocks at the head of the outflowing material (Codella et al. [2009](#page-49-10)). The presence of COMs in molecular outflows strongly suggests that these species were part of the sputtered icy mantles (as the time elapsed since the shock is too short for any gas-phase route to build up COMs) and provides us with another piece of the puzzle regarding their formation. The abundances normalized to methanol are at least one order of magnitude lower in molecular outflows than in hot corinos.

It is worth noticing the presence of species not even detected in other sources, like the phosphorus nitride (PN), whose abundance is only a few times  $10^{-10}$  with respect to  $H<sub>2</sub>$  (Yamaguchi et al. [2011](#page-67-6)). In fact, molecular outflows can be considered, for some aspects, unique laboratories to understand interstellar medium chemistry. For example, hydrogen chloride (HCl) has been recently detected with the Herschel Space Observatory in L1157-B1 (Codella et al. [2012a](#page-50-14)). The measured abundance is 3–6  $\times$ 10<sup>-9</sup>, practically the same value as in high- and low-mass protostellar envelopes (e.g., Peng et al. [2010](#page-60-14)) and about 200 times lower than the Cl elemental abundance. This is a puzzling result, as chemical models predict that HCl would be the major reservoir of chlorine and observational evidence suggests that L1157-B1 is a shock site where grains are sputtered/vaporized and mantles almost entirely destroyed, as also suggested by the large fraction of silicon found in the gas phase as SiO. Therefore, the low measured HCl abundance raises the question "where is chlorine?". It is not in the mantle, but not even in the vaporized refractory material of dust grains where silicates reside. Is then chlorine in a significantly more refractory component than silicates? Which one? All questions that will need more observations to be answered.

#### <span id="page-27-0"></span>5.4 Water and deuterated water

Water and deuterated water are special species, because of the hints on the Earth and Solar System formation that they bring (Sect. [3\)](#page-3-0) and because water plays a leading role in the thermal and chemical evolution of protostellar envelopes (Ceccarelli et al. [1996;](#page-49-11) Doty and Neufeld [1997](#page-51-7); van Dishoeck et al. [2011\)](#page-64-6). However, since water lines can only be observed from out-of-the atmosphere telescopes, the water content in the envelope of solar-type protostars has been estimated only recently.

*Water abundance in hot corinos.* The first estimates based on the Infrared Space Observatory (ISO) suggested that the water abundance in the hot corino region is only a few times  $10^{-6}$  (e.g., Ceccarelli et al. [2000a](#page-49-5)). The more recent observations obtained with Herschel, with a much better spatial and spectral resolution, have confirmed that first claim with an increased reliability and in a larger number of sources (Kristensen et al. [2010,](#page-56-11) [2012;](#page-56-12) Visser et al. [2012;](#page-65-5) Coutens et al. [2012](#page-50-15)). If,

on the one hand, these observations confirm the old theoretical predictions that water should be abundant in the innermost and warmest regions of the envelopes surrounding Class 0 protostars (Ceccarelli et al. [1996](#page-49-11); Crimier et al. [2009\)](#page-50-16), they also raise the question why the measured water abundance is much lower than that expected,  $\sim 10^{-4}$ , based on the ice measurements (Sect. [4\)](#page-12-0). Finally, interferometric observations have shown that a compact  $H_2^{18}O$  emitting region is associated with the hot corinos/disk of a few Class 0 sources (Jørgensen and van Dishoeck [2010a;](#page-55-12) Persson et al. [2012](#page-60-15)).

*Water abundance in molecular outflows* Again, the first estimates of the water abundance in molecular outflows were obtained with ISO and gave abundances varying from  $\sim 10^{-5}$  to  $\sim 10^{-4}$  (Liseau et al. [1996](#page-57-6); Nisini et al. [2000;](#page-59-16) Benedettini et al. [2000\)](#page-46-17). Water in outflows was also the target of the Submillimeter Wave Astronomy Satellite (SWAS) and Odin satellite, which were tuned on the  $H_2O$  ground-state transition at 557 GHz (Franklin et al. [2008;](#page-52-13) Bjerkeli et al. [2009;](#page-47-11) Benedettini et al. [2002\)](#page-46-18). More recently, the new Herschel observations are providing a mine of new information, allowing us to map the water emission along the outflow and to distinguish the water content in low to high velocity shocks. The Herschel maps show bright water emission at the shock sites of the molecular outflows (Nisini et al. [2000;](#page-59-16) Benedettini et al. [2012](#page-46-19); Kristensen et al. [2010](#page-56-11); Bjerkeli et al. [2011,](#page-47-12) [2012\)](#page-47-13). The study of the water abundance as a function of the velocity of the shock then shows that high velocity shocks are associated with larger water abundances (Lefloch et al. [2010;](#page-56-13) Kristensen et al. [2011;](#page-56-14) Bjerkeli et al. [2011;](#page-47-12) Santangelo et al. [2012;](#page-62-14) Vasta et al. [2012;](#page-65-8) Benedettini et al. [2012\)](#page-46-19), as predicted by the C-shock models (Kaufman and Neufeld [1996\)](#page-55-13). These models predict that  $H_2O$  is formed in the gas phase via reactions with large activation barriers (e.g.  $O + H_2$  and  $OH + H_2$ ; see also Hollenbach and McKee [1989\)](#page-54-14). Finally, interferometric observations show that the dense shock very close to the central source produces a large quantity of water (Lefloch et al. [2011\)](#page-57-7).

*Deuterated water* The HDO abundance and HDO*/*H2O abundance ratio have been measured toward a handful of hot corinos, with different techniques. From singledish telescopes (IRAM 30m and ISO first, then Herschel) the HDO*/*H2O has been estimated to be 3 % in IRAS16293-2422 (Parise et al. [2005;](#page-60-16) Coutens et al. [2012\)](#page-50-15) and  $\geq$ 1 % in NGC1333-IRAS2A (Liu et al. [2011](#page-57-8)). Estimates obtained with interferometric observations of HDO and  $H_2^{18}$ O lines give  $\leq$ 0.06 % in NGC1333- IRAS4B (Jørgensen and van Dishoeck  $2010a$ , and 14 % and 22 % toward NGC1333- IRAS2A and NGC1333- IRAS4A, respectively (Taquet et al. [2012c\)](#page-63-14). Note that the interferometric observations provide a direct, almost model-independent, estimate of the HDO*/*H2O abundance ratio as they do measure the extent of the emission and use the rare  $H_2^{18}O$ isotopologue reducing the problem of line opacity. In summary, the HDO/H<sub>2</sub>O ratio has been measured toward four hot corinos: in three of them it is larger than a few percent, whereas in NGC1333- IRAS4B it is at least one order of magnitude lower. Herschel observations have also allowed, for the first time, to estimate the HDO/H<sub>2</sub>O in a molecular outflow shock, L1157-B1 (0.4–2×10<sup>-3</sup>, Codella et al. [2012b](#page-50-17)), a likely direct measure of the deuteration in the ice. The situation is summarised in Fig. [10](#page-29-0). The differences in the HDO*/*H2O abundance ratio probably reflect the different conditions, density and temperature, when the ice was formed (see Sects. [4](#page-12-0) and [7.2\)](#page-40-0).

<span id="page-29-0"></span>

*Doubly deuterated water* Although it has a very low abundance, D<sub>2</sub>O has an important diagnostic power as it sets very tight constraints to models of water formation. So far, thanks to Herschel,  $D_2O/H_2O$  has been measured only toward the cold envelope of IRAS16293-2422, with the observations of both the para and ortho forms of D2O (Butner et al. [2007](#page-48-16); Vastel et al. [2010](#page-65-9)). The D2O*/*H2O abundance ratio as a result is found to be  $1-4 \times 10^{-3}$  (Coutens et al. [2012\)](#page-50-15). Similarly, the para-D<sub>2</sub>O/H<sub>2</sub>O toward the hot corino is  $\sim$ 5 × 10<sup>-5</sup> (Butner et al. [2007](#page-48-16)). Assuming an ortho-to-para ratio equal to 2 gives  $D_2O/H_2O~10^{-4}$ . For example, comparison with the model by Taquet et al. ([2012d\)](#page-63-9) indicates that the bulk of water was formed on grains when the cloud/envelope temperature was 10 K and the density between  $10^4$  and  $10^5$  cm<sup>-3</sup>. In other words, when the density at the center of the IRAS16293-2422 prestellar cloud reached 10<sup>6</sup> cm<sup>−</sup>3, the oxygen not locked into CO was almost entirely already converted into water.

# <span id="page-29-1"></span>5.5 Deuteration of other species

As water, several molecules present large deuteration factors in low-mass protostellar envelopes and molecular outflows (e.g., Parise et al. [2006](#page-60-17) and Codella et al. [2012b](#page-50-17), respectively). Figure [11](#page-30-0) presents a graphic summary of the observations of species with detected doubly or triply deuterated isotopologues. The deuterated ratios are extremely high, with enhancements of the D/H of up to 13 orders of magnitude with respect to the elemental D/H abundance ratio. Given the conditions in the envelopes of the protostars (Sect. [5.1](#page-21-2) and Fig. [7\)](#page-21-0), the observed deuteration is mostly an inherited product of the prestellar phase (Sect. [4\)](#page-12-0). Furthermore, for the typical physical condition where the deuterated molecules have been detected, the measured deuteration ratios likely reflect the deuteration on the grain mantles (e.g., Charnley et al. [1997\)](#page-49-1).

We emphasize here that the deuteration ratio is not the same for all species. As mentioned in Sect. [4](#page-12-0), the lower deuteration ratio of water with respect to formaldehyde and methanol probably reflects the different epoch in which the bulk of the iced species has been formed (during the prestellar phase). Specifically, water is (mostly) formed before formaldehyde, and methanol is the last in the sequence (Cazaux et al.



<span id="page-30-0"></span>**Fig. 11** Measured deuteration ratios of singly, doubly and triply deuterated isotopologues. Based on the modeling of the formation of  $H_2O$ ,  $H_2CO$  and  $CH_3OH$  (Cazaux et al. [2011;](#page-49-3) Taquet et al. [2012d\)](#page-63-9) we speculate that the increasing deuteration reflects the formation time of the species on the ices. References: H2O: Liu et al. [\(2011](#page-57-8)), Coutens et al. ([2012\)](#page-50-15), Taquet et al. ([2012c](#page-63-14)), Butner et al. [\(2007](#page-48-16)), Vastel et al. [\(2010](#page-65-9)); H2S: Vastel et al. [\(2003](#page-65-10)); NH3: Loinard et al. [\(2001](#page-57-9)), van der Tak et al. [\(2002](#page-64-7)); H2CS: Marcelino et al. ([2005](#page-57-10)); H<sub>2</sub>CO: Ceccarelli et al. ([1998\)](#page-49-12), Parise et al. [\(2006](#page-60-17)); CH<sub>3</sub>OH: Parise et al. [\(2002](#page-60-6), [2004](#page-60-7), [2006\)](#page-60-17)

<span id="page-30-1"></span>

[2011;](#page-49-3) Taquet et al. [2012a,](#page-63-8) [2012d\)](#page-63-9). Even though not specific modeling has been published for all observed deuterated species, we speculate that the sequence in the figure represents a temporal sequence of the species formation.

Finally, the comparison between the singly and doubly deuterated isotopologues provides some interesting additional information. First, if the deuterium atoms were purely statistically distributed, namely just proportional to the D/H ratio, then it would hold: D species/D<sub>2</sub> species = 4 (D species/H species)<sup>-1</sup>. As shown in Fig. [12](#page-30-1), this is not the case for the measured deuteration of  $H_2O$ ,  $NH_3$ ,  $H_2CS$  and  $H_2CO$ .

As also noted by Butner et al. ([2007\)](#page-48-16), this points to a change of the atomic D/H ratio during the formation of those species or to an origin from gas-phase reactions. On the contrary, the statistical relation is roughly valid for  $H_2S$  and  $CH_3OH$ . This suggests that these two species have been formed on the grain surfaces in a very short time, when the atomic D/H ratio can be considered roughly constant.

In summary, the observed deuteration ratios tell us that  $H_2O$ ,  $NH_3$ ,  $H_2CS$  and H2CO were formed at various stages during the star-formation process, with different values of the atomic gas D/H ratio. On the other hand,  $H_2S$  and CH<sub>3</sub>OH were formed in a shorter time range. This behaviour roughly agrees with the models of the formation of  $H_2O$ ,  $H_2CO$  and  $CH_3OH$  on grains, that predict that methanol is only formed at very late time, whereas water and formaldehyde are formed over a larger period of time (Cazaux et al. [2011;](#page-49-3) Taquet et al. [2012a,](#page-63-8) [2012b](#page-63-11)). It is, however, possible that the species not close to the statistical value are, at least in part, gas-phase products.

<span id="page-31-0"></span>As a final remark, it is important to emphasize that low- and high-mass protostellar envelopes present important differences in the molecular deuteration. A clear example is provided by the CH2DOH*/*CH3OD abundance ratio, which is at least one order of magnitude larger in low-mass than in high-mass protostellar envelopes (Ratajczak et al. [2011;](#page-61-15) Peng et al. [2012](#page-60-18)).

# **6 Toward planet formation: protoplanetary disks**

Starless and prestellar cores present evidence of overall (slow) rotation (Arquilla and Goldsmith [1986;](#page-46-20) Goodman et al. [1993](#page-53-3); Caselli et al. [2002](#page-48-17)), thus they possess an initial angular momentum. As a natural consequence of angular momentum conservation, the collapse of prestellar cores produces flattened structures which harbor the future protoplanetary disks. Even non-rotating collapsing cores are expected to produce flattened structures in the presence of magnetic fields, as explained in the following. As ionized particles within the core are linked to the magnetic field lines, while neutrals only feel the gravitational field, a drag between ions and neutrals is established during the collapse phase (see Sect. [4\)](#page-12-0). Galli and Shu [\(1993a,](#page-52-14) [1993b\)](#page-52-15) found that during the collapse of a singular isothermal sphere (i.e. an unstable spherical cloud with a density profile proportional to  $r^{-2}$ , thus with a singularity in the center, Shu [1977\)](#page-63-15), the magnetic field, dragged by the flow, deflects the infalling gas toward the midplane, forming a large ( $\simeq$ 2000 AU) "pseudodisk". The magnetic field lines, initially parallel, are shaped as an hourglass, consistent with observations of polarization maps of the dust continuum emission toward young stellar objects (e.g., Girart et al. [2006;](#page-53-12) Frau et al. [2011\)](#page-52-16). The twisting of magnetic field lines in the pseudodisk acts as a "magnetic break", in the sense that it slows down the rotation by transferring angular momentum from the inner regions (which tend to rotate faster for angular momentum conservation) of the pseudodisk toward its outer parts (Basu and Mouschovias [1994\)](#page-46-21). Indeed, magnetic breaking is so efficient, that disks cannot form at all in ideal magneto-hydrodynamic  $(IMHD)^4$  simulations of collapsing cores (e.g., Allen

<span id="page-31-1"></span><sup>&</sup>lt;sup>4</sup>IMHD assumes that the mass to magnetic-flux ratio is constant, which implies that magnetic field lines follow the gas motions, i.e. the magnetic field is "frozen" into the neutral medium.

et al. [2003](#page-45-8); Mellon and Li [2008](#page-58-16); Hennebelle and Fromang [2008\)](#page-53-13). More recently, the inclusion of non-ideal MHD effects, in particular the Hall effect<sup>[5](#page-32-0)</sup> (Braiding and Wardle [2012](#page-47-14); Krasnopolsky et al. [2011\)](#page-56-15), has helped to avoid this so-called magnetic breaking catastrophe, allowing disks of about 100 AU to form (even without initial rotation of the collapsing cloud Braiding and Wardle [2012](#page-47-14)). This has also been shown in simulations by Machida et al. ([2011\)](#page-57-11), who found rapid growth to ≥100 AU of the circumstellar disk when depletion of the infalling envelope is taken into account, and by Joos et al.  $(2012)$  $(2012)$ , who explored the case of magnetic fields non-aligned with the rotation axis and found less efficient angular momentum transport, allowing the formation of  $\simeq$ 100–200 AU disks, with masses as large as 10 % the original core mass. These characteristics are similar to the young self-gravitating protoplanetary disks (we refer to them as "embedded disks") which can become gravitationally unstable (e.g., Laughlin and Bodenheimer [1994;](#page-56-16) Boss [1997](#page-47-15); Durisen et al. [2007](#page-51-8) and references therein; Boley and Durisen [2008;](#page-47-16) Vorobyov [2011](#page-65-11)) and which represent the starting point of our final journey toward the formation of a planetary system. Here we will focus on the chemical evolution (see Armitage [\(2011](#page-45-9)) and Williams and Cieza [\(2011](#page-66-12)) for comprehensive reviews on the physical characteristics and evolution of protoplanetary disks).

# 6.1 Embedded disks: chemistry at the dawn of planet formation

Young disks are embedded within the thick and massive envelopes of Class 0 sources (see Sect. [5](#page-20-0)). Therefore, they are not easy to study and it is hard to put constraints on theoretical predictions. Indirect evidence of young disks in Class 0 sources is given by the presence of collimated outflows, observed with millimeter and sub-millimeter telescopes (Sect. [5](#page-20-0)). ALMA will of course revolutionize this field. After the pioneer work by, e.g., Chandler et al. [\(1995](#page-49-13)), Brown et al. ([2000\)](#page-48-18) and Looney et al. ([2000\)](#page-57-12), further steps toward the characterization of these embedded disks have been made by Jørgensen et al. [\(2007](#page-55-16), [2009](#page-55-17)), and Enoch et al. [\(2011](#page-51-9)). With the help of interferometric observations (able to filter out the surrounding envelopes), these authors found evidence of compact embedded disks in Class 0 sources, with masses ranging from 0.04 to 1.7  $M_{\odot}$ . Choi et al. ([2007\)](#page-49-14) observed NH<sub>3</sub> with the Very Large Array (VLA) and found a 130 AU circumstellar disk around NGC1333 IRAS4A2. With the IRAM Plateau de Bure Interferometer (PdBI), Jørgensen and van Dishoeck [\(2010b](#page-55-14)) measured water vapor  $(H_2^{18}O)$  in the inner 25 AU of the NGC1333 IRAS4B disk, suggesting the presence of a thin warm layer containing about 25 Earth masses of material. Toward the same object, Jørgensen and van Dishoeck [\(2010a\)](#page-55-12) also set a stringent upper limit on the HDO/H<sub>2</sub>O abundance ratio to  $6 \times 10^{-4}$  (Sect. [5](#page-20-0)). Pineda et al. ([2012\)](#page-61-13) observed methyl formate with ALMA toward IRAS16293-2422, a binary Class 0 source in Ophiuchus (Sect. [5](#page-20-0)), and found the first evidence of infall toward source B and evidence of rotation toward source A, consistent with an almost edge-on disk (see also Rodríguez et al. [2005\)](#page-62-15). If confirmed, this could be the first chemically

<span id="page-32-0"></span><sup>&</sup>lt;sup>5</sup>The Hall effect mainly operates at volume densities between  $10^8$  and  $10^{11}$  cm<sup>-3</sup> (Wardle [2004](#page-66-13)), where the more massive charged particles (ions and charged dust grains) decouple from the magnetic field and collisionally couple with the neutral gas.



<span id="page-33-1"></span>**Fig. 13** The earliest stages of a protoplanetary disk. Magnetic fields (*yellow curves*) and the initial rotation of the prestellar core lead to the formation of a flattened structure (the "pseudodisk", size 2000 AU) surrounding the accreting protostar. In the central few hundred AU, the embedded disk can be self-gravitating, develop spiral structure and experience fragmentation. Molecules such as  $H_2O$  and  $H_2CO$  are good tracers of these central regions of young embedded disk (Ilee et al. [2011\)](#page-54-15)

and kinematically characterized embedded disk (discovered with a complex organic molecule!).

What are the chemical model predictions of these embedded disks? Visser et al. [\(2009](#page-65-12), [2011\)](#page-65-13) have been the first to self-consistently follow the chemistry in a twodimensional axisymmetric model of a collapsing (initially) spherical and slowly rotating cloud, on its way toward the formation of a protoplanetary disk. The material infalling in the equatorial plane, within the centrifugal radius,  $6$  forms the disk, whose evolution is also considered assuming no mixing. The disk-envelope boundary and the outflow cavities are well defined. Detailed predictions are given about the ice and gas-phase composition of the cloud-disk system at different evolutionary phases. At the end of the collapse phase, they find that disks can be divided in zones with different chemical history, which will ultimately affect the composition of comets formed in different zones. Different results are found by Ilee et al. [\(2011](#page-54-15)), who used the hydrodynamic simulations of a young and relatively massive (0.39  $M_{\odot}$ ) disk by Boley ([2009\)](#page-47-17) as input in their gas-phase and simple surface chemistry network. Boley's disk resembles in mass and size the embedded disk mentioned above, it is nonaxysimmetric and present complex spiral and physical structure, with shocks moving with the spirals arms (see Fig. [13,](#page-33-1) middle panel in the left, which reports the gas column density map). No accretion of material from the envelope and no outflow is considered. Despite these assumptions, the disk structure is complex and its physi-

<span id="page-33-0"></span> $6$ The radius at which the gravitational force is balanced by the centrifugal force.

cal characteristics are continuously stirred by the rotating spiral arms. Because of this continuous mixing, Ilee et al. ([2011\)](#page-54-15) found no separated chemical zones as in the case of Visser et al.  $(2011)$  $(2011)$ , but they identified species able to trace the inner regions of the disk (such as  $H_2O$ , HNO and NH<sub>3</sub>) and those tracing the spiral arms (e.g. H<sub>2</sub>CO and  $HCO<sup>+</sup>$ ). Examples of these column density maps are given in Fig. [13](#page-33-1) (bottom right panels), which also summarizes the various physical mechanisms to be considered for a comprehensive study of the earliest stages of star formation: the collapsing envelope of a Class 0 source (red semicircle) under the influence of magnetic fields (yellow lines and curves in the figure), the pseudodisk (blue), the central embedded disk (violet) and the outflow (orange) driven by the central protostar (red semicircle). Furuya et al. ([2012\)](#page-52-17) studied the chemical evolution of a molecular core toward the formation of the first hydrostatic core (protostellar precursor) using three-dimensional radiation hydrodynamic simulations. They show that after a first destruction of molecules, simple species such as CO,  $H_2O$  and  $N_2$  reform and more complex molecules (CH<sub>3</sub>OH) and HCOOCH3) can trace the first hydrostatic core, on its way to becoming a protostar. ALMA observations are needed to disentangle the various phenomena at work during the earliest stages of star formation, to test model predictions of collapsing magnetized prestellar cores and to unveil the physical and chemical structure of the embedded disks, precursors to the protoplanetary disks which will be reviewed in the next sections.

### <span id="page-34-0"></span>6.2 "Naked" protoplanetary disks

The embedded phase of disks does not last long. After about 0.5 Myr since the birth of the protostar/disk/outflow system, the parent core envelope quickly disperses and the disk enters a new phase which lasts several Myr (Williams and Cieza [2011](#page-66-12)). This is the T Tauri (or Class II) phase. The disk mass is now only a few % the stellar mass (Williams and Cieza [2011\)](#page-66-12) and the motions are expected to be Keplerian. Despite being "naked" disks, thus easier to observe than during the earlier embedded phase, the physical and chemical processes at work are complex and more (interferometric) data are sorely needed to fully understand them. Figure [14](#page-35-0) shows a schematic picture of a T Tauri disk, compiled from a combination of figures found in Öberg et al. ([2011b\)](#page-60-19), Dullemond and Monnier [\(2010](#page-51-10)); Semenov ([2011](#page-63-16)), Dullemond et al. ([2007b](#page-51-11)), and Bergin et al. ([2007](#page-46-22)): (1) within the central 1 AU from the star, a pure gas disk and the dust inner rim are present. This zone is mainly probed by Br-*γ* lines (e.g. Muzerolle et al. [2003;](#page-59-17) Malbet et al.  $2007$ ; Tatulli et al.  $2007$ ; Goto et al.  $2012$ ),  $H<sub>2</sub>$  (Bergin et al.  $2004$ ; France et al. [2012\)](#page-52-18), as well as near-infrared lines of CO,  $H_2O$ , OH (Salyk et al. [2008;](#page-62-16) Carr and Najita [2008;](#page-48-19) Pontoppidan et al. [2010a](#page-61-16)) and simple organic molecules (Mandell et al. [2012\)](#page-57-14). (2) Moving away from the central star, one finds the "puffed-up" inner dust wall (Natta et al. [2001\)](#page-59-18), clearly seen in the near-infared continuum, where the higher temperature affects its vertical scale height, which is set by hydrostatic equilibrium. Within the central few AU, mid-infrared emission of  $H<sub>2</sub>O$ , CO and the organic molecules HCN and  $C_2H_2$  have been measured (Lahuis et al. [2006;](#page-56-8) Carr and Najita  $2008$ ). Carr and Najita ( $2008$ ) note that the HCN/H<sub>2</sub>O abundance ratio is largest in the most massive disks and speculate that this may be indication



<span id="page-35-0"></span>**Fig. 14** Schematic structure of a "naked" protoplanetary disk, adapted from Öberg et al. [\(2011b](#page-60-19)), Dullemond and Monnier ([2010](#page-51-10)), Semenov [\(2011](#page-63-16)), Dullemond et al. ([2007b\)](#page-51-11), and Bergin et al. ([2007](#page-46-22)). The various regions are labeled. *The black dots* with various sizes represent the coagulated dust in the disk midplane. See text for details

of the sequestration of  $H_2O$  in the outer disk during the process of planetesimal formation. It is interesting to note that toward the disks surrounding the intermediatemass ( $\approx$  2 < M/M<sub> $\odot$ </sub> < 8) Herbig Ae/Be stars, no organic molecules have been detected (Pontoppidan et al. [2010b](#page-61-17); Salyk et al. [2011\)](#page-62-17) and water is only seen in the far-infared at larger radii ( $\approx$ 15–20 AU; Fedele et al. [2012\)](#page-51-12), probably due to the larger UV fluxes compared to T Tauri stars. Beyond the "wall", the disk is thought to have a layered structure. (3) A photon-dominated region (PDR) is present all around the disk, which is exposed to the stellar and interstellar UV field, as well as the stellar Xrays. Here, forbidden line emission from the well-known PDR coolants, [CII]158 µm, [OI]63 µm and 145 µm, are observed (Sturm et al. [2010;](#page-63-17) Podio et al. [2012](#page-61-18)), although the  $\text{[CII]}158 \mu \text{m}$  and the  $\text{[OII]}145 \mu \text{m}$  are not always detected (Mathews et al. [2010;](#page-58-17) Thi et al. [2010a](#page-64-9)). (4) A warm molecular layer. Just below the PDR zone, molecules survive, although photochemistry is still playing an important role (Henning et al. [2010;](#page-53-15) Aresu et al. [2012\)](#page-45-10). The gas and dust are warm and radical and ions dominate the gas composition (Semenov [2011](#page-63-16)). (5) A dark-cloud chemistry zone, where the temperature drops below 20 K, molecular freeze-out becomes important and simple species typically found in dark clouds are detected: CO isotopologues with evidence of depletion (Dutrey et al. [1996,](#page-51-13) [2007a](#page-51-14); Qi et al. [2004](#page-61-19)), CN, HCN, HNC, CS, HCO<sup>+</sup>,  $C<sub>2</sub>H$  and H<sub>2</sub>CO (Dutrey et al. [1997](#page-51-15); van Zadelhoff et al. [2001;](#page-65-14) Thi et al. [2004;](#page-64-10) Chapillon et al.  $2012b$ ), N<sub>2</sub>H<sup>+</sup> (Dutrey et al. [2007b](#page-51-16)), SO (Fuente et al. [2010](#page-52-19)), CS (Dutrey et al. [2011](#page-51-17)), DCO<sup>+</sup> (van Dishoeck et al. [2003\)](#page-64-11),  $H_2D^+$  (Ceccarelli et al. [2004\)](#page-49-16), HDO (Ceccarelli et al. [2005\)](#page-49-17), but see Guilloteau et al. [\(2006](#page-53-16)), HC3N (Chapil-lon et al. [2012a](#page-49-18)). Qi et al.  $(2008)$  $(2008)$  spatially resolved the emission of DCO<sup>+</sup> and measured the deuterium fraction across the disk of TW Hydrae, finding a range between 0.01 and 0.1, with a peak around 70 AU. They also measured the DCN/HCN abundance ratio,  $\approx$  0.02, similar to that measured in the jets of material coming from the nucleus of comet Hale–Bopp (Meier et al. [1998](#page-58-2)). Öberg et al. [\(2010a\)](#page-59-19) used the Sub-Millimeter Array (SMA) to image disks of six Taurus sources with spectral type from M1 to A4, finding similar intensities of CN and HCN lines in T Tauri and Herbig Ae stars, but a significantly different chemical richness: deuterated molecules,  $N<sub>2</sub>H<sup>+</sup>$  and H<sub>2</sub>CO were only detected toward T Tauri star disks, implying a lack of long-lived cold regions in the disks of the more massive Herbig Ae stars (see also Öberg et al. [2011a](#page-60-20)). Water vapor in the cold outer disk has been detected toward TW Hydrae by Hogerheijde et al. [\(2011](#page-54-16)) with Herschel, revealing a hidden large reservoir of water ice at large radii (between 100 and 200 AU). Indeed, ice features have been detected in the direction of edge-on protoplanetary disks by Terada et al. [\(2007](#page-64-12)) and Honda et al. ([2009\)](#page-54-17). More recently, Aikawa et al. ([2012\)](#page-45-11) measured with the AKARI satellite several ice features in edge-on Class II disks, including a faint HDO feature, which allowed them to measure a solid HDO/H<sub>2</sub>O abundance ratio between 2 % and 22 % (significantly larger than the HDO*/*H2O ratio measured in comets and in starforming regions; see Sects. [3](#page-3-0) and [5](#page-20-0)). (6) The midplane, characterized by cold and dense regions, with large amounts of molecular freeze-out, where only light species can survive (Öberg et al. [2011b\)](#page-60-19), in analogy with the central  $\simeq$  1000 AU of prestellar cores (Sect. [4\)](#page-12-0).

Several chemical models of this protoplanetary-disk phase, with various degrees of complexity, have been developed: X-ray chemistry (Glassgold et al. [1997;](#page-53-17) Meijerink et al. [2008;](#page-58-18) Stäuber et al. [2005\)](#page-63-18), surface chemistry (e.g., Willacy and Langer [2000\)](#page-66-14), accretion flows (Aikawa et al. [1999](#page-45-12); Ilgner et al. [2004\)](#page-54-18), thermal balance (Gorti and Hollenbach [2004](#page-53-18)), grain growth (Aikawa and Nomura [2006;](#page-45-13) Vasyunin et al. [2011\)](#page-65-15), UV continuum and Ly*α* radiation (Bergin et al. [2003;](#page-46-24) Fogel et al. [2011](#page-52-20)), turbulence-driven diffusion (Xie et al. [1995;](#page-67-7) Willacy et al. [2006\)](#page-66-15), viscous accretion, turbulence mixing and disk winds (Hersant et al. [2009;](#page-54-19) Heinzeller et al. [2011](#page-53-19)), photochemistry and wavelength-dependent reaction cross sections (Walsh et al. [2012](#page-66-16)), comprehensive physical, chemical and radiative transfer modeling (Gorti and Hollenbach [2008;](#page-53-20) Woitke et al. [2010;](#page-66-17) Kamp et al. [2011\)](#page-55-18). Despite the advances in chemical complexity, large uncertainties are still present on several reaction rates (Vasyunin et al. [2008\)](#page-65-16) and collisional coefficients, so that laboratory studies and theoretical investigations are still sorely needed to improve the reliability of modern astrochemical models. Moreover, the large uncertainties in the process of dust evolution and coagulation in disks are also shaking our understanding of the disk chemical structure. Laboratory experiments (e.g., Güttler et al. [2010;](#page-53-21) Schräpler et al. [2012](#page-63-19)), numerical simulations (e.g., Zsom et al. [2011\)](#page-67-8) and theoretical work (e.g., Dominik et al. [2007](#page-51-18); Windmark et al. [2012\)](#page-66-18) are fundamental to progress in this field and an effort has to be made to link dust coagulation models with astrochemistry.

As schematically shown in Fig. [14](#page-35-0), in the midplane the dust settles and coagulates with its thick icy mantles and larger grains tend to settle first (e.g., Dullemond et al. [2007a](#page-51-19)). The differential dust settling and the presence of some degree of turbulence mixing, maintains a population of small dust grains in the upper layers of the disk (see also D'Alessio et al. [1999\)](#page-50-18). This includes polycyclic aromatic hydrocarbons (PAHs), ubiquitous in active star-forming regions (Tielens [2005\)](#page-64-13) and also present in protoplanetary disks, especially around the intermediatemass Herbig Ae/Be stars (e.g., Habart et al. [2004b;](#page-53-22) Acke and van den Ancker [2004;](#page-45-14) Keller et al. [2008](#page-55-19); see also Kamp [2011](#page-55-20) for a recent review of PAH in disks). PAH features have been detected in only 8 % of the less massive T Tauri stars (Geers et al. [2006\)](#page-52-21). PAHs are not only important from an organic and pre-biotic chemistry point of view, but also for the physical structure of disks, as they can be photoionized, releasing energetic photons which heat the gas, thus maintaining flared disk struc-tures (Kamp [2011](#page-55-20)). Moreover, PAHs boost the formation of  $H_2$  molecules (Habart et al. [2004a\)](#page-53-23), thus the atomic-to-molecular transition in the upper disk atmospheres. Habart et al. [\(2006\)](#page-53-24) spatially resolved the 3.3 µm PAH feature toward Herbig Ae/Be stars, finding that the emission originates from within 30 AU of the star. In T Tauri stars, the less intense stellar UV field makes the detection of PAH features more difficult (as PAH features are excited by photons). Visser et al. ([2007\)](#page-65-17) predict that PAHs in T Tauri disks can survive much closer to the star (down to about 0.01 AU for a 50-carbon atoms PAH) compared to the Herbig disks (down to 5 AU for PAHs with 96 carbon atoms). However, Siebenmorgen and Krügel [\(2010\)](#page-63-20) include the effects of extreme UV and X-ray components in their models and find very efficient PAH destruction also in T Tauri stars; by taking into account typical X-ray luminosities, Siebenmorgen and Heymann ([2012\)](#page-63-21) are able to reproduce the different PAH detection probabilities observed in T Tauri and Herbig Ae disks. Fedele et al. ([2008\)](#page-51-20) found PAH emission co-spatial with the [OI]63  $\mu$ m line, i.e. in the photon-dominated zone of the disk of a Herbig star. As UV photons can break the weaker C-H bonds in PAHs and their carbon skeleton can also brake above a certain threshold of energy intake (Guhathakurta and Draine [1989](#page-53-25)), the presence of PAHs in the upper atmosphere of disks hints at some replenishing mechanism, possibly vertical mixing (Siebenmorgen and Heymann [2012\)](#page-63-21), which maintains a population of small grains mixed with the gas (Dullemond et al. [2007a\)](#page-51-19). Habart et al. ([2004b\)](#page-53-22) suggest that the observed PAHs are evaporated from the icy grain mantles within the disk, while others consider them as the result of fragmentation of larger grains (Rafikov [2006\)](#page-61-21). The mixing of PAHs within the icy mantles of dust grains, could provide an interesting starting point for the formation of more complex molecules, once dust grains start to coagulate and form larger bodies (Bouwman et al. [2011b](#page-47-18), [2011a\)](#page-47-19).

#### 6.3 From debris to icy worlds

The transition between protoplanetary disks and planetary system is far from being understood. As Williams and Cieza [\(2011](#page-66-12)) pointed out, "exactly how and when protoplanetary disks evolve into planetary debris disks remains an open question". In protoplanetary disks, there is plenty of evidence of dust grain growth (Beckwith et al. [1990;](#page-46-25) D'Alessio et al. [2001](#page-50-19); Wood et al. [2002](#page-66-19); Testi et al. [2003;](#page-64-14) Wilner et al. [2005;](#page-66-20) Andrews and Williams [2007](#page-45-15); Isella et al. [2006](#page-54-20); Cortes et al. [2009;](#page-50-20) Lommen et al. [2010;](#page-57-15) Lee et al. [2011](#page-56-17)), dust settling (Duchêne et al. [2003](#page-51-21); Calvet et al. [2005a;](#page-48-20) D'Alessio et al. [2006;](#page-50-21) Furlan et al. [2006](#page-52-22)), dust processing e.g. presence of crystalline silicates (Kessler-Silacci et al. [2005;](#page-55-21) Natta et al. [2007;](#page-59-20) Sargent et al. [2009;](#page-62-18) Merín et al. [2007;](#page-58-19) Olofsson et al. [2012;](#page-60-21) Riaz et al. [2012](#page-62-19)), inner holes (probably carved by a planet or by photoevaporation, Calvet et al. [2005b](#page-48-21); Hughes et al. [2009;](#page-54-21) Andrews et al. [2009](#page-45-16); Andrews et al. [2011;](#page-45-17) Cieza et al. [2012](#page-49-19)). Debris disks are also observed, with their poor gas content and with evidence of large grains and/or planets



<span id="page-38-0"></span>**Fig. 15** Sketch of a debris disk and a speculative history of a debris: 1. Dust grains with their icy mantles (blue rings) coagulate and form a fluffy structure, on top of which more ice can adsorb/form; 2. Exposure to UV photons and X-rays changes the inner structure of the grain and allows the surface icy mantle to be reprocesses and form a refractory carbonaceous material; 3. Further coagulation will lead to small rocks, composed by a mixture of the fluffy grains in  $1 \& 2$  with their refractory organic material and "dirty" ice, glued together by a mixture of amorphous and crystalline dust material

(Wyatt [2008](#page-67-9); Hughes et al. [2011](#page-54-22); Ricci et al. [2012](#page-62-20)). Despite all these measurements, the story behind grain growth and planetesimal formation remains obscure (see also previous subsection). For example, one of the biggest challenges for planet-formation theories is the so-called "meter-size barrier", where models show destructive collisions and rapid inward migration of meter-sized solids (Weidenschilling [1977;](#page-66-21) Williams and Cieza [2011\)](#page-66-12). Nevertheless, the presence of large grains in protoplanetary disks and the structure of our Solar System tell us that dust grains coagulate and evolve toward rocks, comets, asteroids, planetesimals, planets and moons. There are connections between the petrology observed in protoplanetary disks and that in our Solar System bodies. In fact, crystalline grains detected in comets (Wooden et al. [1999,](#page-66-22) [2004;](#page-66-23) Zolensky et al. [2008](#page-67-10)), who also suggest aqueous alterations in the comet P81/Wild2, are mostly made out of Mg-rich olivine grains, consistent with observations of gas-rich T Tauri disks. Fe-rich grains have been observed in several interplanetary dust particles (IDPs, e.g., Brunetto et al. [2011](#page-48-22)) and recently in warm debris disks (Olofsson et al. [2012\)](#page-60-21). Such Fe-rich grains may be due to a secondary alteration of the disk mineralogy (see also Nguyen et al. [2007](#page-59-21)), probably originated within large differentiated bodies (as in the case of the S-type asteroid recently studied with the Hayabusa re-entry module; Nakamura et al. [2011](#page-59-22)). In this scenario, planetesimals form with internal temperatures large enough (from the decay of short-lived radionuclides) to allow the melting and gravitational segregation of silica and metals. Destructive collisions among these planetesimals would then contribute to the production of the Fe-rich particles found in IDPs and in warm debris disks and to the replenishment of small dust grains in our Solar System as well as in exo-zodiacal belts.

Let us now retrace the history of a dust grain during the process of star and planet formation. The starting point has to be found within dense cores, where dust grains have thick icy mantles (see Sect. [4](#page-12-0) and Fig. [6](#page-17-1)) and show some evidence of coagulation (e.g., Keto and Caselli [2010;](#page-55-4) Pagani et al. [2010\)](#page-60-22), also found soon after protostellar birth, in Class 0 objects (Jørgensen et al. [2007;](#page-55-16) Kwon et al. [2009;](#page-56-18) Chiang et al. [2012](#page-49-20)). As we have seen in previous sections, these dust mantles are rich in water and simple organic material and the chemical complexity in ices appears to increase with dynamical evolution. Figure [15](#page-38-0) show a schematic possible scenario of the formation of a debris in the late stages of evolution of protoplanetary disks. (1) Soon after the formation of the protoplanetary disk, dust grains coagulate and become fluffy aggregates of the original icy-dust grains. They may go through shocks during the early "stirring" of the embedded self-gravitating disks (Fig. [13\)](#page-33-1). (2) During the "naked" T Tauri phase, some vertical and radial mixing may expose the fluffy aggregate to stellar and interstellar UV photons and stellar X-rays, so that icy material on the surface can partially be photodesorbed and partially reprocessed, with the production of radicals and formation of an organic residue on the surface (the yellow layer in the figure) and formation of complex organic molecules in the ice trapped within the aggregate. (3) Further processing and coagulation (including some crystalline dust reformed in the inner parts of the disk) could then lead to a cometary-like body, where "dirty ice" (i.e. ice mixed with complex organic molecules) is a major component.

<span id="page-39-0"></span>We are now ready to attempt assembling some pieces of the puzzle.

#### **7 Putting together some pieces of the puzzle**

### 7.1 Molecules in comets and solar-type protostars

All molecules detected in comets are also observed in star-forming regions. However, the measured abundances in comets and Sun-like star-formation regions are not the same. This is clearly shown in Fig. [16](#page-40-1), which reports the abundances, normalized to the methanol abundance, of species detected in various comets (see the reviews Mumma and Charnley [2011](#page-59-2) and Bockelée-Morvan [2011](#page-47-1), and Sect. [3.2\)](#page-7-0) and those in the hot corino and cold envelope of IRAS16293-2422 (see Sect. [5.1](#page-21-2)). A similar plot is obtained also if the normalisation is done with respect to water rather than methanol. In general, species are more abundant with respect to methanol (and water) in IRAS16293-2422, both in the cold envelope and the hot corino, than in comets by more than a factor of ten. In other words, the chemistry in comets seems to be less rich than in both the cold envelope and the hot corino of IRAS16293. It is, therefore, probably fortuitous the rough correlation found in the abundance of a fewer molecules in comets and hot cores (e.g., Bockelée-Morvan [2011](#page-47-1)).

Where does this difference come from? The molecules in the cold envelope of IRAS16293-2422 are likely the product of gas-phase chemistry (but see the com-ments in Sect. [4](#page-12-0)) in cold gas, where CO is largely frozen into the grain mantles. Therefore, the systematic difference between the molecular abundances in comets and the cold envelope may point to different physical conditions, likely warmer, at the time of the comet formation. Similarly, the molecules in the hot corino are thought to mostly reflect the composition of the grain mantles during the pre-collapse phase, so

<span id="page-40-1"></span>

<span id="page-40-0"></span>that the difference in this case also suggests warmer conditions of the material when the cometary ices were formed. There are, however, also other possibilities. It is possible that the cometary ices have undergone a massive reprocessing of the molecular composition due to the long irradiation from cosmic rays and solar wind particles and UV irradiation. Or it is possible that our Sun's progenitor, in fact, did not resemble the IRAS16293-2422 protostar, which is rather isolated, whereas the proto-Sun likely was born in a crowded and much harsher environment (Sect. [3.5\)](#page-11-0). Our census of the molecular composition in comets and in protostellar objects thought to be similar to the proto-Sun is still too poor to have a definitive answer.

# 7.2 Origin of deuterated molecules in comets and chondrites

For a long period it has been though that there is a link between the chemistry in comets, chondrites and interstellar medium, especially because of the enhanced abundance of deuterated molecules (Fig. [17\)](#page-41-0). It is possible that the link is not direct, meaning that it may not be due to the passage of the molecular deuteration from one phase to the next, during the formation of the Solar System. However, the link certainly exists because the chemistry regulating the molecular deuteration is common to all phases and it has to do with the low temperatures occurring during the star and planet formation.

Two key parameters play a major role in the molecular deuteration, regardless of the details which depend on the specific molecule: the ratios of  $H_2D^+/H_3^+$  and of the atomic D/H in the gas (Sects. [4.1](#page-13-1) and [5.5](#page-29-1)). Figure [18](#page-41-1) shows how the  $H_2D^+/H_3^+$  ratio depends on the gas temperature. Another important parameter for this ratio is the abundance of gaseous CO, as CO is a major destroyer of molecular ions, being the most abundant heavy-atom-bearing neutral molecule. In cold and dense regions, CO may freeze-out onto the grain mantles and disappear, therefore, from the gas phase (Sect. [4.1](#page-13-1)). Figure [18](#page-41-1) also shows the dependence of the  $H_2D^+/H_3^+$  and the other isotopologues of  $H_3^+$  as a function of the CO depletion, namely how much the CO abundance is reduced with respect to the standard molecular cloud value. In general,

<span id="page-41-0"></span>

<span id="page-41-1"></span>**Fig. 18** Theoretical abundances of the  $H_3^+$  isotopologues in the gas. *The left panel* (**a**) reports the plot of the ratio  $H_2D^+/H_3^+$  as function of the gas temperature, for gas with no CO depletion. *The right panel* (**b**) shows the abundance ratio of all the  $H_3^+$  isotopologues as a function of CO depletion, for a gas with temperature 10 K. In both cases, the gas density is assumed  $10^5$  cm<sup>-3</sup> (adapted from Ceccarelli et al. [2005\)](#page-49-17)

molecular deuteration exceeding 10 % requires not only cold gas but also a substantial drop of the CO abundance in the gas phase.

Similarly, Fig. [19](#page-42-0) shows how the gaseous D/H ratio, which governs the molecular deuteration of grain-surface product molecules (Sect. [4.2](#page-15-0)), varies with the CO depletion in different situations. Also in this case, large  $(>10\%)$  molecular deuteration can only be achieved in cold gas deprived of CO.

Therefore, the relatively low water deuteration measured on Earth, in comets and in chondrites with respect to the values measured in the prestellar and protostellar

<span id="page-42-0"></span>

phases suggest substantial remixing of water ices since their first formation. How much of the first ices remains in the terrestrial, cometary and chondritic water is difficult to say but cannot be substantial. On the contrary, the extremely large deuteration found in the chondritic organic material, both soluble and insoluble, testifies either the preservation of molecular species since the very first stages (where not only the temperature was very low but also the gas was deprived of CO, Sect. [4.1\)](#page-13-1), or the presence of similar conditions in some zones of the Solar System up to a late stage of the protoplanetary-disk phase.

# 7.3 The <sup>15</sup>N enrichment in comets and chondrites

In our Solar System, the  $15N$  enhancement spans a large range of values. As seen in Sect.  $3.4$ ,  $14$ <sub>N</sub> $/15$ <sub>N</sub> is around 150 in comets, <300 in "primitive" material (such as IDPs and carbonaceous chondrites), *<*100 in interplanetary dust particles (IDPs) and carbonaceous chondrites "hotspots", where the largest D- and <sup>15</sup>N fractions have been measured (e.g., Messenger [2000\)](#page-58-20), ∼450 in Jupiter's atmosphere (representative of the protosolar value), 272 on Earth. In prestellar cores (Sect. [4\)](#page-12-0), current data show a differential 15N fractionation between amine- and nitrile-bearing species, with the largest <sup>15</sup>N enhancement found in the latter (between 70 and 380 in HCN and HNC, Bonal et al. [2012\)](#page-47-20), while no significant enhancement is found in NH<sub>3</sub> and N<sub>2</sub>H<sup>+</sup>, both highly D fractionated. The situation is summarised in Fig. [17](#page-41-0). Thus, D and  $^{15}N$ fractionations do not go hand in hand in all species within prestellar cores, resembling the mixed level of correlation between D and  $15N$  enrichments in primitive material of our Solar System. Moreover, the cometary 15N enhancement has been measured in HCN and CN, again suggesting a prestellar core origin. It will be interesting to find out if amines will ever experience significant 15N at all during the pre- and/or protostellar phase. Wirström et al.  $(2012)$  $(2012)$  predict large <sup>15</sup>N fractionation in NH<sub>3</sub> at late times (*>*a few million years), so maybe only relatively long-lived dense cores will have the chance to have both amines and nitriles highly <sup>15</sup>N fractionated. However, this has all to be tested with observations, which should be extended also to the starless cores found in massive star-forming regions (e.g., Wienen et al. [2012](#page-66-24)) to check if environmental conditions affect the fractionation process. As  $15N$  enhancement

has been measured in IOMs and amino acids trapped in carbonaceous chondrites (Sect. [3.4\)](#page-9-0), amines in prestellar cores should also be able to experience significant enhancement, if a link between these two extreme stages has to be found (Bonal et al. [2012\)](#page-47-20). However, we do not know if further processes within icy mantles or within the "rocks" made out of coagulated icy-dust grains, during the proto-Sun stage, would affect the <sup>15</sup>N fractionation in IOM and amino acids found in carbonaceous chondrites. Experiments are needed here.

# **8 Concluding remarks**

Our chemical heritage is hidden in the large amount of information obtained by observations of Solar System bodies and star and planet-forming regions, and it needs to be deciphered. In this review, glimpses of links between the present star and planet formation in our Galaxy and the remote past of our Solar System have been given. A summary of these glimpses is given here, together with comments/open questions and suggestions for future developments:

- *Water on Earth*. The total amount of water on Earth is  $\geq 2 \times 10^{-3}$  Earth masses, a small fraction of the total amount of water vapor measured in a prestellar core  $(\simeq 800$  Earth masses) and in a protoplanetary disk ( $\simeq 1.5$  Earth masses), and a negligible factor of the deduced water ice mass in the prestellar core and protoplanetary disk (at least three orders of magnitude larger than the water vapor mass). Thus, a large water reservoir was originally available to seed a large number of Solar System bodies, as in fact observed in moons, comets, KBOs and asteroids. Tracing the formation, storage and delivery of water will require more observations as well as a better understanding of the icy-dust coagulation process during the prestellar and protoplanetary-disk phases.
- *Complex organic molecules, COMs.* Organic material in meteorites and IDPs is organized in aromatic and aliphatic compounds, carboxylic acids and amino acids, including those found in all living beings on Earth. PAHs, hydrocarbons and complex organic molecules observed in star-forming regions are a simpler version (building blocks) of the organic material found in Solar System bodies. Thus, interstellar COMs may have contributed to the formation of organic matter during the processing of coagulated icy-dust particles once the proto-Sun was born. More experiments are needed to confirm this statement. Moreover, COMs observed in comets have abundances relative to methanol more than a factor of ten lower than those measured in hot corinos, possibly suggesting that the hot corino conditions and chemical history may not be representative of our Solar System. It is also possible that the difference arises because of a substantial reprocessing of the protostellar material during the protoplanetary disk phase. Finally, the chemical composition of the envelopes of solar-type protostars in crowded environments populated by massive stars, as suggested in the case of the proto-Sun, has not so far been studied, due to the sensitivity of the available instrumentation. The advent of ALMA should clarify this aspect in the near future.
- *D fractionation in water.* The HDO*/*H2O abundance ratio measured in comets is between 1 and 2 times that measured in our oceans  $(1.5 \times 10^{-4})$ , whereas

in cold envelopes and hot corinos a larger spread of this ratio has been found: from  $\leq 6 \times 10^{-4}$  to 0.2. Is the D fraction in water set at the beginning of the starformation process or is it modified during the various phases of star and planet formation? Or does the water D enrichment observed in hot corinos probe only the outer layers of the ices, those that sublimate first, while the bulk of the ice, less deuterated as probably inherited in the previous phases, remains frozen and hidden? Is this the ice that we observe in comets? And which process forms water in comets if it is not inherited? Is it surface chemistry, like in prestellar objects, or gas-phase chemistry? In order to answer all these questions, we will need to measure the HDO*/*H2O in different stages of the protostellar evolution and use observations to constrain detailed chemical models, where gas-phase and surface processes are linked, spanning a broad range of physical conditions.

- *D fractionation in other molecules.* The D fractionation is an active process in the cold gas of molecular clouds and becomes one of the dominant chemical processes within prestellar cores, in regions where abundant neutral species (mainly CO and O) freeze-out onto dust grains. Here, the increase of the D/H elemental ratio in the gas phase is thought to be responsible for the efficient deuteration of methanol, which happens on the surface of dust grains (as no gas-phase routes are available). Organic molecules such as methanol and formaldehyde observed in star-forming regions (in particular toward low-mass protostellar envelopes) display a D fraction orders of magnitude higher than that measured in water. This differential D fractionation of water and organics is also measured in comets, where DCN/HCN ∼10 times HDO/H<sub>2</sub>O. Similarly, in the hot spots of carbonaceous chondrites and IDPs, the D/H associated with organic radicals reaches values as high as 1 %, suggesting, in this case, a direct link with the pre- and protostellar phases of the Solar System's formation.
- <sup>15</sup>N *fractionation*. <sup>15</sup>N enrichments in HCN and HNC are measured in comets, with values similar to those observed in prestellar cores and Galactic star-forming regions. No significant <sup>15</sup>N fractionation is measured in NH<sub>3</sub> and N<sub>2</sub>H<sup>+</sup>, which are, on the other hand, highly deuterated during the prestellar core phase. Thus, no significant correlation is expected between D- and 15N-fractionated material in Solar System bodies, as in fact measured. More observations of <sup>15</sup>N isotopologues of NH<sub>3</sub> and N<sub>2</sub>H<sup>+</sup> in a larger sample of prestellar cores (also including massive prestellar cores) are needed to look for possible fractionations of these species and to understand if different environmental conditions affect the fractionation process.

To further advance in this field, different communities need to join the effort and work together. In particular, the star-formation and Solar System communities should continuously exchange new results and information on new measurements, experiments and theoretical developments. At the same time, laboratory work on molecular spectroscopy to identify the observed lines, on rate coefficients to understand chemical pathways, on surface chemistry and dust coagulation to understand ice formation and ice/dust evolution, as well as calculations of collisional coefficients required for radiative transfer studies are all necessary for a correct interpretation of observations. Finally, theoretical and observational astrophysicists and astrochemists should work together to make sure that, on the one hand, the best physical and dynamical model is used as input for astrochemical modeling and, on the other hand, the best physical parameters derived from the combination of observations, astrochemistry and radiative transfer, are used as input in the physical/dynamical models of star and planet-forming regions. To understand our origins, we cannot work alone!

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