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Carbon isotopes of irradiated methane ices: implications for cometary $^{12}C/^{13}C$ ratio

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Abstract. Frozen CH_4 and CH_4/Ar were irradiated by protons and $^3He^{2+}$ ions at 15 and 77 K in order to simulate the interaction between the solar wind and the surface of comets. After irradiation, polymerised organic matter is left over as solid residues, when warming up the remaining CH_4. The carbon isotopic composition of these residues was determined. Isotopic fractionation between organic residues and methane reveals a two step process in the maturation of organic matter: 1) a polymerisation of methane associated with an isotopic fractionation of 16‰; 2) a sputtering of the polymerised species associated with an isotopic fractionation lying between 8 and 15‰ and with a corresponding conversion yield of the polymers (i.e. the number of carbon atoms converted into refractory polymers relative to those lost by sputtering) between 9 and 5%.

From the present data and assuming that these experiments represent cometary surface conditions, it can be concluded that irradiation of comets by the solar wind does not contribute significantly to the carbon isotopic fractionation between surface ices, surface polymers derived from these ices and their corresponding sputtered gaseous organic species lost in space. Accordingly the mean $^{12}C/^{13}C$ ratio of the gas phase should be regarded as a face value for the bulk cometary nucleus.

Key words: methods: laboratory – comets: general – Sun: solar wind – ISM: cosmic rays

1. Introduction

Comets are probably the most primitive objects of the Solar System (Yamamoto 1985). They were formed at the same time as planets and meteorites and are located at the periphery of the Solar System, in the Oort Cloud, at distances varying from 10 000 to 50 000 A.U. (Wyckoff 1991). At such distances the surface layers of cometary nuclei are modified by ultra-violet radiations, stellar winds (Festou et al. 1993; McSween & Weissman 1989) and cosmic radiations. In addition, the surface of periodic comets is warmed up when they reach their perihelion, leading to the formation of a crust of refractory materials (Mumma et al. 1993) mainly composed of carbon (Festou et al. 1993; Moreels et al. 1994; Wyckoff 1991). Carbon isotopic composition of comet Halley was measured and compared to the mean isotopic composition of the Solar System. Wyckoff (1991) gives a value of $^{12}C/^{13}C = 369 \pm 194$ for comet Halley meanwhile Jaworski and Tatum (1991) rapport a value of $^{12}C/^{13}C = 89 \pm 17$, markedly different from Wyckoff's estimate. The latter value determined on the organic gas phase CN, is clearly in favour of a Solar System origin ($^{12}C/^{13}C = 89 \pm 2$) for this comet.

Kissel et al. (1986a,b) and Sagdeev et al. (1986) have shown that the grains in the coma of Comet Halley are enriched in carbon compared to C1 carbonaceous chondrites and therefore their chemical compositions are closer to solar abundances. The $^{12}C/^{13}C$ ratio of meteorites exhibits extreme variations, i.e. SiC: $^{12}C/^{13}C = 2$ to 200, with a mean value of 60 ± 15 (Ott 1993; Zinner et al. 1989), graphite: $^{12}C/^{13}C = 3$ to 4000 (Anders & Zinner 1993; Ott 1993) and diamond 88 ± 0.3 (Russel et al. 1991). Recent measurements give a larger range of values for SiC and graphite (1.9 up to 2525 for SiC and 2 to 7300 for graphite – Hoppe et al. 1994, 1995). These isotopic variations are interpreted as the presence of preserved interstellar grains embedded in meteorites. The large variations in carbon isotopic material found in interstellar material grains is usually explained to originate from different stellar sources of these grains. For example, the carbon isotopic ratio of silicon carbide grains ($^{12}C/^{13}C = 2$ to 200) can be attributed to the evolution of carbon stars (Ott 1993). Other isotopic anomalies were found in interstellar diamonds and graphite (see review by Robert & Newton 1996). Such isotopic heterogeneities have also been found in the coma of comet Halley for which "in situ" analysis of dust revealed

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$^{12}C/^{13}C$ lying between 1 and 5000 (Jessberger & Kissel 1991; Jessberger et al. 1988).

In carbonaceous meteorites organic matter exhibits typical solar isotopic values. For example, Robert and Epstein (1982) measured carbon isotopic composition of organic macromolecules and found a value of $^{12}C/^{13}C = 90.5$. In soluble organic compounds (amino acids, fatty acids, hydrocarbons etc...) Krishnamurthy et al. (1992) showed that the $^{13}C/^{12}C$ ratio was in the range 85.2 to 90.2. Therefore the situation in carbonaceous meteorites seems quite similar to comet Halley: the main carbon phase consists of organic compounds exhibiting typical solar isotopic values ($^{12}C/^{13}C = 89 \pm 17$) while an extremely small amount of refractory grains have preserved a presolar signature.

In this paper, carbon isotopic compositions of refractory organic polymers synthesised during irradiation experiments simulating the solar wind and/or cosmic ray bombardment on methane ice are presented.

2. Experimental

2.1. Sample preparation and chemical composition

Samples were obtained during the course of other studies. Experiments are described in details by Kaiser and Roessler 1992; Kaiser et al. 1992a,b; Patnaik et al. 1990; Roessler 1992; Roessler et al. 1992a,b. Samples were prepared as follows: CH_4 and CH_4/Ar (1:12) gas mixtures were condensed on Si wafers at 15 and 77 K at a rate of 145 μmole·h^{-1} at a pressure of $2\,10^{-5}$ mbar to give typically a 10 μm thickness. The methane impurity volume concentration was < 5 ppm (Messer Griesheim – Germany). Samples were irradiated with 18 MeV protons and 17 MeV $^3He^{2+}$ ions respectively, during 5 to 90 min. This irradiation corresponds to doses of 0.007 to 16.8 eV per C atom. The fluence at the cometary surfaces being $1 \pm 0.2\,10^{-7}$ eV·y^{-1}, these doses correspond to exposure ages of $7\,10^4$ and $1.7\,10^8$ years respectively.

After warming up, a heterogeneous solid residue with a typical thickness of 0.5 μm remained on the silicon wafer. The chemical composition of these solid residues was obtained in another study (Kaiser & Roessler 1992) by visual microscopic inspection and chromatography. The volatile species outgassed during methane irradiation at 15–30 K were determined: H, H_2, C, CH, CH_2, CH_3, CH_4, C_2H_2, C_2H_4,, up to linear alkanes in C_8. After heating the left over solid residues at room temperature, several mono- and di-subsituted benzene molecules were outgassed from the residues as well as cyclic compounds such as C_3H_6, C_5H_{10} etc... The remaining solid residues consisted of linear alkanes, alkadienes, aromatic species and polycyclic aromatic hydrocarbons.

2.2. Composition and isotopic analysis

Isotopic composition of carbon in the solid residues was analysed as follows: Organic matter was oxidised with an excess of pure oxygen in a vacuum apparatus. CO_2 was collected in a U-trap for which the temperature can be adjusted precisely and then analysed by mass spectrometry. The carbon isotopic composition of methane before irradiation was determined by mass spectrometry after its oxidation, by oxygen released from CuO at 1000 °C.

Table 1. Isotopic composition of carbon in solid residues. $\delta\,^{13}C$ values are expressed in ‰ relatively to PDB and quantities in μmoles. These values are not blank corrected.

sample number	ion beam	target	$\delta\,^{13}C$	quantity (μmoles)
2	p^+	CH_4/Ar	−27.6	3.73
2 d	p^+	CH_4/Ar	−26.6	4.10
			−26.4	2.11
4 d	p^+	CH_4	−27.4	3.02
			−27.1	3.13
5 d	p^+	CH_4	−26.6	2.92
7	p^+	CH_4	−29.9	1.57
7 d	p^+	CH_4	−27.7	2.70
			−24.3	8.15
8 d	p^+	CH_4	−30.3	1.62
			−29.3	1.03
9 d	p^+	CH_4	−27.2	2.48
			−27.2	3.56
12	$^3He^{2+}$	CH_4	−24.9	6.37
blank Pt			−27.9	0.32
blank Si wafer			−27.9	0.76

The main part of the vacuum line was described previously by Lécluse and Robert (1994). Moreover a glass volume was added for the oxygen supply (see Fig. 1). It consisted in a 500 cm^3 reservoir in which industrial O_2 gas was liquefied at 77 K. From this reservoir, a saturated vapour pressure corresponding to room temperature (i.e. pressure equal to 18 cm Hg) could be expended in the vacuum line. Such an apparatus allows the expansion of almost infinite quantities of pure O_2. Samples were sealed in a platinum foil and placed under vacuum in 250 cm^3 quartz reaction tubes. Then a minimum quantity of 280 μmoles of O_2 was expanded into the reaction vessel to ensure a total oxidation of the organic matter. The tubes were maintained in solenoid coils and heated by induction at temperatures above 1000 K during 10 min. Compounds formed by oxidation (CO_2 and H_2O) were condensed in the U-trap at liquid nitrogen temperature and CO_2 was released at temperatures between 113 and 123 K. CO_2 purity was verified by mass spectrometry and its carbon isotopic composition was measured using a ΔE mass spectrometer from Finnigan Mat.

3. Results

Nine samples of the cometary analogue material were analysed. Typical sample size after irradiation and before warming up (i.e. solid residue plus trapped residual methane and/or methane derived volatile gases) was 100 μmoles. After oxidation, all the carbon of the solid residues was converted into the form of CO_2 the amounts varied in the range 0.27 to 7.39 μmoles.

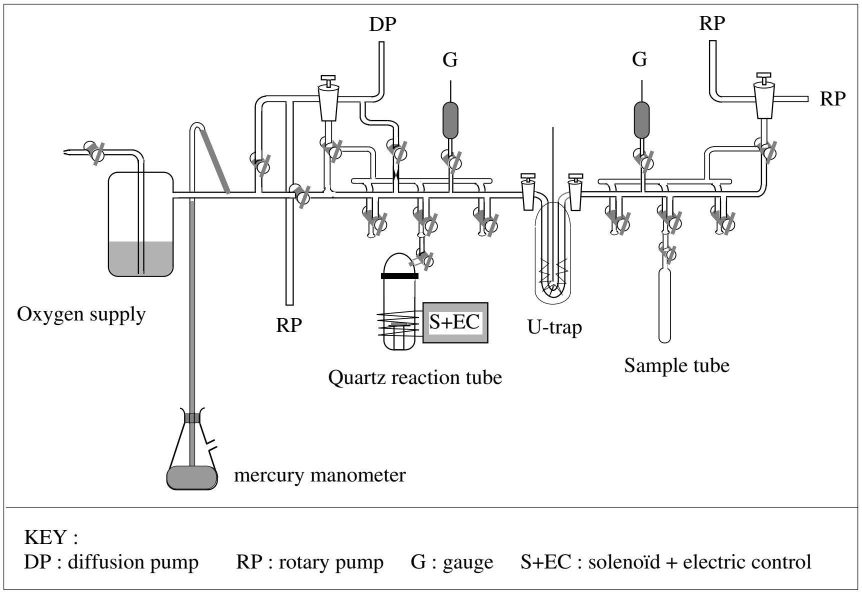

Fig. 1. Oxidation apparatus for organic solid residues. Oxygen supply is ensured by the left part of the line. The oxidation occurred in the quartz reaction tube under oxygen atmosphere at temperature above 1000 K. U-trap allowed the separation of CO_2 from H_2O and sample tube received pure CO_2 for analysis on the mass spectrometer (not represented there). See text for comments.

Carbon isotopic composition for the organic matter are reported in Table 1 and expressed in δ units defined as follows:

$$\delta^{13}C = \left(\frac{R_{\rm sample}}{R_{\rm std}} - 1\right) \times 1000 \qquad (1)$$

with $R_{\rm sample}$ and $R_{\rm std}$ as $^{13}C/^{12}C$ ratios for the sample and the PDB (Pee Dee Belemnite Standard) respectively ($^{13}C/^{12}C_{\rm PDB}$ = 0.0112372). The isotopic composition of the CH_4 before irradiation was -39.9 ± 0.2‰. The carbon isotopic composition of the samples varied from -25 to -35‰. Several samples were analysed in triplicate and give a reproducibility on $\delta^{13}C$ of ± 0.2‰ (2 standard deviations).

The blank contribution was determined to lie between 0.32 and 0.76 μmoles, with carbon isotopic compositions of between -27.95 and -27.87‰, respectively. The two blanks correspond to analyses of the platinum foil and of the silicon wafer sealed in the platinum.

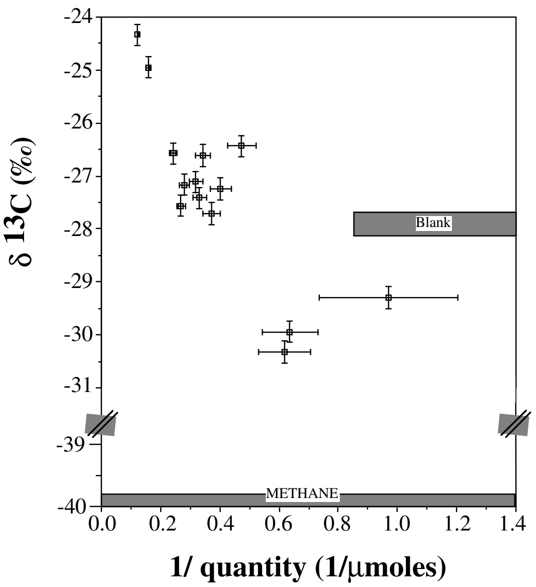

Fig. 2. $\delta\,^{13}C$ (in ‰) versus $1/Q$ (Q in $1/\mu$moles) in organic residues resulting from irradiation of methane ices. Error bars are due to the blank contribution. The initial isotopic composition of methane is also shown. The decrease in $\delta\,^{13}C$ with sample size is interpreted as a progressive maturation by sputtering of initial polymers having $\delta\,^{13}C$ values close to -24‰ (i.e. for $1/Q = 0$).

4. Discussion

In Fig. 2, the isotopic compositions (in δ units) of the residues are reported as a function of $1/Q$ (Q standing for the carbon content expressed in μmole). The isotopic composition of the initial methane is also shown (-39.9‰). All organic residues exhibit an enrichment in ^{13}C relatively to the initial methane and their $\delta^{13}C$ values vary linearly as a function of $1/Q$. According to this correlation, residues appear to reach a fractionation limit of -24‰ for sample size greater than 10 μmoles deposited.

The correlation between the $\delta^{13}C$ and $1/Q$ cannot result from a two component mixing process with the low $\delta^{13}C$ end-member standing for the blank contribution. Indeed, several samples exhibit $\delta\,^{13}C \leq -29.9$‰ clearly lower than those found for blanks ($\delta\,^{13}C = -27.9$‰).

The correlation between the $\delta\,^{13}C$ and the carbon content can be interpreted as a two step process for the formation of the organic polymers. In the first step, methane is polymerised (probably under the form of aliphatic compounds) and the resulting organic polymers (see flow chart in Fig. 3) are isotopically fractionated relative to methane by 16‰ with a mean value of ≈ -24‰ (i.e. 39.9 – 24 = 16‰). In the second step, aliphatic compounds are sputtered by the incoming ion beam (H^+ or He^+). As a consequence, an additional isotopic fractionation occurs and the isotopically heavier species are lost preferentially. Evaporation by sputtering is not supposed to cause any isotopic frac-

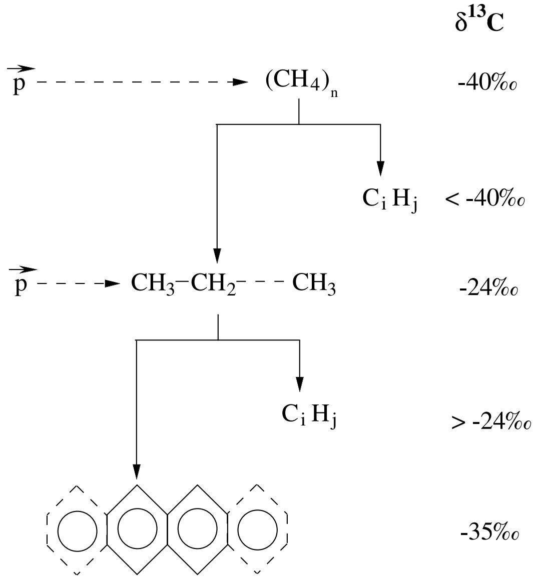

Fig. 3. Flow chart depicting the irradiation model described by Eqs. (1) to (7) (see text). The carbon isotopic composition of each species is indicated in $\delta\,^{13}$C ‰. The species c_{ij} are outgassed form the solid during irradiation. Methane and the other organic compounds remain as solid phases during irradiation.

tionation between the gas and the remaining solids if no chemical reaction takes place between the two phases. Therefore, the observed isotopic evolution must be linked to the loss of carbonaceous fragments, different in isotopic composition from the sputtered solid, implying in turn, that organic matter is rearranged during this second step. Thus one can suppose that this type of isotopic fractionation is caused by the progressive polymerisation of aliphatics into aromatic refractory carbon phases. Simple mass balance equations illustrate this second step:

$$Q_i\delta_i = Q_{\rm aliph.}\delta_{\rm aliph.} + Q_{\rm lost}\delta_{\rm lost} + Q_{\rm arom.}\delta_{\rm arom.} \tag{2}$$

with

$$\delta_i = \delta_{\rm aliph.} \tag{3}$$

and

$$Q_i = Q_{\rm aliph.} + Q_{\rm lost} + Q_{\rm arom.} \tag{4}$$

$$Q_{\rm mes.}\delta_{\rm mes} = Q_{\rm aliph.}\delta_{\rm aliph.} + Q_{\rm arom.}\delta_{\rm arom.} \tag{5}$$

with:

$$Q_{\rm mes.} = Q_{\rm aliph.} + Q_{\rm arom.} \tag{6}$$

The subscripts ‘aliph.’, ‘lost’ and ‘arom.’ stand for the aliphatic carbon produced by the polymerisation of methane, for the carbon lost during irradiation and for the aromatic carbon produced during irradiation, respectively. The subscript ‘i’ designates the initial carbon phases formed by the polymerisation of methane (that is according to Fig. 2, $Q_i \approx 10\,\mu$mole and $\delta_i = -24$‰). The subscript ‘mes.’ stands for the measured values reported in Fig. 2. Since the isotopic fractionation occurs in a solid phase, aliphatic compounds which are not sputtered by the incoming beam are not fractionated relative to their initial values; hence $\delta_i = \delta_{\rm aliph.}$ in Eq. 2. The conversion yield for aromatic compounds can be defined as:

$$Q_{\rm arom.} = kQ_{\rm lost} \tag{7}$$

k in Eq. (6) represents the number of carbon atoms combined into an aromatic structure for 1 carbon atom lost by sputtering.

Eqs. (1) to (6) give:

$$\delta_{\rm mes} = \left[Q_{\rm arom.}/kQ_{\rm mes.}\right]\left[\delta_i - \delta_{\rm lost}\right] + \delta_i \tag{8}$$

In Eq. (7) the measured isotopic composition of the residues (i.e. $\delta_{\rm mes}$) is a linear function of $1/Q_{\rm mes.}$ Numerical simulations of Eq. (7) that fit the results reported in Fig. 2, show that: 1) Assuming that the more ^{13}C depleted samples ($\delta_{\rm mes} = -32$‰; $1/Q_{\rm mes.} = 1.2\,\mu$mole; see Fig. 2) represent almost pure aliphatic free residues, the carbon isotopic fractionation between aliphatic and aromatic is 8‰ (i.e. = 32 − 24) and the conversion yield k cannot be higher than 9%; 2) If the isotopic fractionation is somewhat higher than 8‰, the conversion yield k must be lower than 9%. For example, an isotopic fractionation of 15‰ (i.e. an aromatic polymer with a $\delta_{\rm arom.} = -39$‰) would correspond to a conversion yield k of 5%.

It has been shown by hydrogen nuclear magnetic resonance, that the formation of complex polycyclic aromatic hydrocarbons in solid CH_4 such as coronene ($C_{24}H_{12}$) already takes place at low radiation doses within one collision cascade (Kaiser 1991; Kaiser 1993; Kaiser et al. 1992a,b; Kaiser and Roessler 1992; Patnaik et al. 1990). It is rather a function of linear energy transfer than of the dose. The mechanism discussed here is a multicentre reaction of hot carbon and hydrogen atoms, their intermediate reaction products and free thermal radicals lost in the gas phase being located within a zone of 10 Å radius from the surface (Roessler 1992; Kaiser 1993). As microscopically observed on the wafers (Kaiser et al. 1992; Kaiser and Roessler 1992), the successive transformations of CH_4 into longer and longer aliphatic chains, polycyclic structures and finally amorphous carbon are likely related to the irradiation dose. But even here, multicentre processes will minimise the number of reaction steps. The small isotopic enrichments of ^{13}C in the residues can be considered as an additional evidence for the co-ordinated and concomitant multicentre mechanism.

These observations bear also interesting consequences as far as the origin and evolution of organic material in carbonaceous meteorites is concerned. Gilmour et al. (1991) and Gilmour & Pillinger (1992) detected organic molecule under the form of Poly-Aromatic Hydrocarbons (PAHs) in Murchison and Orgueil meteorites. These authors found that the carbon isotopic composition of PAHs increased with the molecular weight and with the degree of aromatisation. If the present interpretation is correct, isotopic fractionation of carbon linked to irradiation results in a decrease in the $\delta\,^{13}$C values associated with an increase in the degree of aromatisation. This conclusion is opposite to observations reported for PAHs in carbonaceous chondrites, suggesting they were formed by a different process.

5. Conclusion

Organic residues formed by irradiation of CH_4 ice were enriched in ^{13}C by a maximum of 15 ‰ relatively to the CH_4. An evolution of the isotopic composition with the sample size was interpreted as a maturation of organic matter during its irradiation.

In carbonaceous meteorites, $\delta\,^{13}C$ variations up to 75‰ are observed between different organic compounds (e.g. aminoacids, macromolecules etc...). These variations are attributed to the preservation, of a small fraction of interstellar organic matter. Since isotopic fractionation between the gas and the organic residues is markedly smaller (i.e. 15‰ compared with 75‰), the isotopic composition of interstellar matter (if present...) preserved in comets should not be blanked out by an organic maturation taking place at the cometary surface.

In addition, irradiation of comets by the solar wind or cosmic rays does not contribute significantly to the carbon isotopic fractionation between surface ices, surface polymers derived from these ices and their corresponding sputtered gaseous organic species lost in space. Accordingly, the mean $^{12}C/^{13}C$ ratio of the gas phase should be regarded as a face value for the bulk cometary nucleus.

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References

Anders E. and Zinner E., 1993, Meteoritics, 28, 490
Festou M.C., Rickman H. & West R.M., 1993, A&AR, 4, 363 and 5, 37
Gilmour I. & Pillinger C.T., 1992, Meteoritics, 27, 224
Gilmour I., Franchi I.A., Pillinger C.T., Eakin P. & Fallick A., 1991, Meteoritics 26, 337
Hoppe P., Amari S., Zinner E., Ireland T. & Lewis R.S., 1994, AJ 430, 870
Hoppe P., Amari S., Zinner E. & Lewis R.S., 1995, Geochim. Cosmochim. Acta 59, 4029
Jaworski W.A. & Tatum J.B., 1991, AJ 377, 306
Jessberger E. K. & Kissel J., 1991, Chemical properties of the cometary dust and a note on carbon isotopes. in R.L. Newburn etal. (eds) Comets in the Post-Halley era, Vol 2. Kluwer Academic Publishers, 1075
Jesseberger E. K., Christoforidis A. & Kissel J., 1988, Nat 332, 691
Kaiser R.I., 1991, Chemische Prozesse durch Zyklotronionen in festem Methan. Simulation der Wechselwirkung kosmischer Strahlung mit einfachen extraterrestrischen Eiskörpern, Report Jül-2492, Forschungszentrum Jülich GmbH, Germany
Kaiser R.I., 1993, MeV-Ionen induzierte chemische Reaktionen in festem Methan, Ethen und Ethin, Report Jül-2856, Forschungszentrum Jülich GmbH, Germany
Kaiser R.I., Lauterwein J., Müller P. & Roessler K., 1992a, Nucl. Instr. and Meth. B65, 463
Kaiser R.I., Mahfouz R.M. & Roessler K., 1992b, Nucl. Instr. and Meth. B65, 468
Kaiser R.I. & Roessler K., 1992, Ann. Geophys. 10, 222
Kissel J., Sagdeev R.Z., Bertaux J.L. et al., 1986a, Nat 321, 280
Kissel J., Brownlee D.E., Buchler K. et al., 1986b, Nat 321, 336
Krishnamurthy R.V., Epstein S., Cronin J.R., Pizzarello S. and Yuen G.U., 1992, Geochim. Cosmochim. Acta 56, 1045
Lécluse C. & Robert F., 1994, Geochim. Cosmochim. Acta 58, 2927
McSween H.Y. & Weissman P.R., 1989, Geochim. Cosmochim. Acta 53, 3263
Moreels G., Clairemidi J., Hermine P., Brechignac P. & Rousselot P., 1994, A&A 282, 643
Mumma M.J., Weissman P.R. & Stern S.A., 1993, Comet and the origin of the solar system: reading the Rosetta Stone. in E.H. Levy & J.I. Lunine (eds) Protostars and planets III Univ. Arizona Press Tucson, 1177
Ott U., 1993, Nat 364, 25
Patnaik A., Roessler K. & Zádor E., 1990, Radiochim. Acta 50, 75
Robert F. & Newton J., 1996, Condensed Matter News, 5, 8
Robert F. & Epstein S., 1982, Geochim. Cosmochim. Acta 46, 81
Roessler K., 1992, Nucl. Instr. and Meth. B65, 55
Roessler K., Sauer M. & Schulz R., 1992a, Ann. Geophysicae 10, 226
Roessler K., Eich G., Klinger J. & Trimborn P., 1992b, Ann. Geophysicae 10, 232
Russel S.S., Arden J.W. & Pillinger C.T., 1991, Sci 254, 1188
Sagdeev B.Z., Blamont J., Galeev A.A. et al., 1986, Nat 321, 259
Wyckoff S., 1991, Earth. Sci. Rev. 30, 125
Yamamoto T., 1985, Formation History and Environment of Cometary Nuclei. in Klinger et al. (eds) Ices in the Solar System., Reidel Publishing Company, 205
Zinner E., Ming T. & Anders E., 1989, Geochim. Cosmochim. Acta, 53, 3273