

OBSERVATIONS OF CARBON ISOTOPIC FRACTIONATION IN INTERSTELLAR FORMALDEHYDE.

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Introduction: Primitive Solar System materials (e.g. chondrites, IDPs, the Stardust sample) show large variations in isotopic composition of the major volatiles (H, C, N, and O) even within samples, witnessing to various degrees of processing in the protosolar nebula. For example, the very pronounced D enhancements observed in IDPs [1], are only generated in the cold, dense component of the interstellar medium (ISM), or protoplanetary disks, through ion-molecule reactions in the presence of interstellar dust. If this isotopic anomaly has an interstellar origin, this leaves open the possibility for preservation of other isotopic signatures throughout the formation of the Solar System.

The most common form of carbon in the ISM is CO molecules, and there are two potential sources of ¹³C fractionation in this reservoir: low temperature chemistry and selective photodissociation. While gas-phase chemistry in cold interstellar clouds preferentially incorporates ¹³C into CO [2], the effect of self-shielding in the presence of UV radiation instead leads to a relative enhancement of the more abundant isotopologue, ¹²CO. Solar System organic material exhibit rather small fluctuations in $\delta^{13}\text{C}$ as compared to $\delta^{15}\text{N}$ and δD [3][1], the reason for which is still unclear. However, the fact that both ¹³C depleted and enhanced material exists could indicate an interstellar origin where the two fractionation processes have both played a part.

Formaldehyde (H₂CO) is observed in the gas-phase in a wide range of interstellar environments, as well as in cometary comae. It is proposed as an important reactant in the formation of more complex organic molecules in the heated environments around young stars, and formaldehyde polymers have been suggested as the common origin of chondritic insoluble organic matter (IOM) and cometary refractory organic solids [4]. The relatively high gas-phase abundance of H₂CO observed in molecular clouds (10^{-9} – 10^{-8} relative to H₂) makes it feasible to observe its less common isotopologues. As a step in our investigation of ¹³C fractionation patterns in the ISM, we here present comparisons between observations of the ¹³C fraction in formaldehyde, and chemical fractionation models.

Interstellar Chemistry: In classic gas-phase chemistry, formaldehyde is considered to be efficiently formed from the neutral-neutral reaction between CH₃ and atomic oxygen, where CH₃ is built up from carbon ions in the reaction sequence $\text{C}^+ \xrightarrow{\text{H}_2} \text{CH}_2^+ \xrightarrow{\text{H}_2} \text{CH}_3^+ \xrightarrow{\text{H}_2} \text{CH}_5^+ \xrightarrow{\text{e}^-} \text{CH}_3 + \text{H}_2$. However, with dust grains present in the gas there is an alternative formation route: CO is likely to stick to grain surfaces upon collision. There, CO can be successively hydrogenated by mobile H atoms, with

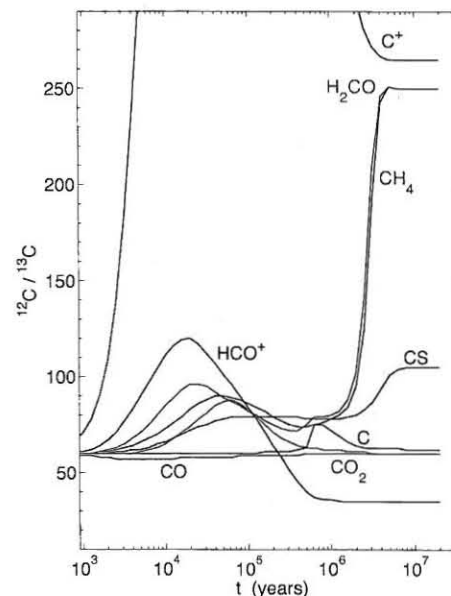


Figure 1: Modeled carbon fractionation evolution at $T_{kin} = 10$ K, $n(\text{H}_2) = 2 \times 10^4 \text{ cm}^{-3}$, $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$, and $A_V = 9$ mag. The $^{12}\text{C}/^{13}\text{C}$ abundance ratio is set to 60 in this example, but the relative characteristics of the $^{12}\text{C}/^{13}\text{C}$ ratio in the different molecules do not depend on the atomic isotopic ratio.

methanol (CH₃OH) as the saturated end-product and formaldehyde formed along the reaction chain. This process has been shown to effectively form methanol and formaldehyde at low temperatures [5]. The relative importance of these two ways of forming formaldehyde in the cold ISM is not currently known.

Since a low temperature environment also is where chemical CO fractionation is expected, the ¹³C fraction in organic molecules should carry some information about the formation. When ¹³C is preferentially incorporated into CO through the reaction $^{13}\text{C}^+ + ^{12}\text{CO} \leftrightarrow ^{12}\text{C}^+ + ^{13}\text{CO}$, modeling of a pure gas-phase chemistry (Fig. 1) show that this fractionation mainly has an effect on other molecules, resulting in a ¹³C deficiency in these. This is because CO is the major carbon reservoir and most other organic molecules, like formaldehyde, form indirectly from C⁺ in the gas-phase. If fractionated CO freezes out onto dust grains and partakes in surface reactions which build up larger organic molecules, these will show $^{12}\text{C}/^{13}\text{C}$ ratios similar to CO. However, if they were formed in the gas-phase, the $^{12}\text{C}/^{13}\text{C}$ ratio would

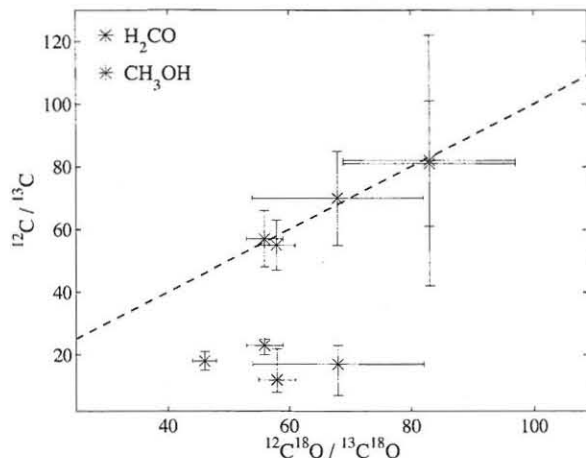


Figure 2: Carbon isotopic ratios in formaldehyde (black stars) and methanol (blue stars) as compared to $C^{18}O$. Methanol data points are from [6].

be much higher. It has been shown that the $^{12}C/^{13}C$ ratio in methanol and CO are very similar in the molecular envelopes of massive young stellar objects [6], supporting the formation of methanol from CO on grains. Likewise, if formaldehyde was formed on grains it would have a similar ratio to CO, but if formed in the gas-phase it would be depleted in ^{13}C .

Observations and Results: In early 2010, three emission lines each from $H_2^{12}CO$ and $H_2^{13}CO$ in the 137–151 GHz range were observed with the Arizona Radio Observatory 12 meter Kitt Peak antenna (ARO12m) towards six massive young stellar objects, most still embedded in cold gas envelopes. The sources are all included in the $^{12}C/^{13}C$ methanol study presented by [6], although a methanol $^{12}C/^{13}C$ ratio could not be determined for all of them. In addition, a higher excitation $H_2^{12}CO$ line at 29 GHz was observed with the Onsala Space Observatory 20 meter antenna towards a couple of the sources, and in early 2012 the line excitation range covered by this study is further extended by observations at the ARO.

Formaldehyde column densities have been derived by means of the reduced χ^2 method, where an excitation temperature and a column density is obtained from a set of emission lines without any assumptions about their optical depth. The derived column densities are divided to arrive at $H_2^{12}CO/H_2^{13}CO$ ratios in the range 15–80. Fig. 2 presents our preliminary ratios compared to those in $C^{18}O$ and CH_3OH , and shows that the formaldehyde in these sources is, unexpectedly, significantly enhanced in ^{13}C as compared to CO and methanol. This is not only in disagreement with most formaldehyde being formed in tandem with methanol on cold grain surfaces, but also contrary to what would be expected if formaldehyde

was formed from a cold, chemically fractionated gas as modeled in Fig. 1.

Discussion: The finding that formaldehyde is enhanced in ^{13}C as compared to methanol and CO would primarily imply that it cannot share a common origin with methanol in these cold environments around massive forming stars. Secondly, either some other fractionation process would have to be active, enriching CH_3 in ^{13}C , or formaldehyde has yet another formation route not considered in common models.

An additional possible source of fractionation to be taken into account is the interaction with grains, i.e. differences in freeze-out and desorption constants for different isotopologues. For CO, there is in theory a tendency for the ices to be enhanced in ^{13}C , which is supported by observations of gas-phase $^{12}CO/^{13}CO$ increasing with decreasing CO gas-fraction [7]. This would however not introduce the observed difference between formaldehyde and methanol fractionation.

In order to interpret the isotopic variations observed in primitive Solar System materials in terms of origin and various degrees of processing, the low-temperature fractionation processes have to be fully understood. Our results indicate that for carbon, this is not yet the case. However, this is work in progress and apart from scheduled complementary observations, we are also constructing a more extensive fractionation network which includes both several isotopes and gas-grain interactions.

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References

- [1] S. Messenger, F. J. Stadermann, C. Floss, L. R. Nittler, and S. Mukhopadhyay, 2003. *Space Sci. Rev.*, 106: 155–172.
- [2] W. D. Langer, T. E. Graedel, M. A. Frerking, and P. B. Armentrout, 1984. *ApJ*, 277:581–590.
- [3] S. Pizzarello, X. Feng, S. Epstein, and J. R. Cronin, 1994. *Geochim. Cosmochim. Acta*, 58:5579–5587.
- [4] G. D. Cody, E. Heying, C. M. O. Alexander, L. R. Nittler, A. L. D. Kilcoyne, S. A. Sandford, and R. M. Stroud, 2011. *PNAS*, 108(48):19171–19176.
- [5] G. W. Fuchs, H. M. Cuppen, S. Ioppolo, C. Romanzin, S. E. Bisschop, S. Andersson, E. F. van Dishoeck, and H. Linnartz, 2009. *A&A*, 505:629–639.
- [6] E. S. Wirström, W. D. Geppert, Å. Hjalmarson, C. M. Persson, J. H. Black, P. Bergman, T. J. Millar, M. Hamberg, and E. Vigren, 2011. *A&A*, 533:A24+.
- [7] R. L. Smith, K. M. Pontoppidan, E. D. Young, and M. R. Morris, 2011. In *Lunar and Planetary Institute Science Conference Abstracts*, volume 42 of *Lunar and Planetary Inst. Technical Report*, page 1281.