Molecular richness in protostars: Lessons learnt from spectral observations

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Abstract. The gas associated with the early stages of star formation contains traces of a large variety of molecular species, many of which are organic in nature. Interestingly, we observe a substantial chemical diversity among protostars, with some objects being enriched in what astrochemists label interstellar complex organic molecules (iCOMs), such as methyl formate ($HCOOCH_3$), while others are overabundant in unsaturated carbon chains such as C_4H. What is the cause of this diversity? And where should we place the proto-solar-system in this chemical context: was it rich in iCOMs, or in carbon chains, or in both? Thanks to the development of sensitive broadband (sub-)millimetre instrumentation, both in single-dish telescopes and interferometers, we are currently witnessing big steps forward in this area. The present contribution summarises what we have learnt, in the past decade or so, about the molecular contents in solar-mass protostellar sources, and suggests a few guidelines to stimulate progress in the field.

1 Introduction: Our chemical origins

Life represents the highest level of chemical complexity that we know of today, yet every single living being is composed of the same basic ingredients: organic molecules. These are essentially carbon-based molecules containing also other elements such as hydrogen, nitrogen, and/or oxygen. The fact that many organic molecules have been detected in comets and other pristine small bodies of the Solar System (e.g. [1, 2]) opens up the appealing possibility that an exogenous delivery of organic matter may have taken place more than 4 billion years ago, when the Earth and the rest of the Solar System had just formed, thus providing substantial quantities of raw material to trigger the origin of life on Earth.

Organic molecules have also been discovered beyond comets, in the interstellar medium (ISM). Most of them have been observed in molecular clouds, which are the birth sites of stellar and planetary systems like our own. This is why star-forming regions (SFRs) are excellent laboratories for astrochemical studies, whose aim is to understand why molecules are present in the ISM, i.e. how they form and how they are destroyed. At the same time, astrochemistry is a powerful tool to understand the process of star formation as a whole.

The present contribution focuses on the organic molecular chemistry present during the early protostellar stages of solar-mass star formation, based primarily on (sub-)millimetre spectral observations of the gas in protostellar cores. Protostars represent the onset of star

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formation, where temperature and density gradients, coupled with infall, outflows, and rotating motions, all leave characteristic molecular imprints on the gas reservoirs surrounding the newly-formed protostellar objects. As we will see in the following sections, protostars are chemically rich sites that can yield precious hints on how our own Solar System chemically looked like during the early phases of its formation.

2 Protostellar chemical diversity: A chronological story

What is the typical chemical composition of protostellar cores? The shortest answer to this question is that there is no such thing as *typical*. As evidenced below, if there is one word to describe the chemistry associated with this phase, it is *diversity*.

2.1 Hot corinos

In terms of organic contents, hot corinos are the first kind of protostars that were discovered and characterised. They contain relatively high abundances of interstellar Complex Organic Molecules (iCOMs), which astrochemists commonly define as carbon-bearing molecules with 6 or more atoms containing other heavy elements such as oxygen or nitrogen. Examples of iCOMs are methyl formate ($HCOOCH_3$), ethanol (CH_2CH_3OH), and formamide (NH_2CHO). Hot corinos are dense ($n > 10^7\,\mathrm{cm}^{-3}$), hot ($T > 100\,\mathrm{K}$), and compact ($< 100\,\mathrm{au}$) regions of gas surrounding the central protostellar object where the icy mantles formed around dust grains during the pre-stellar phase have sublimated and enriched the gas with all the molecules that were previously trapped in these ices. The release of such molecules into the gas triggers further gas-phase chemical reactions that may lead to more iCOMs. The first hot corino that was discovered and characterised in terms of its iCOM contents is IRAS 16293–2242 [3–5]. Broadband spectral surveys of this and other hot corinos in the (sub-)millimetre wavelength regime, first with single dishes such as the IRAM 30-m telescope, and more recently with interferometers such as ALMA and NOEMA, have played a crucial role in unveiling the outstanding chemical richness of these regions. Notable examples are TIMASSS [6], the IRAM large programs ASAI [7] and SOLIS [8], and the ALMA program PILS [9].

2.2 Warm Carbon-Chain Chemistry protostars

It is often assumed that hot corinos are ubiquitous among protostars, which naturally leads to the belief that the Solar System experienced a hot corino phase during its formation. However, it is important to notice that a chemically different type of protostar exists, whose composition differs quite radically from that of hot corinos. Indeed, a few years after the discovery of the iCOM richness associated with hot corinos, the protostar L1527 was thoroughly studied and found to be devoid of iCOM emission. Instead, this source presents a remarkable richness in unsaturated hydrocarbons, carbon chains and rings (hereafter referred to as C-chains for simplicity), such as C_4H, C_4H_2, and c-C_3H_2, whose emission originates in a lukewarm region spanning roughly 1000–3000 au around the central protostellar object [10, 11]. Since then, a few other protostars displaying this kind of chemistry have been discovered [12]. These protostars are known as Warm Carbon-Chain Chemistry (WCCC) objects.

Quantitatively, C-chain abundances are $\sim$10 times higher in WCCC objects than in hot corinos, while their iCOM abundances are about two orders of magnitude lower [13]. Hence, a real chemical diversity exists among protostars in terms of their organic contents. A schematic illustration of a hot corino and a WCCC protostar is shown in Fig. 1 (*left*).

2.3 Hybrid protostars

In 2016, when hot corino and WCCC chemistry were still thought to be exclusive occurrences among protostars, the first hybrid, B335, was discovered [14]. Hybrid protostars display both hot corino and WCCC features: a lukewarm region rich in C-chains surrounding a very compact hot corino enriched in iCOMs. Thanks to this discovery, the idea that hot corinos and WCCC objects represent opposite extremes of what is in reality a continuous chemical spectrum began to take shape. The future research on this front is fully open, as only three hybrid protostars have been unambiguously identified so far: B335, L483, and CB68 [14–16]. Furthermore, while their iCOM abundances have been measured to be comparable to those found in pure hot corinos, their WCCC regions have not been as thoroughly characterised as those of pure WCCC protostars. Dedicated searches for more hybrid protostars will allow us to assess how common they are. These searches will require high sensitivity multi-line interferometric observations sampling both compact and more extended spatial scales, a challenging but far from impossible task with the facilities currently available, such as ALMA and NOEMA interferometers, and their planned spectral capability upgrades.

3 Protostellar chemical diversity explained... partially

The chemical diversity found among protostars is set by the chemical composition of the ice mantles that coat dust grains during the cold phase preceding the formation of a protostellar object. An ice mantle enriched in methane (CH_4) leads to WCCC once it sublimates at a temperature of $\sim$ 25 K, whereas an ice mantle enriched in methanol (CH_3OH) will lead to hot corino chemistry once it sublimates at a temperature of $\sim$ 100 K (see [13] for a review). These two molecules are considered parent species of C-chains and iCOMs, respectively. The tough question, still to be fully answered, is what causes such differences in the compositions of dust grain ices. The first explanation that was proposed concerns the duration timescale of the cold pre-stellar phase: shorter timescales ($\sim 10^5$ yr) would favour CH_4 ice enrichment and subsequent WCCC activity, while longer timescales ($\sim 10^6$ yr) would favour substantial CO depletion onto grains that, once fully hydrogenated, would lead to CH_3OH, triggering hot corino chemistry after ice sublimation. However, recent modelling has challenged this interpretation [17], and various environmental factors present during the cold pre-stellar stage have been proposed as alternative agents that can shape the molecular fate of the future protostar. These include density, temperature, and exposure to either ultraviolet or cosmic ray irradiation. For example, lower density, lower temperature, and higher irradiation favour WCCC (e.g. [17–19]). Even if there has recently been substantial progress in modelling protostellar chemical diversity, some observed features are not fully reproduced yet [17], so model refinement will be needed, with the crucial help of more observational data to provide physical and chemical constraints to such models.

4 Unveiling the chemical past of our Solar System: First baby steps

How common are the different types of protostars described in Sect. 2? Recently, a few statistical surveys were carried out with single-dish telescopes having this question in mind (e.g. [20–22]). This is fortunate because, about five years ago, the statistics were seriously poor: less than 10 hot corinos, less than 5 WCCC objects, and 2 hybrid protostars had been clearly identified and characterised. The results of these first surveys suggest that, as suspected, most protostars display chemical features intermediate between pure hot corinos and WCCC objects [22]. However, [23] found that single dish surveys are not optimal for accurately determining the chemical nature of compact protostellar cores, as the molecular emission measured can be dominated by the parsec-scale photo-dissociation region (PDR) at the edge of the parental molecular cloud hosting the protostars. Clearly, high angular resolution observations are needed for a solid assessment of the chemical nature of protostars. This is what interferometric surveys such as CALYPSO [24], which targeted 26 protostars distributed in several SFRs with NOEMA, and PEACHES [25] have accomplished. In particular, PEACHES targeted 50 protostars with ALMA in the Perseus star formation complex, and identified 56% hot corinos, which is quite a large fraction.

Can the results from PEACHES be generalised to other regions? And perhaps more importantly, how representative of the birth environment of the Solar System is Perseus? This last question is pertinent since, as we have seen in the previous section, the environment of stellar formation can determine the chemical nature of protostars. Therefore, it makes sense to study a SFR that resembles what must have been the birth environment of the Sun and its planets if we want to unveil our own chemical past. What does such a region look like? It turns out that Perseus is not exactly the best analog of what must have been the formation environment of the Solar System. Indeed, several pieces of evidence indicate that the Solar System very likely formed in a relatively large clustered environment with high-mass stars ($> 8\,M_{\odot}$) in its vicinity [26, 27]. One should therefore assess the chemical nature of Solar-mass protostars in high-mass SFRs, which is an observationally challenging feat due to the typically large distances of these regions compared to more isolated and/or looser protostellar clusters such as those in Taurus and Perseus. This motivated us to perform the ORANGES survey, a completely analogous survey to PEACHES in terms of sensitivity, spatial resolution and spectral setup, but this time targeting 19 protostars belonging to the Orion Molecular Cloud (OMC; see Fig. 1, *right*), i.e. the nearest high-mass SFR [28]. The survey revealed that, unlike in Perseus, hot corinos are not dominant in Orion. Indeed, ORANGES measured an occurrence of 26%, indicating that environment does matter and that, bizarrely, ORANGES and PEACHES are not the same.

5 Final remarks and the bright future ahead of us

Surveys such as PEACHES and ORANGES are providing us with the first precious hints towards understanding chemical diversity and its dependence on the environment. Much more work lies ahead of us to fully comprehend what physical properties have a greater impact on the chemical nature of protostars. This naturally includes surveying other regions to have a larger comparative picture of what variables shape the observed chemical diversity. But it also includes tackling the issue of dust opacity at (sub-)mm wavelengths, which may be responsible for hiding iCOM emission in some (or many) hot corinos. This will require resorting to lower frequency observations, as recently shown by [30].

Additionally, looking for hot corino activity (i.e. hot and compact iCOM emission) is not enough. Indeed, while the number of hot corinos discovered has multiplied by five in the past five years, the number of WCCC objects has barely changed. This is due to an observational bias towards iCOMs, which appear as more appealing due to their potential as precursors of more complex molecules with prebiotic interest. But C-chains also deserve their place, and life as we know it cannot exist without hydrocarbon structures. What would cell membranes be made of otherwise? A complete characterisation of the chemical nature of protostars, also in the context of the origin of life, must include C-chains tracing WCCC activity, and this is something that neither PEACHES nor ORANGES were well designed to do, unfortunately. The good news is, it is never late, and it is perfectly doable with current observatories such as NOEMA. This is our next immediate step as a follow up of ORANGES, which we hope will help bridge the gap between hot corino and WCCC studies.

As a final general note, while the present article has focused on observations, and a little bit of modelling, it is necessary to highlight that astrochemistry is a multi-field research domain, and as such, it must rely on the combined effort of observational astronomers, astrochemical modellers, molecular spectroscopists, and theoretical and experimental chemists. In

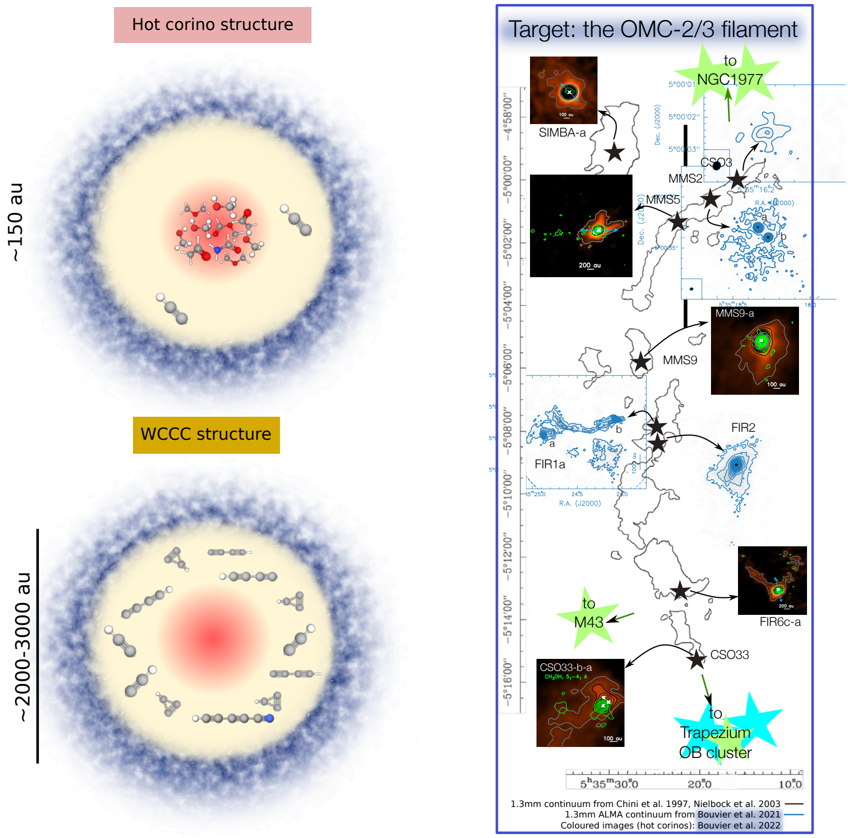

Figure 1. *Left*: Schematic illustration of a hot corino (*top*) and a WCCC protostar (*bottom*). *Right*: The 9 fields targeted with ORANGES (black stars), with zoomed-in emission maps resulting in a total of 19 targets due to source multiplicity within the fields. Five new hot corinos were discovered based on hot and compact CH_3OH emission, shown in green contours overlaid on the 1.2 mm continuum emission maps. For the sources where hot corino activity was not detected, the mm continuum emission is displayed in blue contours (adapted from [28, 29]).

this context, interdisciplinary projects such as ACO (Astro-Chemical origins[1]), funded under the European Community, are optimal frameworks to find a common language to communicate, a common goal to pursue, and with this build a solid community that is as beautifully diverse as protostellar chemistry.

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