ISOTOPIC FRACTIONATION IN INTERSTELLAR CARBON-BEARING MOLECULES UNRELATED TO CARBON MONOXIDE

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ABSTRACT

The isotopic abundance ratio $^{12}C/^{13}C$ in some carbon-bearing molecules is discussed in the context of chemical fractionation via ion-molecule and exchange reactions in dense interstellar clouds. These processes can lead to enhancement of ^{12}C in molecules *not* related to carbon monoxide. The effect is transient and takes place preferentially outside the cores of the interstellar clouds. However, some enhancement of ^{12}C should remain in gases frozen onto dust grains and may be reflected in larger objects such as cometary nuclei.

The somewhat low $^{12}C/^{13}C$ interstellar ratios in the carbon-bearing molecules have been discussed by Watson (1977) on the basis of the fractionation reaction in interstellar gas-phase chemistry (Watson, Anicich and Huntress 1976). The fractionation mechanism involving the carbon isotopes is based on the exchange reaction

$$^{13}C^{+} + {}^{12}CO \rightleftarrows {}^{13}CO + {}^{12}C^{+} + \Delta E.$$

This reaction should enrich CO with ^{13}C when temperature in an interstellar cloud is $T \lesssim \Delta E/k \sim 35$ K. At the same time free C^{+} (and all molecules not closely related to CO) should be enriched by ^{12}C. The rate for the isotopic exchange reaction is 2×10^{-10} exp $(-\Delta E/kT) cm^3 s^{-1}$, which is higher than the rate of the most significant competing neutral-neutral reactions.

Langer 1977 has shown that the fractionation mechanism results in time-dependent isotopic anomalies in diffuse as well as in dense interstellar molecular clouds at low temperatures. Although the effect is transient, and is without significant influence on the isotopic ratio in the long term, the abundance of ^{12}C in molecules *not* related to CO, such as CN, HCN, CH etc., could be considerably enhanced in comparison with the average local ratio of the carbon isotopes.

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We discuss briefly here the numerical results obtained from a calculation in which the most relevant gas-phase reactions are considered (to be published in Bull. of Astr. Inst. of Czech.). The treatment used here is similar to that of Gerola and Glassgold (1978) and of Liszt (1978). Molecules unrelated to CO are formally denoted as species MC, and include molecules such as CN, HCN, and CH_2.

Although the formation mechanisms of these species are not exactly known, it seems reasonable to assume that the molecules are produced by ion-molecule reactions in the gas-phase. These reactions seem to be important not only for smaller polyatomic species but also for the synthesis of larger molecules, especially of those containing the -CN group linked to acetylene-type hydrocarbons (Freeman et al. 1979). The rate coefficient for the formation of the "substituted" molecule MC by reaction with C^+ is assumed to be $2x10^{-9}cm^3s^{-1}$. The most significant competing reaction $C^+(H_2,h\nu)\ CH_2^+$ probably has a rate coefficient no higher than $10^{-16}cm^3s^{-1}$. The relative abundances and isotopic ratios are $[^{12}C] = 8x10^{-5}$, $[O] = 2x10^{-4}$, $[N] = 10^{-4}$ and $^{12}C/^{13}C = 89$. The model of the cloud is isothermal. A temperature of 10K, an initial hydrogen number density of 10^3cm^{-3}, and a radius of 10^{19} cm are adopted. Depletion of light elements including carbon is assumed not to occur during the chemical evolution. The cloud is gravitationally unstable with a free-fall time $\sim 10^6$ years. The numerical results of the "averaged" $^{12}C/^{13}C$ ratio for species unrelated to CO are summarized in Table I.

Table I

$^{12}C/^{13}C$ ratio in a dense cloud for species unrelated to CO. (see text)

time (10^6 year) / optical depth in visual	0.001	0.01	0.1	1
1	89	90	190	250
5	89	95	300	250
10	89	105	260	150

The $^{12}C/^{13}C$ ratios in Table I serve only to demonstrate qualitatively that isotopic fractionation works efficiently during the early evolution of a dense cloud. The actual $^{12}C/^{13}C$ ratio would be modified by gas depletion via gas-grain coupling. Furthermore the fractionation becomes ineffective due to heating of the gas in the late stages of evolution. Therefore the numerical results for elapsed times of 10^6 years from initial formation are probably unrealistic. However, in the regions outside of cloud cores the enhancement of ^{12}C could be preserved in molecules unrelated to CO which freeze onto dust grains during the fractionation phase. Hence there may be some detectable anomalies in the $^{12}C/^{13}C$ ratio in material which has not been processed through the inner part of the pre-solar nebula. If the carbon-bearing molecules were confined in dust grains with mantles, and were later incorporated in comet-like bodies, then the anomalous $^{12}C/^{13}C$ ratio could be preserved in such objects for a very long time.

Since comets are relics of the pre-solar nebula, some enhancement of ^{12}C can be expected in cometary radicals which are products of parent molecules not related to carbon monoxide. The currently available data for $^{12}C/^{13}C$ in comets do indicate that this ratio is higher than 100 i.e. significantly larger than the terrestrial value (Vanysek and Rahe 1978). It must be noted, however that the *average* $^{12}C/^{13}C$ ratio in comets may not be anomalous and could be terrestrial. Unfortunately the available data for comets relates to the isotope ratio in gaseous C_2 only. The $^{12}C/^{13}C$ ratio in comets may exhibit large differences in the various gaseous and solid cometary species. Confirmation of the effect would be significant proof that chemical fractionation takes place in interstellar dense clouds.

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DISCUSSION FOLLOWING VANYSEK

Tatum: There is a difficulty in estimating the ^{13}C abundance in comets. The $^{12}C_2$ bands are strong because $^{12}C_2$ is homonuclear; but $^{12}C^{13}C$ is not homonuclear, and rotational transitions are possible even if the dipole moment is small. Therefore the ^{13}C abundance might be underestimated, and the $^{12}C/^{13}C$ ratio might be much smaller than 120.

Vanysek: So far as I know, this effect in the isotopically shifted C_2 band plays only a secondary role.

Danks: Your suggestion that $^{12}C/^{13}C > 120$ seems unlikely. $^{12}C/^{13}C$ measurements exist for only a few comets, Ikeya 1963 I (Stawikowski and Greenstein), Tago-Sato-Kosaka 1969 IX (Owen), and Kohoutek 1973 XII (Danks, Lambert and Arpigny) which had values of 70±15, 100±20 and 135^{+63}_{-45} respectively. Owen took account of the blending of NH_2 with the $^{12}C^{13}C$ (1-0) bandhead at 4745 Å while Danks et al. resolved

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the NH_2 lines. More recently Danks and Lambert have observed comets Kobayashi-Berger-Milon 1975h and West 1975a. Their measurements suggest ratios equal to or less than the terrestrial value of 89±4.

Any changes in $^{12}C/^{13}C$ seen in comets may indicate the comets' origin. In theory the ratio can be a few hundred down to the equilibrium value ∿5. Values of 89 suggest a comet formed in the solar neighbourhood. Lower values suggest a comet formed later than the sun, and therefore elsewhere in the interstellar medium.

The change in the dipole moment from $^{12}C_2$ to $^{12}C^{13}C$ is unlikely to be significant. The most extreme example is the change from H_2 to HD, yet it is known to be very small. The temperature distribution in the two (1-0) bandheads of $^{12}C_2$ and $^{12}C^{13}C$ is probably not affected.

Vanýsek: The ratio $^{12}C/^{13}C \sim 70$ obtained by Stawikowski and Greenstein in comet Ikeya 1963 I is obviously underestimated owing to NH_2 blending. Although few data exist for comets, the $^{12}C/^{13}C$ values tend to be higher than terrestrial, and the lower limit of the measured values (i.e. ∿90) seems to be exceeded only by Comet West.

Silk: In principle it is possible to test whether the isotopic composition of grains reveals a different fractionation history from cold molecular gas. Grain destruction occurs in interstellar shock fronts, both by sputtering and by grain-grain collisions, and leads to an enhancement of the abundances of several atomic species observed in diffuse clouds with LSR velocities as low as 20-30 km s^{-1}. It would be interesting to measure the isotopic composition of gas that may have been shocked, for example in the molecular cloud associated with the supernova remnant IC 443.

Irvine: Could accurate measurements of isotopic ratios help solve the fundamental question of whether comets were formed in the Oort Cloud or were formed in the region of the planets and then thrown into their present orbits by planetary perturbations?

Vanýsek: One can predict (if the suggestions in my paper are correct) that the varied history of the material in a cometary conglomerate may lead to large differences in the $^{12}C/^{13}C$ ratio obtained either from the gaseous constituents or solid material of a cometary nucleus formed in the periphery zone (i.e. outside the core of a cloud). On the other hand cometary nuclei formed in the chemically and physically processed material of the pre-solar nebula (in the zone of planetary formation) would be isotopically "homogenized". Therefore the cometary isotopic ratios may shed light on the early history of the solar system. They may also indicate the temperature and time at which very primitive large conglomerates can be formed in dense molecular clouds.

Biermann: Some authors have suggested that comets originated during a relatively recent encounter of the solar system with a dense interstellar cloud (say $\sim 10^7$ years ago). A recent origin would imply an isotopic ratio like that of nearby interstellar clouds, whereas an origin along with the solar system would lead us to expect something close to the value 89.

Vanýsek: Yes, I believe that the $^{12}C/^{13}C \gtrsim 100$ ratio in comets is one of the strong arguments against their interstellar origin.