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Memorie della

Our astrochemical heritage

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Abstract. Our Solar System was born about 4.6 billions year ago out of a contracting pre-stellar core, most likely part of a Giant Molecular Cloud where a rich stellar cluster formed. Links to our primordial cloud can be found in the chemical composition of relatively pristine material (such as comets and primitive meteorites), in particular in the isotopic fractionation of hydrogen and nitrogen. Part of the chemical processing happening during the pre-stellar phase may have affected later stages of evolution and some of the pre-stellar fingerprints may be found today in our Solar System. This chapter very briefly summarises part of the review of Caselli & Ceccarelli (2012) and includes some recent updates.

Key words. Astrochemistry – Magnetohydrodynamics (MHD) – Stars: formation – ISM: clouds – ISM: molecules

1. Introduction

Caselli & Ceccarelli (2012) highlighted the five steps which gave rise to our Solar System:

1. the formation of a pre-stellar core, with central densities above $10^5\,cm^{-3}$ and central temperatures below 10 K (e.g. Crapsi et al. 2007), where efficient molecular freeze-out and deuterium fractionation is taking place (e.g. Caselli et al. 1999; Bacmann et al. 2003) and interstellar complex organic molecules (iCOMs) are produced (e.g. Matthews et al. 1985; Vastel et al. 2014; Jiménez-Serra et al. 2016).
2. The protostellar phase, where a rich chemistry is revealed, as part of the dust icy mantles are released back in the gas phase due to thermal desorption nearby the young stellar object (e.g. Cazaux et al. 2003; Pineda et al. 2012; Jørgensen et al. 2016) and/or sputtering due to shocks along the outflow lobes and jets driven by the central protostar (e.g. Arce et al. 2008; Codella et al. 2017).
3. The protoplanetary disk fase, where dust coagulation and gas/ice processing is taking place (e.g. Öberg et al. 2015; Cleeves et al. 2016; Walsh et al. 2016).
4. Planetesimal formation, during which pebbles agglomeration proceeds and part of the icy material produced in step 1 may survive within the larger solid bodies precursors of planets, moons, comets, asteroids.
5. Planet formation and the late bombardment of comets and asteroid debris, during which water and organics may have been delivered to our originally dry Earth (e.g. Bergin et al. 2015; Marty et al. 2016).

Can we trace back our origins to our parent molecular cloud? Can pre-stellar core material be preserved during the various evolutionary steps? How crucial are the first steps to set the stage for the origins of life on Earth? The next sections will try to give some tentative answers to these questions.

2. Interstellar deuteration factories

Earth oceans are enriched in heavy water (HDO), and the derived D/H ratio is about 10 times larger than the cosmic abundance of deuterium (1.6×10^{-5}; Linsky 2007). Comets show D-enrichment in water, with values ranging from those of our oceans (Hartogh et al. 2011) up to about 30 times the D/H cosmic abundance (Altwegg et al. 2015). Carbonaceous chondrites also show D-enrichments in water to levels very close to those of our oceans (Robert 2003). Ehrenfreund et al. (2002) noticed that in Solar-System objects, such as interplanetary dust particles (IDPs), various chondrites and comets, the D-fraction measured in organic matter is significantly larger than that measured in water. Interestingly, this different level of D-fraction between water and organics is also found in young protostellar objects, where icy mantles have been recently evaporated back into the gas phase (see Ceccarelli et al. 2014, for a comprehensive review on this topic). A way to explain this is to have at least partial delivery of pre-stellar core material to the late stages of planet formation (see also Cleeves et al. 2014, 2016).

Indeed, pre-stellar cores can be considered as deuteration factories (e.g. Vastel et al. 2006), because of the low temperatures (about 7 K in their centers; Crapsi et al. 2007; Pagani et al. 2007) and the high volume densities (larger than 10^6 H_2 molecules cm^{-3}; e.g. Keto & Caselli 2010). These conditions favour the freeze-out of CO and other heavy molecules onto dust grains (e.g. Caselli et al. 1999; Tafalla et al. 2002), the drop of the ortho-to-para ratio of H_2, and the boost of deuterium fractionation (Dalgarno & Lepp 1984; Pagani et al. 1992; Sipilä et al. 2010; Kong et al. 2015). The main chemical processes are reported in Figure 1, where the paths to H_3^+ deuteration are shown, assuming most of H_2 molecules are in para form (Flower et al. 2006). The formation of H_2D^+, D_2H^+ and D_3^+ induces gas phase deuteration of molecules such as HCO^+, N_2H^+ (upon collisions with the parent species CO and N_2, respectively) and also provides a mechanism to increase the D/H abundance ratio in the gas phase (upon dissociative recombination of the deuterated molecular ions). It is the enhanced gas-phase D/H ratio that drives surface deuteration and the formation of copious amounts of deuterated methanol (produced by successive H/D-atom addition reactions with surface CO) in the central regions of pre-stellar cores. Indeed, Parise et al. (2004) detected triply deuterated methanol toward the young protostar IRAS 16293-2422, and deduced a D-fraction of 13 orders of magnitude (!). On the other hand, deuteration of water in star forming regions is typically below 10% (see e.g. Coutens et al. 2013). These findings toward star forming regions resemble those in Solar System objects described by Ehrenfreund et al. (2002).

3. ^{15}N fractionation

An overview of the $^{14}N/^{15}N$ abundance ratio in our Solar System, as well as in different star and planet forming regions is shown in Figure 2, taken from Zeng et al. (2017). The terrestrial atmospheric value (∼272; Junk & Svec 1958) is indicated by the horizontal 'TA' black line and this is very close to the value measured toward nearby diffuse clouds using HCN and HNC (237±25; Lucas & Liszt 1998); the proto-Solar Nebula value is considered to be the one measured in Jupiter atmosphere (450±100; Fouchet et al. 2004), which, within errors, is the same as the one found in the Solar wind (441±6; Marty et al. 2010). Large ^{15}N excesses are found in primitive material in our Solar System (meteorites, IDPs, cometary dust particles returned by *Stardust*), with extreme $^{14}N/^{15}N$ ratios as low as ∼50 measured in small areas within meteorites (the so-called 'hot spots'; Messenger 2000; Busemann et al. 2006; Bonal et al. 2010). ^{15}N-enriched 'hot spots' do not always coincide with D-enriched 'hot spots' (Busemann et al. 2006; Mandt et al. 2014) and, similarly, no correlation has been found toward a large sample of high-mass star forming regions (Colzi et al., sub.). Hily-Blant et al. (2013) pointed out that in pre-stellar cores there is a systematic differ-

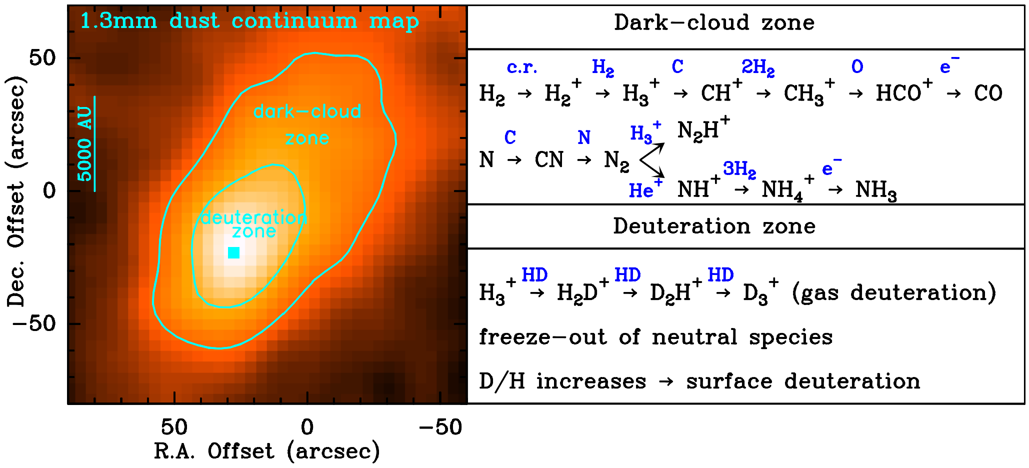

Fig. 1. From Caselli & Ceccarelli (2012). The chemical zones of the prototypical pre-stellar core L1544, embedded in the Taurus Molecular Cloud Complex, at a distance of 140pc. The background color image is the 1.3mm dust continuum emission map obtained with the IRAM-30m antenna Ward-Thompson et al. (1999). The cyan contours show the different chemical zones, with the corresponding main chemical processes listed in the right panel. Blue labels indicate reaction partners.

ential ^{15}N-enhancement between nitriles and amines (nitriles being more fractionated than amines) which has been recently also found in meteoritic material analysed by van Kooten et al. (2017). These two observational facts (no correlation between D and ^{15}N fractionation and differential ^{15}N-enhancement between nitriles and amines) can be reproduced by chemical modelling inclusive of spin-state chemistry (Wirström et al. 2012). However, the large ^{14}N/^{15}N values measured in N_2H^+ in the pre-stellar core L1544 (1050±220 and 1110±240; Bizzocchi et al. 2013) as well as in high-mass star forming regions (up to ∼1300; Fontani et al. 2015) cannot be reproduced by current models (see also Roueff et al. 2015) and more work needs to be dedicated to understand the ^{15}N fractionation in N_2H^+.

In summary, Figure 2 shows that Solar System values of ^{14}N/^{15}N are reached by all objects studied so far: pre-stellar core, low-mass protostars (Wampfler et al. 2014), protoplanetary disks (Guzmán et al. 2017) high-mass star forming regions (Adande & Ziurys 2012; Fontani et al. 2015). Zeng et al. (2017) interestingly found that the lowest ^{14}N/^{15}N ratio was found toward the least dense cloud in their sample, which suggests that environmental conditions may play an important role in setting the the level of ^{15}N fractionation.

4. Complex organic molecules

Interstellar Complex Organic Molecules (iCOMs), i.e. organic molecules detected in space with at least 6 atoms, are known to exist in the interstellar medium since decades and they are copiously found in the vicinity of high-mass (e.g. Blake et al. 1987; Belloche et al. 2014) and low-mass (e.g. Cazaux et al. 2003; Jørgensen et al. 2016) young stellar objects, and recently one iCOM (methanol, CH_3OH) has been detected in protoplanetary disks (Walsh et al. 2016). Surface chemistry during the cold collapse phase, followed by radical diffusion within warm ices and UV irradiation in the vicinity of protostars are thought to be important processes for the surface production of iCOMs (e.g. Garrod & Widicus Weaver 2013). It is however more challenging for chemical models to reproduce the iCOMs detected in cold dark clouds and pre-stellar cores, as dust grains are kept cold and UV illumination is limited

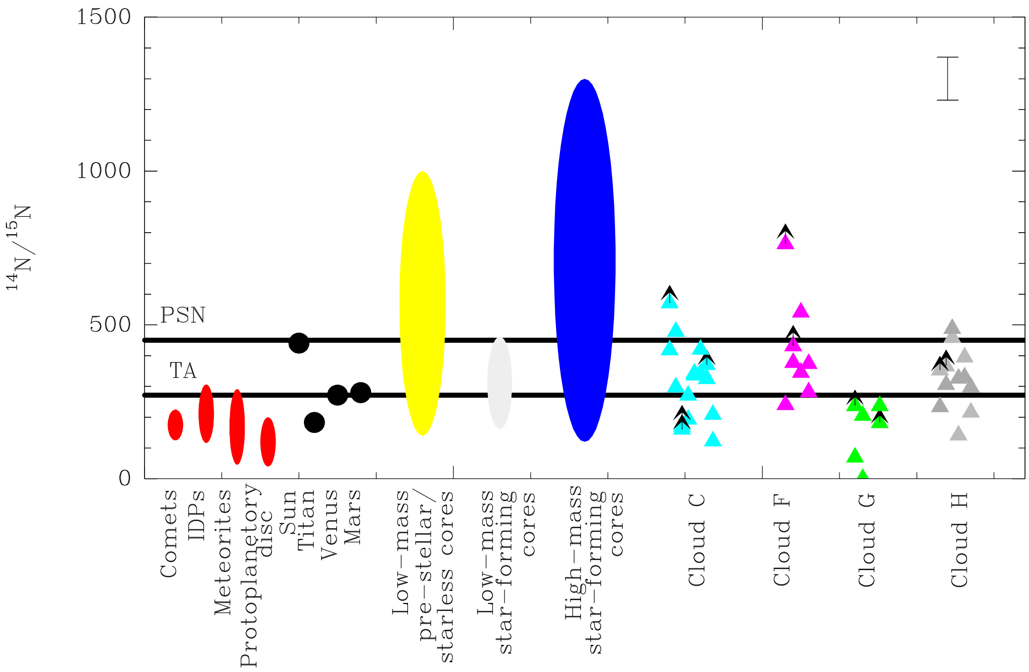

Fig. 2. Nitrogen isotope ratio measured in Solar System bodies and protoplanetary disks (red), planets (black), low-mass pre-stellar cores (yellow), low-mass star-forming cores (light grey), high-mass star-forming cores (blue). Zeng et al. (2017) measurements are shown on the right, with the representative error bar on the upper right corner. This figure is from Zeng et al. (2017), where all references for the data used to build this picture can be found.

(but see Fedoseev et al. 2015, 2017). The presence of iCOMs in dark clouds, starless and pre-stellar cores[1] is also known since the 80s: e.g. Broten et al. (1984) detected methylcyanoacetylene, CH_3C_3N, toward the starless core TMC-1; Matthews et al. (1985) detected acetaldehyde, CH_3CHO, toward the pre-stellar core L134N and TMC-1. More recently, methylcyanodiacetylene (CH_3C_5N) and propylene (CH_2CHCH_3) were found in TMC-1 (Snyder et al. 2006; Marcelino et al. 2007), methyl formate ($HCOOCH_3$) and CH_3CHO were detected toward the cold core B1-b (Öberg et al. 2010), $HCOOCH_3$ and dimethyl ether (CH_3OCH_3) were found toward the starless core L1689B (Bacmann et al. 2012); the prototypical pre-stellar core L1544 is also rich in iCOMs (Vastel et al. 2014; Jiménez-Serra et al. 2016).

Jiménez-Serra et al. (2016) found that the O-bearing iCOMs in L1544 are significantly more abundant toward the CH_3OH peak, about 4000 AU away from the dust peak of L1544 (Bizzocchi et al. 2014), thus suggesting that CH_3OH plays an important role in the chemistry of at least some iCOMs. Indeed, the location of the iCOM abundance peak and the link to methanol has been successfully reproduced by Vasyunin et al. (2017), who developed a gas-grain model where icy mantles are divided into surface layers (where desorption can happen and diffusion is fast) and bulk (no desorption and slow diffusion). This model also takes into account reactive desorption (desorption of surface molecules upon formation) and its efficiency variation as a function of the ice surface

[1] Pre-stellar cores are a sub-sample of starless cores (Crapsi et al. 2005): they are dynamically evolved structures on the verge of star formation, characterised by large amount of CO freeze-out and D-fraction (see also Keto & Caselli 2008).

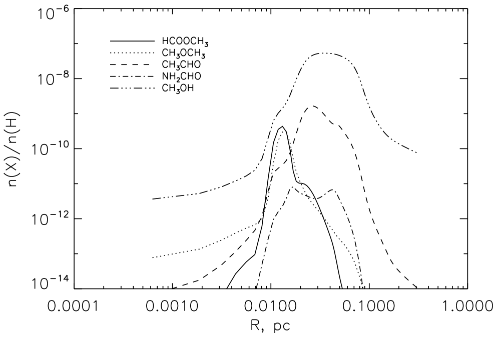

Fig. 3. Fractional abundances (w.r.t. H_2 molecules) of methyl formate ($HCOOCH_3$), dimethyl ether (CH_3OCH_3), acethaldehyde (CH_3CHO), formamide (NH_2CHO) and methanol (CH_3OH) as a function of radial distance across the pre-stellar core L1544, as calculated by Vasyunin et al. (2017). iCOMs peak at radii larger than 2000 AU, in agreement with observations (Jiménez-Serra et al. 2016).

composition (based on Minissale et al. 2016), crucial to allow efficient reactive desorption of methanol and other iCOM precursors away from the dust peak, at the outer edge of the CO-depleted zone (Caselli et al. 1999). Finally, another important ingredient of the model are gas-phase neutral-neutral reactions, some of which have been recently found to proceed fast at low temperatures (e.g. Shannon et al. 2013; Balucani et al. 2015; Skouteris et al. 2017). Figure 3 shows the fractional abundance of selected iCOMs as a function of radius across L1544, showing that indeed their abundance peaks at radii larger than 0.01 pc or 2000 AU.

Complex organic molecules (with abundances roughly similar to those found in star and planet forming regions) are also found in comets (e.g. Altwegg et al. 2016; Biver et al. 2015; Mumma & Charnley 2011; Öberg et al. 2015), suggesting that at least part of the pre-stellar core ices may have been preserved all the way through the planet formation phase, presumably protected within pebbles and planetesimals. The discovery of the simplest amino acid glycine in comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2016) as well the well known presence of amino acids, fatty acids and nucleobases in primitive meteorites (Botta & Bada 2002)[2] rises the question: which role does pre-stellar chemistry have in the production of pre-biotic molecules in small bodies of the Solar System which may have seeded our early Earth? To answer this question, one would need to simulate the processing of pre-stellar ices in protoplanetary disks during dust coagulation and planetesimal formation. Although this is a daunting problem, interactions between (theoretical and experimental) astro-, geo-, bio-physicists and chemists should help us in this endeavour.

5. The dawn of protoplanetary disks

Another important problem in current astrophysical models is the formation of our Solar Nebula or, more in general, of protoplanetary disks, which should be the natural outcome of the contraction of magnetised and rotating pre-stellar cores. However, simulations of this process (especially in the ideal MHD limit) typically end up with the so-called 'magnetic breaking catastrophe' (Galli et al. 2006): the strong magnetic field, accumulated at small radii during the process of material accretion toward the central object, removes the angular momentum of the accreting flow, thus preventing the formation of disks (see Li et al. 2014, for a comprehensive review on the topic and possible ways to overcome the problem). Recently, Zhao et al. (2016) performed 2D non-ideal MHD simulations of contracting dense cores with the inclusion of simple (but comprehensive ionisation) chemistry and grain size distribution, showing that the removal of very small dust grains (VSGs, with sizes between 10 and 100 Å) enables disk formation. In fact, the negatively charged VSGs are highly conductive, thus well-coupled to the magnetic field lines and able to drag neutral molecules more efficiently than ions. Removing VSGs enhances ambipolar diffusion by 1-2 orders of magnitude at densities below 10^{10} cm^{-3}, thus reducing the amount of magnetic flux being

[2] See also Cobb & Pudritz (2014) and Pearce & Pudritz (2015) for a comprehensive collection of references on amino acid and nucleobases measurements, respectively, in meteorites.

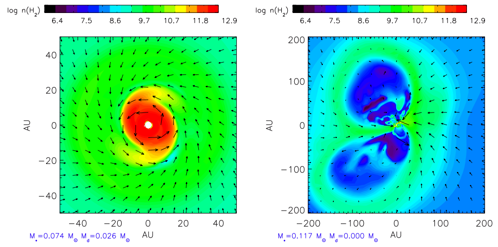

Fig. 4. Face on view of young protostellar objects formed in the 3D non-ideal MHD simulations of Zhao et al. (2017). The left panel shows the result of a model where Very Small Grains (VSGs) are removed from the dust grain size distribution (a rotationally supported disk is formed), whereas the right panel shows the result of the same model when VSGs are included (no disk is present). Black arrows show the velocity field and the color scale refers to the gas volume density. Because of their high conductivity, the negatively charged VSGs act as a break to the magnetised material that accretes toward the central protostar; only their removal enables disk formation.

dragged by the collapsing flow, which can then retain enough angular momentum to sustain a rotationally supported disk of tens of AU. These findings have also been recently proved to be valid in 3D non-ideal MHD simulations (Zhao et al. 2017) and Figure 4 shows the results for a collapsing core without (left) and with (right) VSGs. Interestingly, VSG removal allows the formation of gravitationally unstable disks, such as those studied by Ilee et al. (2011) and (Evans et al. 2015), and the formation of Jupiter-mass fragments, a fraction of which accretes onto the protostar producing bursts (Zhao et al. 2017), maybe at the origin of the episodic accretion phenomenon observed toward young stellar objects (e.g. Safron et al. 2015).

The removal of VSGs could be due to a process similar to the molecular freeze-out in cold dense gas, and it could imply an interesting enrichment of the chemistry of icy mantles, where carbonaceous material (e.g. Polycyclic Aromatic Hydrocarbons, PAHs) could be mixed with water and CO ice, ready to be processed at later stages of stellar system evolution.

6. Conclusions

The previous sections highlight the importance of the pre-stellar phase in the process of star and planet formation, as it is in the dense (n_{H_2} $>10^5\,cm^{-3}$) and cold ($T\leq10\,K$) central regions of pre-stellar cores that efficient deuteration of molecules in the gas phase and on ice surfaces take place. Complex organic molecules are also produced in these early phases and possibly stored in icy mantles in later stages of star and planet formation. It is also in pre-stellar cores that the differential deuteration of water and organics found in Solar System pristine bodies and in star/planet forming regions could originate. The iCOMs detected in comets have abundances similar to those measured in star and planet forming regions, thus suggesting that Solar-System chemistry is not unique. ^{15}N-fractionation is taking place in pre-stellar cores and it is more efficient for CN-bearing (compared to NH-bearing) molecules. This ^{15}N-enrichment differentiation between nitriles and amines has also been recently measured in meteorites. Finally, chemical processes (in particular ionisation and dust evolution) are also crucial for the dynamical evolution of contracting pre-stellar cores; in particular, the removal of very small grains enables the formation of rotationally supported and gravitationally unstable disks, possibly the precursors of the protoplanetary disks observed around pre-main-sequence stars and of our own Solar System.

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