SOLAR SYSTEM - INTERSTELLAR MEDIUM

A Chemical Memory of the Origins

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Abstract. The growing body of data on solar system objects and interstellar space provides us with new tests of the connection between the two. We emphasize here the role played by the study of comets through the properties of the dust, the chemical composition of volatiles and the elemental abundances. These data inform us on cometary matter formation, and hence on conditions in the protosolar nebula. Under the adopted scenario of formation in a cold environment, with little further processing, cometary abundances are even new constraints to interstellar (gas and solid phase) abundances. Several points specific to the chemical modelling of the collapsing cloud and of the protosolar nebula are listed.

1. Introduction

Due to the constant influx of new data from both ground-based research and spacecraft, one can trace better and better the primitive connection between the Interstellar Medium (ISM) and the Protosolar Nebula (PSN). We will focus here on the implications of recent results from cometary studies (see A'Hearn 1992 ; Snyder 1992), as comets are thought to be among the most pristine bodies in the solar system. We will further assume *as a working hypothesis* a close connection between interstellar and cometary matter, following Yamamoto and coworkers (1983,1985).

Recent reviews address related fields : meteorite properties (Meteorites and the Early Solar System, Kerridge and Matthews eds. 1988) ; giant planet atmospheres (T.Owen 1992) ; ice/rock ratio in Pluto and outer planets satellites (McKinnon and Mueller 1988). The very important issue of the D/H ratio and other isotopic ratios in the Solar System is addressed also by T.Owen (1992). Much information on cometary composition and its relation to ISM can be found in the recent works of Irvine and Knacke (1989), Yamamoto (1991), Encrenaz et al. (1991), Mumma et al. (1992), and in Comets in the Post-Halley Era (Newburn et al. eds. 1991).

Shu and Adams (1987) describe a possible scenario of the formation of solar-type stars. The four main steps are : the inside-out collapse of a gas condensation ; the formation of a central star surrounded by an accretion disk ; the emergence of a bipolar outflow perpendicular to the disk ; the final T Tauri stage where most of the gas has been blown out by the stellar wind. The history of cometary matter starts even earlier. Refractory grains form in the envelopes of evolved stars, and are eventually coated by ices, which are later processed to organic refractories when the grains are released into the diffuse interstellar medium. When the diffuse medium condenses into dense clouds, molecules begin to form a new ice mantle on the grain surface ; these mantles are believed to reevaporate partially into the gas phase due to some continuous or occasional phenomena (e.g. Tielens and Allamandola 1987, Williams 1990, Walmsley 1990).

In the collapse phase, the medium gets denser and denser, and condensation will probably dominate any reevaporation mechanism until the grain reaches the central regions. There, reheated in the accretion disk, it loses partially its mantle. The gas has now typically a density of 10^{13} cm^{-3}, and undergoes a quite specific chemistry. Some authors (e.g. Prinn and Fegley 1989) see in the gas of the protosolar nebula and the planetary subnebulae major contributors to cometary matter ; we will not discuss these models here (see Yamamoto

P. D. Singh (ed.), Astrochemistry of Cosmic Phenomena, 451–458.

1991 for a presentation and references) and follow the hypothesis favoured by Yamamoto that the condensation of interstellar gas in a cold environment and the subsequent partial sublimation in the PSN are the main phenomena determining cometary composition. Grains grow also by coagulation to form cometesimals, which will aggregate to form cometary nuclei (e.g. Donn 1991). These nuclei, soon ejected by 3 body interactions with the planets toward the Oort cloud will endure only superficial alteration by UV and energetic particles from the Sun and the Galaxy during the 4 Gyr before their eventual return close to the Sun as an active comet.

To test the different models of solar system formation, comets provide us with the following tools : study of their orbits (likelihood of the formation of the Oort cloud and the Kuiper belt) ; isotopic abundances, especially D/H enrichment ; elemental abundances ; chemical abundances ; ortho/para ratios ; microstructure.

We concentrate below on the dust and volatile composition of comets. The dynamical aspects are presented by Weissman (1991) and isotopic ratios by T.Owen (1992). Species like H_2O, H_2CO, H_2S ... have two different hydrogen nuclear spin states (ortho and para) which are not easily converted one into the other and differ in energy ; the ratio of their abundances should thus inform us on the formation or last equilibration temperature of the molecule. The determination of this ratio has been attempted on H_2O in Halley (Mumma et al. 1988), but, according to the reanalysis made by Bockelée-Morvan and Crovisier (1990), there is no clear evidence of any departure from the value expected in the high temperature limit. Recent works on meteorites (see e.g. Kerridge and Matthews, eds. 1988) show that their microstructure is extremely rich in information, and a similar wealth is to be expected from the study of cometary samples.

2. Refractories : Interstellar versus cometary dust

Greenberg and Hage (1990) have proposed a detailed model of coma dust based on the interstellar dust model of Greenberg (1985). The larger interstellar grains, made of silicate cores surrounded by organic refractories, accrete molecules in a very cold region to form precometary grains. Many smaller grains, some made of carbon, others of silicates or PAHs get included in the molecular mantle. Precometary grains stick together to form a very porous structure ("bird's nest"). When the cometary matter is exposed to the sun in the active comet phase, volatiles and part of the organic refractories are released in the coma, where they can be observed ; the remaining solid particles form the cometary dust.

This model explains the low albedo observed in Halley's nucleus, the presence of many low-mass particles, the large organic component (CHON particles, e.g. Jenniskens et al. 1991), and the IR properties of coma dust. It leads to a porosity (empty space/total volume) of at least 0.6 for the nucleus.

Recently, Clairemidi et al. (1991) have proposed a tentative identification of PAHs in Halleys's coma from UV spectra ; the PAHs have been proposed as a major component of the ISM (15% of total carbon) by Léger and Puget (1984). Strong isotopic anomalies have been found by in situ analysis in individual dust grains ($^{12}C/^{13}C$ from 1 to 5000 ; Jessberger and Kissel 1991) suggesting the aggregation of unmodified solid material formed in a variety of places in the galaxy.

All these features give support to the idea of the formation of cometary matter from little processed IS material in a cold environment.

H_2O	152	SO_2	83	CH_3C_2H	65	CH_4	31
HCOOH	112	NH_3	78	H_2CO	64	CO	25
CH_3OH	99	CS_2	78	C_2H_2	57	O_2	24
HCN	95	HC_3N	74	H_2S	57	N_2	22
CH_3CN	91	CO_2	72	C_2H_4	42	H_2	5

TABLE I
Sublimation temperatures in Kelvin for major molecular species under PSN conditions (gas density 10^{13} cm^{-3}). After Yamamoto 1985.

3. Volatiles

In a series of paper Yamamoto and coworkers (1983, 1985, 1991) have studied a two stages model to explain the molecular abundances encountered in comets. First, interstellar gas freezes on grains to form ice mantles in the early stages of Solar system formation. Second, the temperature rise toward the center of the protosolar nebula evaporates partially or totally the most volatile species. In this view, cometary ices should have the same relative abundances as in the interstellar medium, with the major exception of CO and N_2 , which have especially low sublimation temperatures. The abundances of CO, CO_2, N_2 are used to constrain the temperature at the final steps of cometary nuclei formation to 20-70K (for pressures corresponding to the expected typical density, 10^{13} cm^{-3}). Table 1 gives the sublimation temperature for important molecules under PSN conditions (Yamamoto 1985).

Recent advances in ground-based comet observations (cf A'Hearn 1992 ; Snyder 1992 ; Crovisier 1991a ; Weaver et al. 1991), together with Halley's results have enabled an increasing number of tests of this scenario. We assume here that gas production rates from the nucleus give a good picture of its internal composition (a noticeable departure from this is however predicted in some models, due for example to differential sublimation, Espinasse et al. 1991).

The abundance of sulfur species is a new tool made available by recent radio and visible observations (Crovisier et al. 1991, Kim and A'Hearn 1991). We summarize briefly the results of the comparison with ISM (see Despois et al. 1992). The present inventory of the sulfur volatile compounds in comets seems essentially complete (in terms of fraction of total S) ; H_2S and the parent of CS (proposed to be CS_2) dominate, with comparable amounts (0.1-0.2 % of H_2O). S is thus depleted in the volatiles, compared to solar S/O value, 2% , but not in the comet as a whole (i.e. including the dust). Unlike what is presently observed in many places in IS gas, where these species are of comparable abundances (ratio 0.1-10), H_2S strongly dominates sulfur oxides (SO and SO_2) by 2 to 3 orders of magnitude. To interpret this in the frame of the above model seems to require the conversion into H_2S of a large fraction of atomic sulfur (predicted to be the dominant S species in ISM) through grain surface reaction during the formation of cometary matter.

A summary of other cometary volatiles is given in Table 2 ; this list is rather conservative, and the species quoted are fairly securely identified. The derived abundances are however sensitive to some extent to model parameters concerning the excitation of the molecule and its spatial distribution (some species like H_2CO seem to originate at least in part from an extended source, grains or heavier parent molecule ; regarding excitation, atomic sulfur — a decay product — is one of the difficult cases) (Bockelee-Morvan and Crovisier 1992 ; Roettger 1991). On the other hand, new molecules help constraining the models ; for example, the numerous mm lines of methanol will permit to constrain rotational and kinetic

CO	40-200 (a)	NH_3	2	H_2S	2
CO_2	35	HCN	1 (a)	$CS(CS_2)$	1 (a)
CH_3OH	10-40 (c)	N_2	0.2	OCS	<2
H_2CO	0.4-40 (b)	CH_3CN	<0.1	H_2CS	<1
CH_4	<3	HC_3N	<0.05	S_2	0.2/<0.05 (b)
C_2H_2	?			SO	<0.005-0.005
				SO_2	<0.001-0.01

TABLE II

Production rates of major known or expected constituents of the nucleus, normalized to the production rate of H_2O . Unit : $H_2O = 1000$. See Crovisier 1991b and Mumma et al. 1992 for references. Notes: a) variable from comet to comet b) may be variable ; spatial distribution not completely understood c) still under interpretation

temperature in the coma, which previously relied mainly on hydrodynamical modelling (Bockelee-Morvan et al. 1990).

Note in particular the high CH_3OH/H_2CO ratio (with the above caveat!), the low CO/H_2O, the very low abundances of N_2 and NH_3 , as well as of CH_4 . Important to mention also is the apparent variability from comet to comet of *some* of the species : CO (seen in many comets with different relative abundances to H_2O) ; S_2 seen in only one comet (but with high S/N) and absent to very good limits in others.

4. Elemental abundances

If comets are a real pristine sample of PSN material, their elemental composition should be close to solar. Recent summaries (Encrenaz et al. 1991; Wyckoff et al., 1991) using Vega and Giotto dust analyser results together with careful (but in some cases indirect) measurements of coma gas composition from ground-based observations have both concluded that nitrogen is depleted globally (by a factor ~ 6) ; this is mainly due to the N depletion in the volatiles (~ 75). Although not directly observable, the abundances of the two main N bearing species, N_2 and NH_3 have been carefully derived from their daughter species N_2^+, NH_2 and NH, and the reality of these depletions seems certain. Note however that some components like NH_4^+,X^- and $(HCN)_n$ have not been measured, and that another abundance summary (Delsemme 1987) is consistent with a solar value for nitrogen (mostly because of the adoption of a high N_2 abundance).

A simple explanation of this depletion is obtained in Yamamoto's model : above ~ 20 K, pure N_2 would begin to sublimate in the PSN, and N_2 is considered to be a (the ?) major nitrogen depository in the gas phase. Note however that O_2 has also a low sublimation temperature. The fact that O is not underabundant would imply that comets formed from a gas where O_2 was not a major species. This is important, as the oxygen budget of the ISM is not yet understood ; it would favor atomic O, or H_2O (gas or solid), but not O_2 , as main oxygen reservoir in molecular clouds. Another possibility is that of reactions destroying O_2 in the PSN (to form H_2O ?) ; in that case, cometary abundances are expected to depart noticeably from interstellar ones.

Other noticeable features regarding elemental abundances can be seen in Fig. 1. In P/Halley, there are, beside the expected H deficiency, a slight deficiency of C and a larger deficiency of S in the gas phase, which are roughly compensated by higher dust abundances, and a marginal indication of non solar Si/Fe. The latter, if confirmed by future spacecraft measurements with higher S/N, would be difficult to explain in the frame of a formation

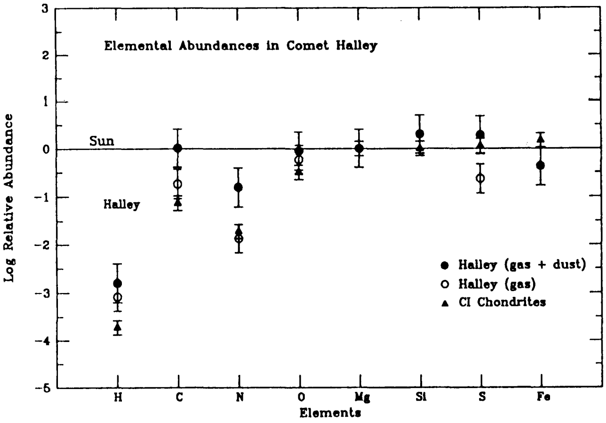

Fig. 1. Elemental abundances in the gas and the combined gas+dust components of P/Halley relative to solar photospheric abundances and normalized to Mg. After Wyckoff et al. 1991.

at cold temperature from homogeneous IS matter.

5. Some remarks on the modelling of the transition from ISM to PSN

To understand the chemical composition of solar sytem objects, especially little evolved objects like comets, one needs to model the evolution of the collapsing gas and its subsequent evolution in the outer fringes of the nebula. This is a quite complex task, as many competing phenomena are involved. However the rapid increase in the amount of data calls for such work, and makes it a very exciting subject. We comment here briefly on some aspects of this new field.

The density and temperature evolution could be taken from the numerical models of solar system formation (see Boss et al. 1989 for a summary). The results are however rarely given in Lagrangian (comoving) coordinates which are more convenient for the study of mostly local processes like chemical evolution. Such a comoving evolution of physical parameters can be more easily retrieved from approximate analytical models. The inside-out model of collapse (Shu 1977 ; Adams et al. 1987) although quite simplified, seems to include much of the relevant physics, according to its success (IR spectra of YSOs and spatial distribution of the matter around them : Adams et al. 1987 ; Butner et al. 1991). Regarding the PSN accretion disk, a quite manageable model is given by Wood and Morfill (1988).

Another question is that of the chemistry in the gas. Ion-molecule chemistry, dominant in the IS medium, will remain limited by its energy input, ionisation through cosmic rays, which has no reason to grow and will eventually decline in the innermost part of the protostellar core due to opacity effects (e.g. Ginzburg 1978). The increase in density will favor the recombination of preexisting ions and radical species, and, even with a modest increase in temperature, neutral-neutral reactions will take place preferentially. Shock chemistry may take place at the boundary of the disk, if there is an accretion shock as in the model of Hollenbach and Neufeld (1990) ; shocked gas will also be present around the bipolar flow which -in the present view -should accompany the early solar evolution. Other high-T chemistry is expected in the inner solar nebula (cf. Prinn and Fegley 1989), but the species produced there should not contaminate much the outer nebula through diffusion (Stevenson 1990). Flares have even been proposed as the origin of the rapidly heated and cooled inclusions found in meteorites (chondrules)(Levy and Araki 1990). Other effects may be produced by the early sun.

Grain surface chemistry, as was suggested in the study of sulfur species, may become the dominant chemistry. Condensation of molecules on grains is an increasingly efficient process as collapse proceeds. Molecule encounters with grains grow linearly with density ; in a cold medium with H_2 density higher than 10^9 cm^{-3}, molecules will condense on grains in less than a year in the absence of any reevaporation process. It appears clearly compulsory now to take into account ice mixture properties in order to discuss the condensation and evaporation of the ices (Schmitt et al. 1989, Sandford and Allamandola 1990, Yamamoto 1991). *Some* CO for example may be retained at temperatures as high as 50 K on an H_2O ice surface, contrasting with the 10-20K for a pure CO layer ; a comparison of solid versus gas phase CO abundances in dark clouds is given in Whittet and Duley (1991).

The surface available for molecule condensation and reaction is however decreased to an unknown extent by grain coagulation (e.g. Cassen and Boss 1988). This phenomenon, first and essential step in the formation of larger bodies, is extremely difficult to model. Grain-grain velocities depend on the (unknown) turbulent properties of the gas, and aggregated grains are likely to have a fractal structure as is common in such processes. Such structures have already been considered in the ISM (to explain dust emission properties, Wright 1987) and in a PSN context (e.g. Weidenschilling et al. 1989). Important also are : the temperature of the grains, which is expected to be different from the gas, the eventual ejection processes releasing molecular mantles into the gas phase, and the surface reaction rates.

In the recent years, some models have already taken into account part of the above complexity : Tielens and Hagen (1982), d'Hendecourt et al. (1985) (grain surface chemistry) ; Boland (1982), Tarafdar et al. (1985), Brown et al (1988), Rawlings et al. (1992) (chemistry in a collapsing cloud).

6. Conclusions

Our knowledge of cometary abundances has considerably grown recently. We now have good estimates or significant upper limits on critical molecular abundance ratios like CO/H_2O, CO/CH_4, NH_3/N_2, $H_2S/(SO+SO_2)$, H_2S/H_2O, ... We have also through the combination of ground based and space results indications for a significant departure from solar elemental abundances in the case of nitrogen. With all these new data, we begin to be able to constrain models of solar system formation. If one admits further, as was done above, the scenario in which cometary matter results from condensation of interstellar matter with little processing, these abundances even give new constraints to ISM chemical models. It is thus desirable that IS chemical models including grains provide mantle composition for comparison. Due to the large range of phenomena occuring, many molecular abundance ratios should be considered together to test the various theories ; among them, minor species such as S-bearing species are extremely useful diagnostic tools. Processes linking IS abundances and cometary/solar system abundances need to be investigated, like gas phase chemistry at densities higher than $10^7 - 10^8$ cm-3, and non-LTE condensation of ice mixtures. Grain surface chemistry plays probably a dominant role, but other possiblities (accretion shock chemistry,...) have also to be investigated. To go further, more data is needed. This is fortunately what the next years should bring, through high spatial and spectral resolution mm and IR investigation of low-mass star forming region by means of millimetric interferometers and infrared satellites, through on-going ground based observation of comets, and ultimately return to Earth of a comet sample by the Rosetta spacecraft.

Acknowledgements

This work owes much to my collaboration with J.Crovisier, D. Bockelee-Morvan, P.Colom and G.Paubert on radio observations of comets. I acknowledge very stimulating discussion with M.Walmsley and enlightening remarks by T.Owen and M.Guélin. I would also like to thank A.Baudry for detailed comments on the manuscript and P.D.Singh for his patience as an editor.

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QUESTIONS AND ANSWERS

B.Foing: In its early evolution in the T-Tauri and past T-Tauri phase, the Sun has an enhanced activity in terms of UV flux (~100 times higher than now), intense flaring and strong winds, as well as energetic particles. How do you expect this active early Sun to affect and alter grains before them being integrated into cometesimals?

D.Despois: We don't know yet. Several groups are investigating the effects of UV and energetic particles on ices. It is precisely the study of the chemical composition of comet nuclei which will inform us on the importance of these effects, and hence on the duration and relative starting time of the various phases of cometary matter formation, cometesimal accretion, clearing of the nebula and exposure to early Sun radiations.