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## ORIGIN OF ORGANIC MATTER IN THE PROTOSOLAR NEBULA AND IN COMETS

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### ABSTRACT

Comet organics are traced to their origin in interstellar space. Possible sources of comet organics from solar nebula chemistry are briefly discussed. The infrared spectra of interstellar dust are compared with spectra of solar (space) irradiated laboratory organic residues and with meteorites. The spectra compare very favorably. The atomic composition of first generation laboratory organic residues compares favorably with that of comet Halley organics if divided into appropriate “volatile” (less refractory) and “refractory” (more refractory) complex organics.

### INTRODUCTION

While it is now well recognized from space experiments that comets contain a large amount of organic matter in the form of both complex molecules /1/ and simple molecules /2,3/ it is still being argued whether these molecules originated in interstellar space in the collapsing interstellar cloud or were formed in the protosolar nebula following partial evaporation of the dust. The former point of view has been proposed by Greenberg and coworkers /4,5/ while the latter point of view has its own proponents (see Fegley /6/ and references therein). The picture that appears to be emerging based on both theoretical and observational evidence is that comets are almost, perhaps fully, representative of pre protosolar nebula interstellar dust. It is the purpose of this paper to summarize a few of the critical arguments supporting this view. We will also point out the need for more theoretical and observational work as well as laboratory studies. The importance of a Rosetta mission to study cometary material, at least in situ, with a comet nucleus retrieval effort as the ultimate goal can not be overemphasized.

### INTERSTELLAR ORGANICS

The evidence that complex organics (organic refractory molecules) are a major ubiquitous component of interstellar dust is now generally accepted. The first observational *clue* to their existence was adduced in 1971 by Greenberg /7/ from the *absence* of an H<sub>2</sub>O ice band in the line of sight to VI Cygni no.# 12. It was noted that ultraviolet photoprocessing of dirty ice grains should lead to the formation of complex organic molecules. Observational

*proof* was delayed until 1980 when a distinctive  $3.4 \mu\text{m}$  feature was seen towards IRS7 in the galactic center /8/ although its presence was already noted by Willner *et al.* /9/ in the galactic center (SgrA W). However it was only recently that the  $3.4 \mu\text{m}$  feature was seen /10/ towards VI Cygni no. # 12 where it was first *predicted*. The detailed structure of the feature seen in diffuse cloud dust is characterized by subfeatures corresponding to  $\text{CH}_2$  and  $\text{CH}_3$  stretches which are now determined with some detail /11,12/ and seen in a multitude of sources including extragalactic ones /13/. The question as to whether these organics are preserved and representative of cometary complex organics will be discussed, both directly and indirectly in the following sections.

### PRESERVATION OF INTERSTELLAR VOLATILE ICES

The molecules detected by radio-astronomical observations in interstellar clouds, although they are well represented in comets via the presence of such molecules as  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{CO}$  and many others, their relative proportions are generally very different. An obvious discrepancy is in the  $\text{H}_2\text{O}:\text{CO}$  ratio which, in the interstellar gas, is less than 1:10 while, in comets, it is at least 5:1; i.e., a factor of 50 higher. On the other hand the  $\text{H}_2\text{O}:\text{CO}$  ratio in the interstellar dust found in molecular clouds is, in fact, very similar to that found in the comet coma /2/. This, is already a strong indication of the preservation of the volatile ices of interstellar dust. Additional proof can be deduced from the fact that if the  $\text{H}_2\text{O}$  were to evaporate and reform in the protosolar nebula it can be shown that upon recondensing it would be crystalline rather than amorphous /14/. It is currently believed that the ice in the interior of comet nuclei is amorphous (see /14/ and references therein) so that it can not have condensed in the protosolar nebula. Additional proof of interstellar ice preservation is in the ortho to para ratio of  $\text{H}_2\text{O}$  coming from comets which indicates a very low condensation temperature consistent with the 10K temperature of interstellar dust (see /3/). The point to be taken here is that if the interstellar ice did not evaporate, the organic refractories certainly did not evaporate.

### ORGANIC FORMATION IN THE PROTOSOLAR NEBULA

Allowing for the possibility that some volatile interstellar dust components did evaporate in the inner region of the protosolar nebula and even some of the organics, are there chemical processes which could reconstitute organics in the form observed in comets? The answer to this may be found by comparing the result of the most reasonable protosolar process with the composition of asteroids as reflected in such primitive meteorites as the Murchison meteorite. Cronin and Chang /14/ have compared the FTT (Fischer Tropsch Type) reaction products with those found in Murchison and have concluded that there are several basic *inconsistencies*, a very important one being the fact that the carbon isotope fractionations are different. They have been led to conclude that the formation of chondrite organic matter owes its origin to surviving *interstellar* compounds. Since comets formed and remained at much lower temperatures than asteroids what is true for asteroids *must* be true for comets.

### LABORATORY AND SPACE STUDIES OF INTERSTELLAR DUST ANALOGUES AND ORGANIC RESIDUES

A longstanding effort, begun in 1970, has been devoted to the production and study of complex organic molecules in processes simulating those occurring in the ice mantles of grains in interstellar clouds. In recent years chemical analyses of organic residues produced by ultraviolet irradiation of low temperature ices followed by warmup have given

evidence for a wide range of molecular species, both aliphatic and aromatic. Some of the results of those analyses have been reported elsewhere /16,17,18/. Comparison with comet Halley data shows a wide range of correspondences but it is not possible to be completely positive about the degree of closeness because of incomplete data. One basis for comparison is the 3.4  $\mu\text{m}$  emission by comet dust /19/. A simpler basis for comparisons can be made using the relative atomic compositions. This is being studied now both for the laboratory residues and the space irradiated residues discussed later in this section. A preliminary estimate of the relative atomic composition of the various laboratory residues of  $\text{H}_2\text{O}:\text{CO}:\text{NH}_3 = 5:5:1$  is as follows:

1) Products evaporated and collected at  $100\text{K} < T < 300\text{K}$  /17,18/

C : O : N : H = 1 : 1.2 : 0.03 : 1.4

2) Organic residue material remaining at room temperature and analyzed by GCMS /16/

C : O : N : H = 1 : 1.06 : 0.1 : 2.2

3) Organic residue remaining at room temperature analyzed by mass spectroscopy (relatively more refractory than portion (2) /17,18/)

C : O : N : H = 1 : 0.06 : 0.001 : 1.1

4) Unanalyzed organic residue (estimates based on the *overall* structure of the background mass spectra)

C : O : N : H = 1 : 0.06 : >0.001 : 1.1

There have been no direct measurements of the relative amount of products 1, 2 and 3 but somewhat subjective estimates have been made. From the surface appearance of the cold finger on which the residues have been created and which remain after various stages in the analysis procedures we may assume roughly equal amounts of (1) and (2), and of (3) and (4). The molecules in (1) may be labeled as volatile (V) with respect to the temperatures at which Halley material was measured at or about 1 AU; i.e. the dust at 1 AU has a temperature well above 300K. Some of the organic residue molecules in (2) sublime at temperatures  $\gtrsim 350\text{-}400\text{K}$  which is required for them to be the probable sources of some of the CO in comet Halley as well as other molecules like  $\text{C}_2$  and CN /5,19,20/. Some would remain solid at even higher temperatures /12/. Approximately 1/2 of the mass of the molecules in (2) are required to provide the distributed source of CO in the comet Halley coma /5,19/. On this basis we assign 1/2 of (2) to the category (V) and 1/2 to the refractory (R) category. The total volatile component is then estimated to be (1) + 1/2 (2) and the total refractory component is 1/2 (2) + (3) + (4). These approximations lead to V:- C:O:N:H = 1: 1.2 : 0.05 : 1.7 and R:- C:O:N:H = 1: 0.6 : > 0.01: 1.28

The *total* relative composition using equal masses of V and R as implied by Halley mass spectra is (V+R) = 1: 0.91: 0.03: 1.49

According to Krueger /21/ the stoichiometric distribution of elements in comet Halley mass spectra /22/ are as follow: dust = C:O:N:H  $\simeq$  1:0.5:0.04:1 and PICCA gas = C:O:N:H  $\simeq$  1:0.8:0.04:1.5 and, assuming equal amounts of gas and dust gives a *total* for the organics C:O:N:H = 1:0.6:0.04:1.2. The above results are summarized in Table 1. The comparison between the laboratory and comet Halley complex organics in term of stoichiometric ratio is well within the expected errors described by Krueger /21/. We have not yet answered the question of where the missing nitrogen is to be found but the overall consistency is reasonable. The 3.4  $\mu\text{m}$  features in the infrared spectra of "first generation" laboratory residues although they bear a reasonably close resemblance to those of the interstellar dust, have not provided a *really* good fit /13,23/. A recent comparison has also been made with the spectrum of the orgueil meteorite /24/. *Still* more recently, infrared spectra have been taken of laboratory residues exposed to *long term* solar ultraviolet irradiation equivalent to  $\sim 10^6$  years in diffuse clouds where the volatile molecules are absent from

the grain mantles. These experiments will be reported on in more detail elsewhere but it is worthwhile noting that not only do their spectra more closely resemble those of interstellar dust in the  $3.4 \mu\text{m}$  region than *any other* laboratory analogue refractory /13/, but also their overall spectra bear a remarkably close resemblance to that of the organic component of the Murchison meteorite (See Figs. 1 and 2). The  $3.4 \mu\text{m}$  feature in the Murchison meteorite (not shown here) is almost the same as the space irradiated residue, EURECA B. Exactly what this implies in terms of chemical processing of interstellar dust in the parent asteroid is yet to be investigated in detail. However the explanation (at least in part) for some differences is immediately evident. A major difference between the laboratory spectra and that of the meteorite is in the  $3 \mu\text{m}$  broad feature and the height of the "6"  $\mu\text{m}$  features which are substantially less conspicuous in the latter. Both may be largely attributed to the carboxylic acid OH and CO groups respectively which would tend to be reduced upon heating and thus would be expected to be less in meteorites than in interstellar dust or comets. The strong organics features between 5 and  $8 \mu\text{m}$  will be accessible to the Infrared Space Observatory (ISO) and may eventually be used to compare interstellar organics with laboratory organics. How strong they will turn out to be relative to the  $3.4 \mu\text{m}$  feature will probably indicate the degree of processing of organics in the diffuse interstellar medium.

**Table 1.** Stoichiometric distribution of the elements in laboratory organics compared with the comet Halley mass spectra normalized to carbon.

	Lab Organics			Halley		
	Volatile <sup>a</sup>	Refractory <sup>a</sup>	Total	PICCA(gas)	dust	total <sup>b</sup>
C	1.0	1.0	1.0	1.0	1.0	1.0
O	1.2	0.6	0.9	0.8	0.5	0.6
N	0.05	> 0.01	>0.03	0.04	0.04	0.04
H	1.70	1.3	1.5	1.5	1.0	1.2

<sup>a</sup> Division between calculated refractory is here taken at a sublimation temperature less than or greater than  $\sim 350\text{K}$  respectively.

<sup>b</sup> Assuming equal amounts of dust and gas.

## COMPLEX ORGANICS IN NEW COMETS

Observations of dynamically new comets show evidence for cosmic ray processing for  $5 \times 10^9$  years of the ices in the outer layer of a comet. This produces organic refractories out of the ices while the comet has been in the Oort cloud (see /25/, and references therein). The properties of comet Yanaka 1988r can be explained in terms of their extra surface processing /20/.

## VOLATILE ORGANICS

The most conspicuous volatile organic observed in interstellar dust ice mantles is methanol with formaldehyde a somewhat distant second. Both of these are observed in comet comas. Exactly how much of these molecules will be present in the collapsing cloud before comet formation remains to be studied. Theoretical work on this is underway by two of us (Shalabiea and Greenberg) and, hopefully, more will be learned from the Infrared Space Observatory (ISO) scheduled for launch in 1995.

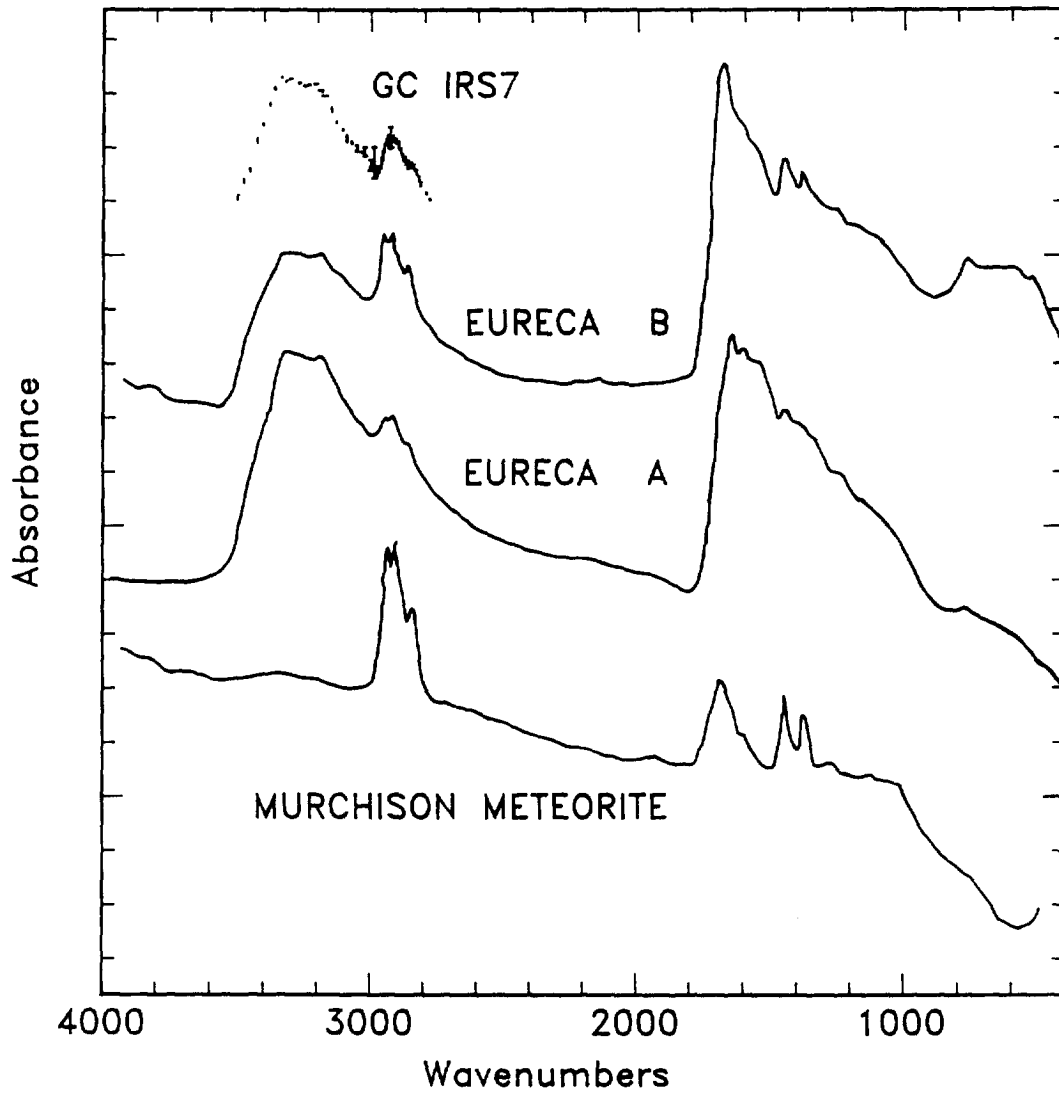


Figure 1: Comparison of the spectra of two laboratory residues subjected to solar ultraviolet irradiation for 4 months (EURECA satellite) with interstellar and meteoritic spectra. A and B are solar irradiated residues resulting from photoprocessing of ice mixtures  $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{CH}_4 = 5:2:2:2$  and  $\text{H}_2\text{O}:\text{CO}:\text{NH}_3:\text{C}_2\text{H}_2 = 5:2:2:1$  respectively. The interstellar spectrum is that of IRS7 in the galactic center.

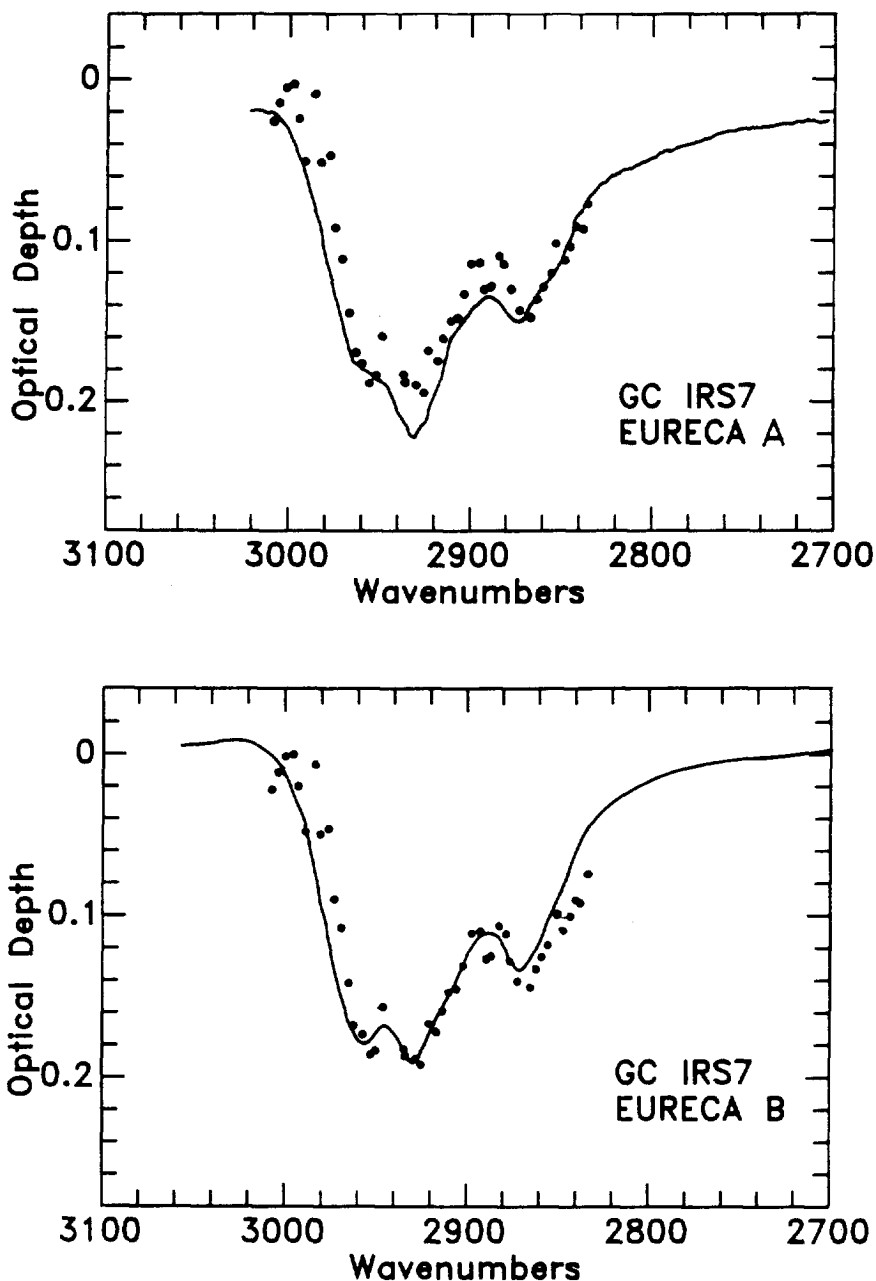


Figure 2: Detailed comparison of the  $3.4 \mu\text{m}$  features of space irradiated residues A and B with the diffuse cloud dust. Observed values are dots, residues are solid lines.

### CONCLUDING REMARKS

Evidence is accumulating in support of the interstellar dust model of comets and, in particular, the preservation of interstellar organics in comet nuclei. The exact nature of these organics will not be definitely known until a comet nucleus sample return mission is achieved. But until then a considerable effort on theoretical modelling and observations of collapsing pre-stellar clouds must be pursued in order to understand when and how these organics have been created. Basic laboratory studies of photoprocessing of interstellar grain mantles in clouds are a required ingredient to provide both a data base for observations as well as a basis for use in the theoretical modelling of dust/gas interactions and evolution in collapsing clouds.

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