# ISOTOPIC ABUNDANCES IN COMETS

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ABSTRACT: It is belived that the unprocessed material of the solar nebula may be preserved in comets. Thus the data concerning the chemical composition and the abundance of stable isotopes in these primitive bodies are of some importance in cosmological and cosmogonical context. Although the isotopic abundance in the small bodies of the Solar System are poorly known, owing to the forthcoming Halley fly-by missions, the discussion as whether or not the comets have preserved the cosmic isotopic ratio in their nuclei became more relevant. From this point of view expected data of the cosmologically and cosmogonically significant isotopic ratios of stable isotopes of the light elements in comets are discussed.

## 1. INTRODUCTION

It is generally assumed that the comets are composed from the pristine material left over from the presolar nebula. Although there are no evidences that cometary nuclei retain exactly the molecular composition inherited from the interstellar matter, it is believed that in terms of the cosmic abundance there is a direct relation of the cometary material to that of an interstellar cloud. Moreover, recent observation of the sulphur dimer $S_2$ in the spectrum of comet IRAS-Akari-Alcock implies that comets may be formed from the interstellar dust grains (A´Hearn and Feldman 1985, Greenberg 1985). It indicates that even the cometary ice did not condense during the formation of the Solar System, but in the interstellar environment. Thus comets appear to be relatively or absolutely unaltered condensates which contain a key information about processes that took place in an interstellar cloud preceeding the early stage of the solar nebula. The most interesting and significant could be data concerning the isotopic ratios in comets. The isotopic abundances depend on the universal evolution of elements and the individual history of the particular object; it can be used as one of the independent tests for cosmological models, theories of the general chemical evolution of the Galaxy, and theories of the Solar System evolution. The ratios of stable isotopes in comets were directly determined from observations only for carbon, for other isotopes such data are still



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unknown. Nevertheless, the question as to whether or not these bodies may provide a representative information for the cosmology and cosmogony studies become a relevant topic (see Fallik 1982).

In the following review is discussed the status of this problem on the eve of the era of space missions to comets. Space experiments aimed to determine "in situ" the elemental and isotopic abundances in comets have a high priority in the present VEGA and GIOTTO missions to Comet Halley. Therefore, it should be logical and not at all surprising, that many - if not all - conclusions of this review will be approved or disapproved very soon by results provided by the mass spectrometry during the Halley´s fly-by of both above mentioned spacecrafts in March 1986.

## 2. DATA RELIABILITY AND CONSTRAINTS

Since the cometary nucleus contains volatile and refractory material, the abundance derived from comets are those derived from non-uniformly mixed constituents There are no reasonable arguments to belive that in the solid particles the same isotopic abundances prevail as in frozen volatiles. The cometary dust should be regarded as a material with an evolutionary history that precedes entirely the development of the planetesimals and even the formation of the solar nebula.

The dust grains growing in the interstellar environment keep their chemical composition virtually unchanged as far as only minor changes of the grain temperature can be expected during the formation of the cometary nucleus. Consequently, like the chemical composition, the isotopic abundances in the refractory component of cometary dust are inherited from those in the interstellar matter. On the other hand, the condensable volatile constituents in the ice component have been most likely a subject to a modification and redistribution of particular chemical compounds. Therefore, the isotopic ratios in dust grains may be different from those in the evaporable cometary material, even if the isotopic abundance in the very early stage of the grains and ice formation was almost uniform throughout the primeval interstellar cloud.

The abundances of various chemical species in the interstellar space are predominantly controlled by the reaction rates and less by chemical equilibria. Under the conditions generally prevailing in the interstellar environment, isotopic fractionation are more pronouced (see Smith 1981, Adams and Smith 1981, 1987), This effect that is suggested in interstellar clouds may control to some extent the final isotopic ratios in cometary volatiles. Therefore, the isotopic data derived from the evaporated molecular compounds cannot be considered as representative for the entire cometary nucleus.

It must be noted, however, that even the data obtained in near future by the "in situ" mass-spectrometry of dust particles may be slightly hampered by the contamination of the atomic vapor released from the dust grains by the remaining molecules. Particularly, the binding varieties of H, O, N with carbon should be source of the mass ambiguities - for instance $^{13}C$ and $^{12}C^{1}H$ - owing to relatively low mass resolution of the dust impact mass spectroscopy. In comparison to that, the neutral gas spectroscopy is more precise. The resolving power of

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the mass spectrographs on the VEGA and GIOTTO spacecraft is about ± 0.2 amu. Thus the ratio of stable elements, dominant in volatile material as H, D, C, N and O, will be known with higher accuracy than those of the refractory material. The chance to obtain significant data concerning the ratio of nuclear species with cosmological and cosmogonical implications, as H/D, $^{6}Li/^{7}Li$, $^{12}C/^{13}C$, $^{14}N/^{15}N$, $^{16}O/^{18}O$ are discussed in following sections of this paper.

## 3. DEUTERIUM

There does not yet exist a direct identification of D in the cometary spectra. Since most of the hydrogen in comets is probably contained in $H_2O$ a determination of [HDO / $H_2O$] or of [OD / OH] is likely to be good representative data for the estimation of [D/H]. Because the basic structure i.e. electronic, vibrational and rotational of OD is identical to that of OH, A'Hearn et al (1985) applied the same program for the computation of the fluorescence of OD as was used for OH. From the theoreticaly derived strongest features of OD 0-0 band line intensity and from the IUE spectra of OH obtained of comets 1978 XV, 1979 X, 1980 X, 1982 VI and 1983 d were estimated upper limits of OD/OH line intensity ranging from 0.004 (Comet Austin 1982 IV) up to 0.1 (Comet Bradfield 1979 X). The most favorable result for the molecular ratio seems to be [OD / OH] $\approx 4\ 10^{-3}$, which indicates enhancement of D/H ratio by a factor up to 100 relative to the upper limit $2.5\ 10^{-5}$ in the interstellar matter (Vidal-Madjar 1983) as well as in the giant planets, where [D/H] range from about $10^{-5}$ to $6\ 10^{-5}$ (see Encrenaz 1984 and references therein). It would be not surprising if a future mass-spectrometry of the neutral gas confirmes an enhancement of deuterium in comets. Many processes in interstellar clouds and, presumably, also in the solar nebula may led to the isotopic fractionation in molecules at low temperatures. Thus the relative abundances of isotopes, including [D/H] ratio may deviate from their primordial values. The estimation of the deuterium in the solar nebula have been topics of many studies (Geiss and Reeves 1972, Black 1973, Robert et al 1979). This problem was discussed extensively by Gautier and Owen (1983). As was shown by Richet et al (1977) enrichment via the deuterium fractionation suggested that equilibrium process is strongly sensitive to the temperature. Thus in principle the observed [D/H] ratio might be used as a temperature indicator of the environment where the protoplanetary bodies were formed.

Since comets were obviously formed at very low temperature and the volatile material in cometary nuclei is in a form of ices, the fractionation of deuterated molecules in these objects should be significant. Assuming that the formation of comets occured at temperature about 50 K, the enhancement of [D/H] relative to primordial value could be of a factor of order 1000, if the ultimate equilibrium during the condensation of ices was reached. However this is an "ordinary" fractionation process which requires relatively long time scale. More likely some other processes as ion-molecule reactions, or surface reactions on the dust grains may control the deuterium abundance in cometary vol-

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atiles. An indirect support for the assumption that the deuterium in comets could be enhanced follows from results concerning the isotopic ratios in primitive meteorites. Hydrogen released from carbonaceous chondrites is enriched by deuterium by factor 5 relatively to SMOW (standart mean ocean water). See discussion by Pillinger 1982 who favors also the idea of ion-molecule reactions as a fractionation process.

Recently Vanysek and Vanysek (1985) suggested that ion-neutral reactions may led to an enhancement of [D/H] in comets at least of a factor 10. Ip (1985) who suggests that the surface reactions proposed by Tielens 1983 are main channels for the deuteration of water in cometary volatiles predicted even larger [D/H] ratio up to a factor 1000 . Although these predictions are based on different assumptions regarding to the dominant reaction, the results indicate a tendency toward a substantial enhancement of the [D/H] in cometary ice. Since in a hot gas $T > 500$ K all fractionation effects are negligible, above the mentioned upper limit of the deuterium relative abundance implies that the temperature of the environment where the formation of cometary precursors take place was low. It is congruent with the current viewpoints on the origin of comets. On the other hand, however, the [D/H] ratio would be definitely not the best source of data for determination of primordial abundance. Threshold of the VEGA and GIOTTO neutral gas mass spectrometry for [D/H] is about $10^{-4}$ which corresponds with the upper limit of primordial value or to a value which may be yielded by the isotope fractionation.

## 4. CARBON STABLE ISOTOPES

The only isotopic ratio in comets which was determined from observation is the ratio of stable carbon isotopes (see Owen 1973, Danks et al 1974, Vanysek 1977). The average $^{12}C/^{13}C$ ratio found from spectra of four comets is $\geq 100$ which is higher than, but within error of, the Solar System value of 89.

The chemical evolution of the Galaxy lead to the enrichment of $^{13}C$ in the interstellar matter. If comets were formed about 4.5 $10^9$ years ago, then cometary $^{12}C/^{13}C$ ratio should be slightly higher than that of present interstellar clouds; this is indeed in agreement with observations. However, the carbon isotope ratio in comets is derived from emission spectra of $C_2$ in the gaseous coma and is not representative for dust particles. Besides, the ratio of $^{12}C/^{13}C$ in comets tends to be higher than for other objects in the Solar System (Vanysek and Rahe 1978).

Only in the case of Jupiter, the Voyager data provided a suprisingly high ratio $^{12}C/^{13}C \approx 160$ (Courtin et al 1983), which is almost the upper limit estimated for comets. There is no explanation to this discrepancy at present time (Encrenaz 1984). On the other hand, the possible depletion of $^{13}C$ in comets may be an indication that some kind of fractionation has been involved in the condensation of cometary volatiles (Vanysek 1978). The $^{13}C$ enhancement in interstellar clouds via ion-neutral reactions depend strongly on CO abundance and on abundance of CO--related species, as $CO_2$, HCO, $H_2CO$. Because the potential parent molecules of $C_2$ in comets - spectra of which were used for the $^{12}C/^{13}C$

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determination - are probably not related to CO, they could be depleted from $^{13}C$. However, an opposite tendency - i.e. an enrichment by $^{13}C$ follows from the $^{12}C/^{13}C$ ratio $\approx 50$ derived from high-resolution spectra of the 0-0 band of Comet West 1976 VI (Lambert and Danks 1983). Available data seem to indicate that either the $^{12}C/^{13}C$ ratio in comets may be after all very close to the Solar System ratio, or $^{13}C$ isotope is in some comets enriched up to relative abundances observed in the interstellar gas.

An enrichment of $^{13}C$ may be also expected in the cometary dust. Whereas in the meteoric graphite the carbon isotopic ratio is almost exactly terrestrial, the carbon phase in primitive carbonaceous meteorites has anomalous low ratio $^{12}C/^{13}C \approx 50$. This relatively stable refractory carbon component is most likely a relict of the interstellar dust formed in $^{13}C$-enriched atmosphere of a red giant star (Swart et al 1983).

## 5. LITHIUM

From the cosmological point of view one of the most important isotopes is $^{7}Li$. According to Spite and Spite (1982) the Li/H ratio at the formation of the Solar System was about $10^{-9}$, while the primordial ratio was $10^{-10}$. Therefore, $^{7}Li$ ought to be produced during the galactic evolution. The substantial abundances of elements which cannot be formed cosmologically and are destroyed by the nuclear reactions in stars at low temperatures, such as lithium 6, beryllium and boron, can result from the interaction of cosmic rays protons and alpha particles with $^{4}He$ and heavier nuclides more abundant in the interstellar matter. However, the terrestrial $^{7}Li/^{6}Li$ ratio is about 12 and the spallation of light elements by cosmic rays is unable to maintain such a high abundance of $^{7}Li$. This isotope is likely formed in a sufficient amount in novae and/or red giant stars (see Audouze 1983 and references therein). Since two stable lithium nuclides are produced under different conditions, the $^{6}Li/^{7}Li$ ratio was a subject of considerable variation over the life of the Galaxy. Thus, the determination of the lithium isotopic ratio in any objects could be significant for the study of this problem.

Unfortunately, lithium in comets is most likely chemically bound to the refractory material. Owing to low Li abundance and low sensitivity of the dust-mass-spectrometry one does not expect to obtain representative data of the $^{6}Li/^{7}Li$ ratio in comets. Nevertheless, because Li is an easy ionizable alkali element some gross data about the relative ratio of Li to the Si and Fe peaks could be obtained.

## 6. NITROGEN AND OXYGEN

Beside hydrogen the most abundant species in cometary volatiles are compounds of N and O. The isotopic ratio of $^{14}N/^{15}N$ and $^{16}O/^{18}O$ in comets is unknown. The Solar System and interstellar values in the solar neighborhood of $^{14}N/^{15}N$ range from 270 to 330 and the $^{16}O/^{18}O$ ratio is

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roughly 500 Wannier (1980). The abundance of $^{15}N$ is definitely higher than can be expected from the CNO cycle nucleosynthesis. It implies that this isotope, as well as other rare isotopic species, as $^{25}Mg$, $^{26}Mg$, $^{29}S$, $^{30}S$ etc., are products of an explosive nucleosynthesis. The explosive event of a massive star may leave trace in the isotopic composition of the interstellar matter surviving in the cometary nuclei. However, any possible anomalies resulting from such a process will be recognized by the "in situ" measurements only if they occur on a gross scale. Thus there are no reason to expect some conclusive results from the cometary data of the $^{14}N/^{15}N$ and $^{16}O/^{18}O$ ratios.

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## DISCUSSION

JACKSON: Can you tell something about the evolution of comets from the $^{32}S/^{34}S$ ratio?
VANYSEK: Until now the $^{32}S/^{34}S$ is not known. (Note that terrestrial ratio of $^{32}S/^{34}S \sim 120$). However if in the dust particles are some inclusions from an explosion of very massive star ($M > 15\ M_\odot$), then there may be an enhancement of S nuclides relative to <Fe> group and in S isotope ratio.

TATUM: One must be careful in estimating isotope ratios from the Swan bands, because $^{12}C\ ^{13}C$ is heteronuclear and therefore can rotationally depopulate. The $^{12}C/^{13}C$ ratio obtained by neglecting this is always too high. It is possible to estimate the $^{12}C/^{13}C$ dipole moment from the known HD dipole moment and the dependence of dipole moment on reduced mass. Fluorescence calculations on $^{12}C/^{13}C$ need to be done including rotational depopulation.

SHAPIRO: For the ratio $^{7}Li/H$ in the Big-Bang epoch, you quoted an estimate of $10^{-10}$; for the time when the solar system was formed, you gave a value of $5 \times 10^{-10}$. To what is this 5-fold increase attributed?
VANYSEK: The terrestrial $^{7}Li/^{6}Li$ ratio is about 12 and the production of light elements (by cosmic rays in interstellar matter) is insufficient to maintain such a high abundance of $^{7}Li$. This lithium is likely formed in sufficient amount in novae and red giant stars (cf Audouze 1983). From this it follows that during the galaxy evolution the ratio of $^{7}Li/H$ increased by a factor between 5 to 10 relative to the Big Bang ratio of $\sim 10^{-10}$.

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