CLOUDS, CLUMPS, CORES & COMETS -
A COSMIC CHEMICAL CONNECTION?

S.B. CHARNLEY & S.D. RODGERS
Space Science & Astrobiology Division, MS 245-3, NASA Ames Research Center
Moffett Field, CA 94035-1000, USA
E-mail: charnley@dusty.arc.nasa.gov

We discuss the connection between the chemistry of dense interstellar
clouds and those characteristics of cometary matter that could be remnants
of it. The chemical evolution observed to occur in molecular clouds is summa-
rized and a model for dense core collapse that can plausibly account for the
isotopic fractionation of hydrogen, nitrogen, oxygen and carbon measured in
primitive solar system materials is presented.

Keywords: comets; radio lines: solar system; ISM: molecules; solar system: for-
mation; astrochemistry

1. Introduction

Comets have probably retained some material that originated in the molec-
ular cloud from which the Sun formed. Determining how much pristine inter-
stellar material is in comets will help answer many important questions
relating to the origin of our Solar System and, as comets are strong can-
didates for seeding planets with complex organic molecules, understanding
the details of the interstellar-comet connection will have important implica-
tions for astrobiology. Recent data from the Stardust mission, and ground-
based observations, indicate that some materials present in cometary
dust experienced very high temperatures (~ 800 K), relative to those typically found in molecular clouds (~ 10 K). Nevertheless, the organic inventory and isotopic signatures measured for cometary molecules do provide a tantalizing connection with interstellar chemistry.

In this paper we discuss the chemical structure and evolution of in-
terstellar matter prior to its incorporation into protoplanetary disks. We
outline a model whereby many of the key cosmogonic markers in cometary
matter can be explained as being of interstellar origin.
2. Molecular clouds and star formation

The Sun, the planets, and other small solar system bodies, originate from the protostar and gaseous dusty disk produced by the gravitational collapse of molecular cloud material. Prior to incorporation into a protostellar/protoplanetary disk, the chemistry of dense interstellar matter can be tracked by monitoring the evolutionary state of the cloud and embedded protostar(s). We can identify 5 stages of direct interest. First, there is the ambient dense cloud material. This is found to be clumpy and turbulent, with hydrogen densities of $\sim 10^3 - 10^4 \text{cm}^{-3}$ and kinetic temperatures of $\sim 10^5 \text{K}$. In dense clouds, pre-stellar (or starless) cores are apparently globular structures with pronounced density gradient towards the center ($>10^5 \text{cm}^{-3}$), and are where low-mass protostars can eventually form. Protostars at the earliest stage of evolution, the Class 0 sources, are deeply embedded in their parent core from which they, and their associated disks, accrete mass at a very high rate. As sources undergo transition into the Class I epoch, the optically invisible protostar has accumulated most of its mass from the circumstellar envelope and a gaseous disk is in Keplerian orbit around it. Objects at the Class II stage are optically visible T Tauri stars and most of their circumstellar gas is contained in the disk.

![Evolution of protostellar and disk masses](image.png)

Fig. 1. Evolution of protostellar and disk masses.

Figure 1 illustrates the time-scales associated with protostar-disk mass accumulation (see Ref. 10). Detailed observational studies and chemical modelling have led to a deeper understanding of the chemistry of the evolutionary sequence from pre-collapse (and pre-stellar) cores, through to Class 0 and I sources, Class II and III objects and their related ‘protoplanetary’ and ‘debris’ disks. Such studies can also shed light on the state of the
interstellar material available to disks during the comet-formation epoch (e.g. Ref. 11). As most of the mass accreted up to early in the Class I epoch was consumed by growth of the protosun (Figure 1), the volatile disk material now retained in comets probably accreted during the Class I-Class II evolutionary phases, where the lower mass accretion rates also favour much weaker accretion shock strengths over the disk surface.\textsuperscript{23} Thus, the chemistry in molecular clouds containing protostars at the Class 0/I boundary, and later, is that which may be best associated with the most pristine cometary matter.

\subsection*{2.1. Observations of cloud chemical evolution}

The Barnard 5 molecular cloud in Perseus (B5) is a region in which low-mass protostars are forming.\textsuperscript{25,26} Of the four identified protostars,\textsuperscript{27} B5 IRS 1 resides in the dense central core and is classified as a Class I source that may just be at the Class 0/I transition.\textsuperscript{28} Interferometric maps of IRS1 confirm the presence of a circumstellar disk of $\sim 0.16 - 0.27$ solar masses.\textsuperscript{29} Mapping of clouds like B5 in various molecular lines allows us to understand the physical and chemical evolution that occurs in cloud material prior to incorporation into a circumstellar disk.

High resolution C$^{18}$O mapping of the B5 core (Figure 2) shows a clumpy...
morphology for both the extended ambient gas and the dense central core. Maps of the B5 core (Figure 3) demonstrate that other molecular distributions are also very clumpy and chemically differentiated. This chemical anticorrelation between the emission peaks of many molecules is evident in other high-resolution maps of the B5 core (e.g., CH₃OH, H¹³CO⁺), and other dark clouds. In particular, Figure 3 shows that emission from various carbon-chain species is anti-correlated with that of ammonia, as observed in TMC-1 and several other dense cores. Chemical models indicate that carbon-chain species such as C₂S, C₄H, and the cyanopolyynes (HC₂n₊₁N, n =1-5) are ‘early time’ species - they reach their peak abundances in ~10⁵ years - whereas ‘late time’ species, including N₂H⁺ and NH₃, peak much later. This has led to the idea that observed spatial compositional gradients (e.g., involving the carbon-chains and ammonia) are due to differing chemical ages within individual clouds. Thus, the two C-chain peaks (CP1&2), near δ ~ +150″, are probably at an earlier stage of evolution relative to the material surrounding IRS1, as one would expect.

In B5 we can observe the chemistry at three distinct phases in the star formation sequence: the clumpy ambient medium, dense prestellar clumps and a core containing a Class I protostar. However, in B5 we do not appear
Since we have observed single transitions in C18O, SO and HC3N, and detect only one or two CH3OH transitions in a large ... the N2H+ peak.37

Fig. 4. Integrated intensity map of the HC3N J=10-9 emission in the TMC-1C cloud (K km/sec levels indicated by the scale to the right). The peak in the N2H+ emission found by Caselli et al.38 is indicated by a cross. The approximate peak in the diffuse submillimetre emission is indicated by a triangle. From Ref. 30.

... to see the chemistry at two intervening phases.

Maps of starless globules in lines of carbon chain molecules show that they can have a reasonably smooth emission.39,40 An apparently common subsequent step from such dense prestellar clumps is the formation of a depletion core where observations indicate that almost all the heavy molecules, particularly CO, become depleted into the solid state.41–43 and strong emission from deuterated molecules becomes evident.15 Hence, all the elemental C, O, N and S can be available for grain-surface chemistry. For example, Figure 4 shows the dense core of the starless dark globule TMC-1C mapped in its HC3N emission.30 This morphology can be explained as resulting from the increasingly efficient sticking of HC3N molecules on dust as the density increases, the end-point being a core with all the HC3N molecules frozen out in the center. Comparison with an N2H+ map of this source38 indicates that the N2H+ emission actually peaks at the central ‘hole’ in the HC3N emission (see Figure 4). This is an example of selective depletion where the enhancement of N-bearing species (such as N2H+ and N2D+) in CO-poor regions is thought to be related to the relative depletion of CO and N2.44–46

Although depletion cores are very difficult to study both in molecular lines (except perhaps for N2H+, N2D+, H2D+ and HD2+) and also in solid state absorption, the chemistry occurring in their ices can be revealed later...
in the star formation sequence. Many cores at the prestellar stage show
evidence for gravitational infall\cite{14} and the next step should be formation of a
protostar in the deeply embedded Class 0 phase\cite{14}. During the Class 0 phase,
the protostar and disk accrete mass at a high rate; the consequent increase
in luminosity and the present of outflows and shock waves means that it
heats its immediate environment and a hot corino is formed.\cite{15} Observations
of hot corinos show that, like their massive counterparts, the hot molecular
cores\cite{2} they are very rich in complex organic molecules and exhibit extremely
pronounced deuterium fractionation characteristics.\cite{15} This is believed to
be due to the evaporation and/or sputtering of molecular ices into the
gas.\cite{47} Well-studied ‘hot corinos’ are IRAS 16293-2422, NGC1333-IRAS4A,
NGC1333-IRAS4B and NGC1333-IRAS2A.\cite{48–54}

Hence, the protostellar disk of a source such as B5 IRS 1 may, in
principle, accrete material with chemical characteristics representative of
a prestellar core, a depletion core, the Class 0 hot corino, and the remnant
envelope at the Class I phase. The actual relative proportion of each chem-
istry that could end up unaltered in comets is unknown. Comparison with
the measured volatile composition of comets can help us better understand
this putative connection and to develop and constrain chemical models of
the passage of interstellar material into disks.

3. Measured characteristics of cometary material

The inventory of molecules observed in comets is, in general, a subset of
the $\sim 150$ molecules detected in the ISM. Table 1 lists species detected
in interstellar and circumstellar environments, with those also detected in
comets highlighted. The extensive overlap between cometary and interstel-
lar molecules has long suggested a connection between the two.\cite{55} A thor-
ough description of all cometary characteristics and their possible links with
the ISM is beyond the scope of this paper, and has been discussed in detail
elsewhere\cite{1,2,56,57}. In the following discussion, we focus on isotopic ratios in
specific molecules, and their potential role as tracers of the cometary–ISM
connection.

3.1. Hydrogen and deuterium

Cometary D/H ratios are not significantly altered in the coma,\cite{58} and are
not thought to be altered during sublimation, or during their long deep-

\footnote{A candidate Class 0 source has recently been identified in B5 (J.V. Buckle, priv. comm.)
that would be coincident with a putative depletion core identified in CH$_3$OH maps\cite{24}}
Table 1.  Interstellar, circumstellar, and cometary molecules

| Number of Atoms | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------------|---|---|---|---|---|---|---|---|----|
| $\text{H}_2$  | C$_1$ | c-H$_3$ | C$_2$ | C$_3$ | C$_4$ | C$_5$ | C$_6$ | C$_7$ | C$_8$ |
| $\text{AlF}$ | C$_2$H | C$_3$H | C$_4$H | C$_5$H | C$_6$H | C$_7$H | C$_8$H | C$_9$H | C$_{10}$H |
| $\text{AICI}$ | C$_2$O | C$_3$H | C$_4$H | C$_5$H | C$_6$H | C$_7$H | C$_8$H | C$_9$H | C$_{10}$H |
| $\text{C}$      | C$_2$ | C$_3$ | C$_4$ | C$_5$ | C$_6$ | C$_7$ | C$_8$ | C$_9$ | C$_{10}$ |
| $\text{CH}$    | CH$_2$ | CH$_3$ | CH$_4$ | CH$_5$ | CH$_6$ | CH$_7$ | CH$_8$ | CH$_9$ | CH$_{10}$ |
| $\text{CH}^+$  | HCN | C$_2$H | C$_3$H | C$_4$H | C$_5$H | C$_6$H | C$_7$H | C$_8$H | C$_9$H |
| $\text{CN}$    | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{CN}^+$ | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{CO}$    | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{CO}^+$ | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{CP}$    | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{SIC}$   | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{HCl}$   | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{HNO}_3$ | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{HNO}_2$ | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{H}$      | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{NaCN}$  | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{SO}$    | OCS | OCS | OCS | OCS | OCS | OCS | OCS | OCS | OCS |
| $\text{SO}^+$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ | SO$_2$ |
| $\text{Si}$     | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ |
| $\text{SiO}$   | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ | CO$_2$ |
| $\text{SiS}$   | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ |
| $\text{CS}$    | H$_2$ | H$_2$ | H$_2$ | H$_2$ | H$_2$ | H$_2$ | H$_2$ | H$_2$ | H$_2$ |
| $\text{HF}$    | SCN | SCN | SCN | SCN | SCN | SCN | SCN | SCN | SCN |
| $\text{SH}$    | SNC | SNC | SNC | SNC | SNC | SNC | SNC | SNC | SNC |
| $\text{F}$      | AINC | AINC | AINC | AINC | AINC | AINC | AINC | AINC | AINC |
| $\text{H}$      | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{H}$      | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{O}_2$    | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" | "CO$_2$" |
| $\text{C}$      | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{H}_2$    | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{CH}_3$   | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN | HCN |
| $\text{Si}$     | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ | SiC$_2$ |
| $\text{S}$      | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ | NH$_3$ |

Note: Molecules in blue are detected in comets. Those marked with an asterisk are uniquely detected in comets. Data from [www.cv.nrao.edu/~avootten/allmols.html](http://www.cv.nrao.edu/~avootten/allmols.html) and [www.astrochemist.org](http://www.astrochemist.org)

freeze storage over the age of the Solar System. Enhanced D/H ratios are a hallmark of interstellar material, and the presence of highly-fractionated material in comets would be strong evidence for the preservation of interstellar material. D/H ratios have been observed in a handful of molecules in a total of five different comets, and are summarized in Table 2. In contrast, large numbers of deuterated species have been observed in the ISM, including several multiply-deuterated species. Deuterium enrichments have also been seen in cometary dust grains returned by the *Stardust* mission, and in interplanetary dust particles thought to originate from comets. This D-enrichment is also thought to originate in the ISM, but as it resides in complex organic refractory material it is not possible to trace a direct link to specific interstellar molecules.
Table 2. D/H ratios in comets and the ISM

| Molecule       | Cometary D/H Ratio | Comet | Interstellar a D/H Ratio | Refs. a |
|----------------|--------------------|-------|--------------------------|---------|
| HDO/H_2O       | 0.0003             | Several b | 0.0004 – 0.01 b | 65      |
| DCN/HCN        | 0.002              | Hale-Bopp | 0.01 – 0.1 | 62      |
| HDCO/H_2CO     | 0.28               | T7 (LINEAR) | 0.07 – 0.3 | 63      |
| CH_3D/CH_4     | < 0.04             | Q4 (NEAT) | <0.06 | 64      |
| NH_2D/NH_3     | < 0.04             | Hale-Bopp | 0.01 – 0.08 | 65      |
| CH_2OD/CH_3OH  | < 0.03             | Hale-Bopp | 0.01 – 0.06 | 65      |
| CH_2DOH/CH_3OH | < 0.008            | Hale-Bopp | 0.04 | 65      |
| HDS/H_2S       | < 0.2              | Hale-Bopp | 0.01 – 0.1 | 65      |

*Note: a Representative interstellar values are from Ref. 59. b HDO/H_2O ratios were measured in Halley, Hyakutake, & Hale-Bopp, with three further tentative detections in comets Ikeya-Zhang, LINEAR A2, and Lee 69*

With the exception of the large HDCO/H_2CO measured by Kuan *et al.*, cometary D/H ratios are somewhat smaller than those measured in dark interstellar clouds and low-mass star-forming regions (hot coronas), but are in line with those found in massive hot cores. The HDO and DCN fractionation in the ISM is understood to result from ion-molecule isotope-exchange reactions at 10 K, whereas the cometary values are more in line with a somewhat warmer temperature of ≈ 30 K.

### 3.2. Nitrogen

$^{15}$N/$^{14}$N ratios have only been observed in two cometary molecules: hydrogen cyanide and the related cyanogen radical. HC$^{15}$N/HC$^{14}$N ratios of 0.003 were seen in Hale-Bopp, roughly equal to the terrestrial nitrogen isotope ratio, and slightly larger than the elemental protosolar ratio. C$^{15}$N/C$^{14}$N ratios have been measured in eight comets, including Hale-Bopp, with an apparently constant value of 0.007 in every comet. The discrepancy between the isotope ratios in HCN and CN shows that HCN cannot be the sole parent of CN, and demonstrates the importance of isotope ratios in testing putative ‘parent-daughter’ relationships between coma species. The CN is thought to originate from the break-up of $^{15}$N-enriched organic refractory (CHON) material in the coma. Interestingly, $^{15}$N-rich organics have been discovered in *Stardust* samples, and also in meteorites and IDPs.

Cometary (and meteoritic) $^{15}$N fractionation is often assumed to origi-
nate in the ISM via low-temperature chemistry, in analogy with enhanced D/H ratios, as there are no known nebular processes that can produce such effects. However, there have been very few observational studies of nitrogen fractionation in the ISM. Theoretical calculations predicted only small $^{15}$N-enhancements of $\sim 25$ per cent in a ‘typical’ dark interstellar cloud. More recent studies indicate that, if CO is depleted from the gas-phase, much larger enhancements are possible. In this scenario, $^{15}$N is preferentially incorporated into ammonia ice, and bulk ice $^{15}$N-enhancements of 80 per cent are possible. Following the isotopic ratios in individual monolayers (ML) as they accrete sequentially, these models also show that most of the $^{15}$N-enhancement is due to highly-fractionated uppermost ML which accrete at late times. These layers are also the most likely to be altered by subsequent processing of the ices by UV and cosmic ray irradiation into more refractory material, although the details of this processing are unclear. If this mechanism is in fact the origin of the $^{15}$N anomalies in primitive solar system material, this indicates that at least some cometary organics originally formed in cold (10 K) interstellar gas.

### 3.3. Oxygen and carbon

Gas-phase $^{13}$C/$^{12}$C ratios have been measured in cometary $\mathrm{C}_2$, CN, and HCN. To date, the only $^{18}$O-bearing isotopologue detected in a comet is $\mathrm{H}_2^{18}$O. For both elements, the isotopic ratios are all ‘normal’ (i.e., Solar), although the error bars in each case are sufficiently large that small deviations from the Solar ratio would not have been identified. More accurate laboratory analysis of the *Stardust* samples did in fact reveal the presence of some cometary grains with small $^{18}$O and $^{17}$O depletions, of the order forty parts per mil. This material is isotopically identical to many particles found in meteorites and IDPs, and presumably shares a common origin. Similarly small $^{13}$C-anomalies are present in many *Stardust* particles, also in line with those observed in other primitive solar system material.

Low temperature interstellar fractionation of oxygen and carbon via ion-molecule reactions was modeled by Langer et al., who showed that relatively small effects are to be expected. For carbon, $^{13}$C becomes preferentially incorporated into CO, whereas other C-bearing species become $^{13}$C-deficient. Subsequent freeze-out and surface chemistry will preserve these differences in specific molecules. For example, formaldehyde and
methanol are thought to be formed via hydrogenation of CO, so one would expect these species to have a slight $^{13}$C excess. Ion-molecule reactions are apparently unable to account for the observed oxygen isotope anomalies, which instead have been interpreted as arising from self-shielding of the more abundant $^{12}$C$^{16}$O molecule compared to its isotopologues. This shielding may have occurred at the surface of the interstellar cloud from which the solar system was formed, or at the surface of the protosolar nebula. In either case, the fractionation occurred in UV-irradiated gas, which models of photon-dominated regions (PDRs) predict to have temperatures of $\sim 30–70$ K. Thus, the presence of oxygen isotope anomalies in cometary material is evidence for the formation of some cometary matter in warm gas.

### 4. From the pre-Solar core to comets: tracing the chemical heritage of cometary material

In the previous section we described the isotopic ratios seen in cometary material, and the possible relations between cometary and interstellar material. In this section, we briefly describe a model of core collapse and isotope fractionation that can plausibly account for the observational data. Figure 5 illustrates the chemical structure of a pre-stellar core, immediately prior to the onset of collapse and beginning of the Class 0 phase. The core contains strong chemical gradients, and we expect these gradients will result in related chemical differentiation (both spatial and temporal) during the subsequent gravitational collapse.

In the coldest, most dense, regions toward the center all heavy elements are frozen on to grains. Here, D$_3^+$ dominates the gas-phase, and accretion of gas with high atomic D/H ratios leads to ices containing highly-deuterated molecules. However, once the core begins to collapse, most of the material in this centermost region will end up in the newborn protostar. Hence, we may expect the most heavily-deuterated molecules detected in the ISM to generally be only a minor constituent of comets. Surrounding this region, a shell of CO-depleted gas is the site of efficient $^{15}$N-fractionation, which produces $^{15}$N-enriched ammonia ice after about a few times $10^5$ yr - this time-scale is of sufficient duration that, for the collapse of a 1 $M_\odot$ core, this shell will collapse during early Class I phase. Farther out, CO remains in the gas phase and the chemical composition can be understood from ‘standard’ models of dark cloud chemistry. This region will however contain a temperature gradient, with those shells immediately behind the PDR being warmed by infrared reradiation of the
UV absorbed at the surface, and so having gas and dust temperatures of \( \approx 25–35 \) K. As these regions are almost the last to accrete, during the Class I/ Class II epochs, they are a major source of material in the disk at the time when comets were formed and will be characterised by reduced deuterium fractionation and molecular ortho:para spin ratios characteristic of these temperatures\(^8\)

The interstellar UV field to which the surface of the core is exposed may actually be much stronger than the mean interstellar flux if the core is in close proximity to newborn massive O and B stars,\(^9\) and so warm gas and dust may exist to greater depths. In any case, self-shielding of CO in these surface layers leads to mass-independent fractionation of atomic \(^{13}\)C, \(^{17}\)O, and \(^{18}\)O. The UV flux also results in increased gas and dust temperatures interior to the surface PDR, with \( T_{\text{gas}} \sim 70–150 \) K and \( T_{\text{dust}} \sim 30–35 \) K\(^9\). Previous models of CO self-shielding in clouds and disks have relied on rapid transport (e.g. turbulent diffusion) from the PDR to cold regions, where atom sticking and hydrogenation on dust fixes the oxygen isotopic anomalies in water\(^8\),\(^9\),\(^2\). At the elevated dust temperatures in our model (Figure 5), atoms do not stick to the surfaces of dust grains,\(^4\) so surface chemistry is unable to convert the isotope fractionation in the atoms into fractionation of more refractory species. However, as the gravitational col-
Fig. 6. Physical conditions in a collapsing protostellar envelope (see Ref. 21).

Lapse proceeds and the central luminosity increases, neutral chemistry in the hot infalling gas provides an alternative gas phase route to $\text{O} \rightarrow \text{H}_2\text{O}$ conversion.

Modelling the chemistry in the collapsing protostellar cocoon requires a physical model in order to derive density, temperature, and infall velocity profiles in the envelope as a function of time. We have adapted the dynamical-chemical model of Rodgers and Charnley\textsuperscript{21}, based on the ‘inside-out’ collapse of Shu,\textsuperscript{98,99} to include a static PDR at the outer edge of the envelope. This work will be reported in detail elsewhere\textsuperscript{100} and here we present some preliminary results to demonstrate how interstellar fractionation patterns in $^{13}\text{C}$, $^{17}\text{O}$, and $^{18}\text{O}$ may be transported from the distant outer envelope to the central protostar and disk.

Figure 6 shows the density and temperature profiles used in this model, with conditions appropriate for a $1\,\text{M}_\odot$ star accreting material at a rate of $10^{-5}\,\text{M}_\odot\,\text{yr}^{-1}$. Clearly, at late times when most of the mass is in the central star, the luminosity is large enough to significantly heat material in the innermost regions of the collapsing envelope. However, by this point the infall velocities are sufficiently large to ensure that the dynamical time-scale for material to pass through this hot zone is much less than the typical time-scales for chemical reactions to alter the composition of the gas\textsuperscript{21}. Important exceptions are the reactions of O and OH with $\text{H}_2$ which rapidly convert atomic oxygen into water.

This is illustrated in Fig. 7 which shows the C and O chemistry in material initially located at a radius of $10^4\,\text{AU}$. The far right panel is a blow-up of the final ten years, showing how high-$T$ chemistry drives O into
H$_2$O near the protostar. Thus, the material that rains down onto the disk, during the epoch that cometsimals and planetesimals are forming, contains isotopically-enhanced water derived from the isotopic anomalies in neutral oxygen atoms generated by CO self-shielding in the surface PDR.

5. Conclusions

We have reviewed the putative contribution of interstellar chemistry to the volatile composition of comets. In doing so, we have purposely neglected discussion of the possible contribution of nebular chemistry as a source of cometary volatiles - either from the warm inner nebula or from an essential continuation of interstellar chemistry in the cold outer disk; these have been reviewed elsewhere.$^{11,101}$

Comets could contain material from several different stages of molecular cloud evolution and we have illustrated the related chemistry with some recent observations. Many of the molecules detected in comets, including several organics, are either directly observed in interstellar ices (e.g. methanol, formic acid) or are believed to form on interstellar grains (e.g. formamide).$^2$ A direct comparison of the organic inventories is however complicated by the fact that, in comets, additional sources of simple molecules appear to...
contribute to their coma abundances (e.g. CO, CS, CN, formaldehyde). These so-called extended sources are believed to be due to the thermal or photolytic break-up of large organic macromolecules and have no readily identifiable parallel in interstellar chemistry. Interstellar isotopic fractionation in dense gas with temperatures in the range $\sim 10^{-35}$ K could account for the currently known, albeit meagre, fractionation ratios measured in comets.

We have presented the outline of a model that may account for all these characteristics as arising in the prestellar core from which the Sun formed. As observed in many galactic sources, such cores can develop very strong chemical gradients. Gravitational collapse of such a core may deliver chemically distinct regions (i.e. mass shells) onto the central disk during the Class 0/I epoch, and later, to the extent that all the 'interstellar' characteristics of comets are delivered during this infall.

Finally, future observations of more bright comets, especially short-period ones, as well as of protoplanetary disks, are necessary (e.g. 103). The advent of the Atacama Large Millimetre Array promises a great advances in further investigating the ISM-comet connection.

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