# THE <sup>12</sup>C/<sup>13</sup>C ISOTOPE RATIO IN COMETS, STARS AND INTERSTELLAR MATTER\*

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Abstract. The  ${}^{12}C/{}^{13}C$  isotope ratio in the interstellar medium and in stellar atmospheres is discussed and compared to the value found in the solar system and especially in comets. The cometary value ( $\geq 100$ ) tends to be slightly above the terrestrial value and is definitively higher than that for interstellar molecular clouds (about 30 to 50).

This result implies that comets are not of interstellar origin; that the "original" isotopic abundances of the primitive solar nebula has been preserved in the cometary material; and that due to an enrichment of the interstellar medium in <sup>13</sup>C, the <sup>12</sup>C/<sup>13</sup>C isotope ratio has decreased by a factor of about 2.5 since the formation of the solar system (i.e., during the past  $4.5 \times 10^9$  years) – a result which is roughly in agreement with present theories of the chemical evolution of our Galaxy. The relatively high cometary carbon isotope ratio (as compared to the terrestrial value) indicates that some correction should be applied to the semi-empirical models describing the <sup>13</sup>C enrichment in the Galaxy.

#### 1. Introduction

The abundance ratio of stable isotopoes in old objects is one of the most significant sources for our understanding of the chemical evolution of our Galaxy, and especially the conditions prevailing in the primeval solar nebula which condensed from interstellar matter about  $4.5 \times 10^9$  years ago. Comets are probably the only observable bodies in the solar system in which the original abundances have been preserved; their material seems to be identical to that of the planetesimals of the first kind, and from their study one might thus obtain some insight into the chemical evolution of the solar neighborhood.

If comets were originally formed in fragmented interstellar clouds, then the carbon isotopic ratio in these objects may provide some clues for the <sup>13</sup>C enrichment of interstellar matter during the past  $4.5 \times 10^9$  years. The original isotope ratios might even have been changed in the outer layers of the Sun due to large scale convection and other processes occurring during the pre-Main-Sequence stage of evolution.

Until now only <sup>12</sup>C and <sup>13</sup>C have been observed with sufficient accuracy in comets as well as in other objects of the solar system, in red giant stars and in the interstellar medium, the cometary <sup>12</sup>C/<sup>13</sup>C ratio is compared to the interstellar and stellar value.

<sup>\*</sup> Paper dedicated to Professor Hannes Alfvén, on the occasion of his 70th birthday, 30 May, 1978.

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### 2. The <sup>12</sup>C/<sup>13</sup>C Ratio in the Interstellar Medium

Among the rare isotopes present in our Galaxy, such as D, <sup>13</sup>C, <sup>15</sup>N, <sup>17</sup>O, <sup>18</sup>O, <sup>29</sup>Si, etc., <sup>13</sup>C is the most abundant species – in the planetary system as well as in the interstellar medium.

Optical determination of the relative abundances of both stable <sup>12</sup>C and <sup>13</sup>C carbon isotopes based on measurements of the equivalent width of interstellar bands of <sup>12</sup>CH<sup>+</sup> and <sup>13</sup>CH<sup>+</sup> (Bortolot and Thaddeus, 1969; Van den Bount, 1972) in the direction of  $\zeta$  Oph yield a carbon isotope ratio which, although rather uncertain, seems to be below the terrestrial value. It is definitely higher than the extremely low ratio shown by some carbon stars. A value of 105 is obtained by Smith and Stecher (1971) from ultraviolet observations of absorption lines of <sup>12</sup>C<sup>16</sup>O and <sup>13</sup>C<sup>16</sup>O towards the same star; but also this value has a large uncertainty.

Interstellar molecular clouds are mostly dense, massive and extemely young objects where the abundance of <sup>13</sup>C is enhanced by mass-loss from red giant stars and by supernova outbursts. The <sup>12</sup>C/<sup>13</sup>C isotrope ratio in the interstellar medium has been derived from radioastronomical observations of different rotational transitions of carbon-containing interstellar molecules such as CO, CS, HCN, HNC, H<sub>2</sub>CO, HCO<sup>+</sup>, and HC<sub>3</sub>N. According to Wilson and Bieging (1977), the mean <sup>12</sup>C/<sup>13</sup>C ratios are about 50 and thus considerably lower than the terrestrial value of 89. The values determined for the same source from different molecules show, however, a large variation, and there might also be some variations between different clouds. From observations of the 4.6 GHz absorption line of H<sub>2</sub><sup>13</sup>CO in ten clouds outside the galactic center, Wilson *et al.* (1976) find an average value of 46 ± 18. Their data seem to indicate that the <sup>12</sup>C/<sup>13</sup>C ratio may slightly vary with distance from the galactic center.

In deducing abundance ratios, optical depth effects have to be considered. It is usually assumed that no chemical fraction occurs that would enhance the abundance of one species relative to another, and that the opacity in the <sup>12</sup>C lines is small ( $\tau_L \ll 1$ ) so that the integrated line intensity is proportional to the column density; the intensity ratio of the <sup>12</sup>C and <sup>13</sup>C lines should then lead to realistic <sup>12</sup>C/<sup>13</sup>C abundance ratios. Since the <sup>12</sup>C<sup>16</sup>O line is nearly always saturated, the <sup>12</sup>C/<sup>13</sup>C ratio is generally determined from the observed intensity ratio of the two rare (and therefore probably optically thin) isotopes <sup>12</sup>C<sup>18</sup>O and <sup>13</sup>C<sup>16</sup>O. In this case, the <sup>16</sup>O/<sup>18</sup>O ratio has to be assumed; usually the terrestrial value of <sup>16</sup>O/<sup>18</sup>O of about 500 is taken.

Linke *et al.* (1977) have measured the molecular abundance ratio  $(H^{12}C^{15}N)/(H^{13}C^{14}N)$  in six dense molecule clouds and find it everywhere smaller than that implied for terrestrial abundances where  $({}^{12}C^{15}N)/({}^{13}C^{14}N) = 0.327$ . For the sources found in the galactic disk the authors determine an average ratio of 0.187, and for those associated with the galactic center the ratio drops to 0.026.

For the integrated intensity ratio  $(HC_3N \equiv H^{12}C^{12}C^{12}C^{14}N)/(H^{13}CCCN)$ , Churchwell *et al.* (1977) find a value of 21 ± 3, whereas for the blended lines of HC<sup>13</sup>CCN and HCC<sup>13</sup>CN, they obtain 56 ± 10, indicating that the true  ${}^{12}C/{}^{13}C$  value is between 20 and 60. The

intensity of the H<sup>13</sup>C<sup>12</sup>C<sup>12</sup>CN line is more than twice as large as that of the H<sup>12</sup>C<sup>13</sup>C<sup>12</sup>CN and H<sup>12</sup>C<sup>12</sup>C<sup>13</sup>CN isotopes. Assuming that the excitation temperature for all three <sup>13</sup>C species of HC<sub>3</sub>N is the same, the authors conclude that there are real abundance differences between the <sup>13</sup>C species and that chemical fractionation takes place in HC<sub>3</sub>N. In that case, the <sup>12</sup>C/<sup>13</sup>C abundance measurements from other molecules could similarly be affected and the obtained results might be too low and should thus be treated with caution. In a comprehensive review on radio measurements of isotope ratios in interstellar molecular clouds, Winnewisser (1976) and Winnewisser *et al.* (1977) give a detailed discussion on the problems involved and conclude that the interstellar <sup>12</sup>C/<sup>13</sup>C ratio lies most probably in the range of 30 to 50.

### 3. The <sup>12</sup>C/<sup>13</sup>C Ratio in Atmospheres of Red Giants

Recent high-resolution spectroscopic observations of lines due to CN and CO molecules in red and infrared spectra of red giants and supergiants of spectral type G, K and M have shown that these stars have a markedly enhanced <sup>13</sup>C abundance relative to the solar system value. The observed <sup>12</sup>C/<sup>13</sup>C isotope ratios extend from values of about 10 for the brightest red giants and supergiants with luminosities of log  $(L/L_{\odot}) \ge 1.6$ , and a mean value of about 20 for less luminous giants with  $1 \le \log (L/L_{\odot}) \le 1.6$ , to over 30 for subgiants with  $\log (L/L_{\odot}) \le 1.0$  (Lambert, 1975; Tomkin *et al.*, 1975; Dearborn *et al.*, 1975 and 1976; Reimers, 1976). In some stars as e.g., in the supergiant  $\epsilon$  Peg where the ratio of <sup>12</sup>C/<sup>13</sup>C = 5.1 is probably attained during helium burning, this ratio is close to the equilibrium value for the CNO-cycle of about 4, whereas in the young subgiant  $\nu^2$  CMa, the ratio of 50 is comparable to the interstellar value.

According to Audouze *et al.* (1975), Vigroux *et al.* (1976), and Reimers (1976), about 5 to 15% of the present interstellar gas (which is about 5% of the total mass of the Galaxy) has been ejected by red giants during the past  $4.5 \times 10^9$  years, the major part being contributed by the brighter stars with  ${}^{12}C/{}^{13}C \approx 10$ , but with additional mass losses from other (including low-mass) stars, during nova outbursts, etc. Due to the enrichment of the  ${}^{13}C$  isotope in the interstellar medium since the formation of the solar system, the isotopic  ${}^{12}C/{}^{13}C$  ratio could thus have easily decreased from less than 100 some  $4.5 \times 10^9$  years ago to the earlier discussed value of 30 to 50 which is presently observed in various galactic clouds.

## 4. The ${}^{12}C/{}^{13}C$ Ratio in the Planetary System and in Comets

Interstellar isotope abundances are characteristic for the present condition of the interstellar gas, whereas the abundances derived for stellar atmospheres correspond to galactic abundances at the time of star formation. Similarly, abundances determined in the planetary system correspond to the conditions prevailing some  $4.5 \times 10^9$  years ago.

Let us assume that <sup>13</sup>C has been formed predominantly by the CNO-cycle in stellar interiors where, in equilibrium, the  ${}^{12}C/{}^{13}C$  ratio is about 4 (i.e., about 5% of the terres-

trial value); by some other processes such as heavy neutron irradiation of <sup>12</sup>C atoms in circumstellar or interstellar gas and solids during the early stage of stellar evolution; or by supernova outbursts. This process would produce <sup>13</sup>C by the reaction <sup>12</sup>C( $n, \gamma$ )<sup>13</sup>C, but only in close vicinity of the neutron flux source due to the limited life time of the neutrons. In addition, hydrogen is a strong absorber for the neutron flux. If neutron bombardment would indeed occur, it would slightly enhance the <sup>13</sup>C abundance in the innermost region of the young solar nebula; the carbon isotope ratio would be somewhat lower for the Earth's and the Moon's crust than for asteroids, but it would remain essentially unchanged on the periphery of the solar system.

Except for comets, the  ${}^{12}C/{}^{13}C$  value is about the same for the other objects in the solar system (Table I), and the same holds for the  ${}^{16}O/{}^{18}O$  ratio which is about 500 ± 25 for Earth, Venus, meteorites and Moon; and about 460 ± 150 for the Sun.

Object	<sup>12</sup> C/ <sup>13</sup> C	Method	Reference
Earth	89 ± 4	_	Wedepohl (1969)
Meteorites	89 ± 2		Boato (1954)
Moon	~ 89	~	Epstein et al. (1972)
Jupiter	$110 \pm 35$	CH₄	Fox et al. (1972)
Venus	$\sim 100$	CO	Connes et al. (1968)
Mars	~ 100	CO	Kaplan et al. (1969)
Sun	90 ± 15	СО	Hall et al. (1972)
Comets:			
Ikeya 1963 I	70 ± 15 <sup>a</sup>	С,	Stawikowski and Greenstein (1964)
Tago-Sato-Kosaka 1969 IX	$100 \pm 20$	C <sub>2</sub>	Owen (1973)
Kohoutek 1973 XII	115 + 30 - 20	C <sub>2</sub>	Danks et al. (1974)
	135 + 65 - 45	C <sub>2</sub>	
Kobayashi-Berger-Milon 1975 h	110 + 20 - 30	C <sub>2</sub>	Vanýsek (1976)
Interstellar Matter	30–50	Radio- Observ.	Winnewisser (1977)

TABLE I Observed isotope ratios of  $({}^{12}C){}^{13}C)$  in the solar system and in interstellar matter

<sup>a</sup> Low value since NH<sub>2</sub> contribution was underestimated; the corrected value amounts to > 100.

If comets are indeed relicts of the most remote parts of the primordial nebula, then they should have a high  ${}^{12}C/{}^{13}C$  ratio. Consequently, if the general chemical evolution of the Galaxy means enrichment of  ${}^{13}C$  in interstellar clouds and young objects, the cometary  ${}^{12}C/{}^{13}C$  ratio should be higher by a factor of 2 or 3 than that of interstellar molecular clouds.

In practice, the intensity of the  ${}^{12}C{}^{13}C(1-0)$  band head at 475.4 nm is compared with that of the  ${}^{12}C{}^{12}C(2-0)$  band head at 438.2 nm or with the triplets of  ${}^{12}C{}^{12}C(1-0)$  at 473.0 and 473.1 nm. This method was described and first applied by Stawikowski and

Greenstein (1964) for Comet Ikeya 1963 I, later also by Owen (1973) for Comet Tago-Sato-Kosaka 1969 IX, by Kikuchi and Okazaki (1975) for Comet Kohoutek 1973 XII, and by Vanýsek (1977) for Comet Kobayashi-Berger-Milon 1975h.

All these studies were based on spectrograms with a linear dispersion of about 18 Å/mm. High-resolution spectrophotometry was applied by Danks *et al.* (1974) who derived the carbon isotope ratio of Comet 1973 XII by scanning the  ${}^{12}C^{12}C$  and  ${}^{12}C^{13}C$  (1–0) bands and the nearby ammonia bands with a spectral resolution of 0.5 and 0.16 Å, respectively. The results of all these observations are summarized in Table I.

The most serious disadvantage of such studies is the blending of the  ${}^{12}C^{13}C$  emission with four lines of NH<sub>2</sub> at 474.428, 474.446, 474.484, and 474.519 nm. Stawikowski and Greenstein (1964) noted the presence of NH<sub>2</sub> but underestimated its influence. A detailed account of the NH<sub>2</sub> contribution was given by Owen (1973), but the most comprehensive analysis of this problem was presented in the above mentioned paper by Danks *et al.* (1974).

### 5. Conclusions

Although the carbon isotopic ratio in comets can be determined only with rather low accuracy, the resulting values of  ${}^{12}C/{}^{13}C$  tend to be  $\geq 100$  in all cases studied so far, and are thus slightly above the terrestrial value of 89. They are certainly higher than those found for interstellar molecular clouds (30 to 50). This result is perhaps one of the most important observational evidences of the growing abundance of  ${}^{13}C$  in the course of the chemical evolution of our Galaxy.

The obvious differences between  ${}^{12}C/{}^{13}C$  ratios found in comets and in interstellar clouds lead to the following implications:

(1) Suggestions concerning an interstellar origin of comets (i.e., in contemporaneous interstellar dense clouds) are incompatible with the observational evidence.

(2) In cometary material the same isotopic abundances have been preserved which were originally present in the primitive solar nebula and in the interstellar matter of the young Galaxy (i.e.,  $4.5 \times 10^9$  or more, years ago).

(3) Due to an enrichment of the interstellar medium in  ${}^{13}C$ , the isotopic ratio of  ${}^{12}C/{}^{13}C$  decreased during the past  $4.5 \times 10^9$  years (i.e., since the formation of the solar system) by a factor of about 2.5 – a result which is roughly in agreement with present hypotheses of the chemical evolution of our Galaxy.

(4) The average value of the carbon isotope ratio in comets tends to be higher than the corresponding value for the Sun or the terrestrial planets. The characteristic time scale for the gas evolution of our Galaxy should therefore be chosen in such a way that the  ${}^{12}C/{}^{13}C$  ratio is 100–120 at the galactic time of  $2.8 \times 10^9$  years (counting from the formation of the Galaxy and corresponding to the birth of the Sun) rather than 89 which is usually assumed (Audouze *et al.*, 1975) in current models of the chemical evolution of the Galaxy.

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