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LOW-TEMPERATURE CONDENSATES IN COMETS

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Recent observational data on the volatile fraction of comets are confronted with a model based on the fractional condensation, in the 80-100 °K range, of a higher-temperature equilibrium obtained from a solar mixture, more or less depleted in oxygen and in hydrogen. It is possible to almost duplicate the observational data, only by assuming that the solar ratio of C/O is at least as large as 0.66 and that the hydrogen was drastically depleted by an unknown process in the primitive solar nebula. Although none of these two assumptions is at variance with present knowledge, the latter is sufficiently exotic to propose a simpler explanation, namely that comets could be made of interstellar grains relatively unprocessed by heat.

INTRODUCTION

As a first approximation, chemical equilibrium models of the primitive solar nebula have been used (Grossman 1977) to predict the element fractionation accompanying the condensation of different crystalline phases at temperatures from 1300 to 400 °K. Chemical kinetics (example: catalysis of Fischer-Tropsch type reactions, Anders 1971) has been used *only* to explain those observations that are obviously at variance with the chemical equilibrium hypothesis (for instance, the presence in carbonaceous chondrites, of straight-chain hydrocarbons, mainly with 15 to 20 carbon atoms).

This approach confirms *a posteriori* that the pressures inferred for the solar nebula (10^{-6} to 10^{-2} atm, Larimer and Anders 1970) allow triple collisions and that classical chemical thermodynamics is applicable, as opposed to interstellar clouds, where the pressure is too low for triple collisions to happen, and where the low temperature implies that a new type of chemical kinetics must be used (charge-exchange reactions prevail). The very success of the chemical equilibrium approach to explain most of the chemical differences among chondrites from a small number of fractionation processes in a cooling solar nebula (Grossman 1977) suggests to investigate whether it could be extended to the low-temperature range in order to explain the chemistry of the volatile (H, C, N, O) molecules in comets.

CHEMICAL NATURE OF COMETS

Whipple's (1950) remarkable insight on the cometary nucleus: "a matrix of meteoritic material with little structural strength, mixed together with the

frozen gases" has withstood the passage of time extremely well, since it has been confirmed by numerous circumstantial considerations. In his paper II, Whipple (1951) assumed cosmic abundances, implied a very low formation temperature, and concluded that meteoritic material should constitute about one third or less the mass of cometary nuclei, the other two thirds being made up largely of hydrides of C, N, O. Lacking enough information on these molecules, he arbitrarily assumed that the major mass was in the form of CH₄, NH₃ and H₂O. This model is shown in Table I, assuming modern solar abundances (Ross and Aller 1976 for C, N, O, normalized to Cameron 1973 for Si) and about 1/3 of the oxygen in silicates and solid oxides (meteoritic material).

TABLE I
MASS DISTRIBUTION OF MOLECULAR COMPOUNDS IN THE COMETARY NUCLEUS
(Normalized to Solar Abundances = 100 Parts)

Model I (Whipple 1952)		Model II (Delsemme 1977)	
Solar Abundances and Thermal Equilibrium At Low Temperature		Observational Data from Four Recent Comets	
Silicates	34	Silicates	34
Water	34	Water	30
CH ₄	26	CO ₂ (and some CO)	6
NH ₃	6	HCN, CH ₃ CN, and Parents of C ₂ , C ₃ etc.	1
Total	100	Total observed	71
Dust/gas ratio	0.5	Dust/gas ratio from observed gases	0.9

In his discussion of observational data from four recent comets, Delsemme (1977) concludes that their oxygen must reach solar abundances, whereas some carbon and nitrogen is clearly missing or unaccounted for. This remark sets the ratio of silicates to (H₂O + CO₂) and yields model II. The dust-to-gas ratio in comets (Delsemme 1977) shows that no major component is missing; the 29 parts that are unaccounted for in model II may imply that some carbon (for instance in CH₄) and nitrogen (in N₂) did not condense out of the solar nebula. Of course it could be suggested that HCN and/or CH₃CN is not a parent molecule present in the cometary snows, but that it was produced after vaporization, by one of the charge-exchange reactions working in the inner coma. This alternate possibility is not very likely. Huebner (1977) has not succeeded in producing large amounts of HCN or of CH₃CN in his charge-exchange model of the coma.

Whatever the case, the simultaneous presence of HCN and CH₃CN and CO₂ suggests a rather exotic origin. Before making different assumptions, we felt however that all possibilities of thermal equilibrium should be exhausted first, if only to rule it out with hard numerical data.

We will therefore investigate here, whether model II can be duplicated by the low-temperature condensation of a solar mixture, more or less depleted in oxygen and in hydrogen (see next section), but still at thermodynamic equilibrium.

The C, N, O solar abundances are of a fundamental importance for our model of the primitive solar nebula. From Ross and Aller's (1976) review, the solar (number) ratios are C/O = 0.60 and N/O = 0.13. Lambert's (1977) comprehensive discussion of all atomic and molecular solar lines, does not appreciably change these ratios. (He gives C/O = 0.59 and N/O = 0.12). Both reviews also agree more or less on the error bars. They should be about ±0.20 dex for the ratios (that is, from 63% to 158% of the nominal values). In particular, the solar

C/O lies between 0.38 and 0.95. This uncertainty has an important consequence for the condensation of the solar nebula. The high-temperature condensation of the solid oxides and silicates removes first approximately 1/3 of the available oxygen. We will call "primitive," the C/O ratio in the gas, after condensation of the solid oxides and silicates. The primitive C/O ratio therefore lies between 0.57 and 1.42, which means that the uncertainty of the present solar data does not rule out reducing conditions in the primitive nebula (that are going to appear automatically when $C/O > 1$). Even if we ignore this uncertainty, and use only the "best" value $C/O = 0.60$, the primitive ratio may vary from 0.87 to 1.05 depending on which silicates we condense. In particular, the formation of hydrated silicates, in the general range of 300 °K, could shift the C/O gas ratio beyond 1.00. The fact that it seems so easy to do so at least in some parts of the nebula, may have played a considerable role in different circumstances; (presence of graphite grains in carbonaceous chondrites, absence of oxidized iron in enstatite chondrites, etc.). To take into account some of the present uncertainty of the solar C/O ratio, as well as the supplementary variation of the primitive C/O ratio, we have explored the consequences of the variation of the primitive C/O ratio between 0.5 and 1.5 and even to 1.7 in some special cases (see Table II later).

WAS THERE A PRIMITIVE HYDROGEN DEPLETION?

The presence of CO₂ (and perhaps some CO) in model II, is one more clue suggesting a possible hydrogen depletion in the solar nebula. For instance, it is known that a likely place for the origin of comets, is a ring at the distance of Uranus and Neptune, or beyond (Kuiper 1951, Whipple 1964). From the spectra of these planets, namely from the 5760, 5430 and 4860 Å bands of methane, Owen and Cess (1975) have deduced a lower limit for the CH₄/H₂ ratio, that indicates that H₂ is depleted by *more than* a factor of 20 from solar abundances in Uranus and Neptune. Polodak's (1976) model of Uranus, suggests a factor of 100. Of course, the origin of this depletion depends very much on the scenario accepted for the early condensation of the solar nebula and the formation of the planets. For instance, Hoyle (1963) suggested that H₂ might have escaped from a nebular "exocone" (by analogy to thermal escape of low-mass molecules from planetary exospheres). Opik's (1963) criticism applies only to straightforward, uncomplicated models. Of course, the T Tauri wind of the young sun may have also played an important *selective* role in the dissipation of the solar nebula.

Without trying to solve this problem here, we have explored the consequences of a hydrogen depletion by varying the primitive H/O ratio between 1500 (solar) and 1.2 (Table II).

TABLE II
RANGE OF THE PARAMETERS COVERED IN THE PRESENT WORK

H/O ratio	from 1.2 to 1500
C/O ratio	from 0.5 to 1.5, (to 1.7 in special cases)
Gas Temperature	from 300 to 1500 °K
Gas Pressure	from 10 ⁻¹⁰ to 10 ⁻⁴ atm
Condensation Temperature	from 60 to 200 °K
Graphite Formation	alternatively included and excluded

CONDENSATION MODEL OF THE PRIMITIVE SOLAR NEBULA

We start from a primitive solar nebula in which silicates have already

condensed into fine grains (for instance from 0.1 to 100 microns). The gaseous phase is considered to contain molecular compounds of H, C, N, O only, and assumed to reach thermodynamic equilibrium at a given temperature and pressure. At all places where the nebula is optically thick, the grains remain at the same temperature as the gas; however wherever the nebula becomes optically thin, grains cool faster than the gas, because they radiate more in the infrared out into space. This temperature difference grows considerably at the edge of the nebula, and grains can condense a larger and larger part of the condensable fraction of the nebula. Condensation has been assumed to be rapid compared to the time scale of the gas chemical reactions. The grains and their icy mantles of solidified gases have been also assumed to have coalesced eventually into cometary nuclei, without further modification.

The equilibria were computed on the IBM 360/75 and UNIVAC 1110 available at The University of Toledo, by using the method of minimization of free energy developed by White, Johnson and Dantzig (1958) and improved by Levin (1962). A list of 82 different molecules including 38 hydrocarbons, 27 (H,C,O) compounds, 14 (H,C,N) compounds, and H₂, O₂ and N₂, was used in the calculations, but we discovered that only 10 species occur in amounts large enough to really determine the overall chemical balance and change appreciably the total free energy. They are: H₂, H₂O, CH₄, NH₃, N₂, CO, CO₂, HCN, CH₃CN, C₂H₆, to which a possible sink of carbon (into graphite) must be added. The amount of any other molecule reaching the threshold level of 10⁻¹⁶ atmosphere was established for each equilibrium worth consideration (see below); the fraction of the gas condensable at a given temperature was then computed as a function of this temperature.

The ranges of the parameters used as independent variables are listed in Table II. The phase space defined by the combination of all these ranges is so immense that we had to establish a searching procedure, to identify only those condensates that were not too far away from Model II; in particular, they had to contain H₂O, CO₂, HCN and CH₃CN in non-negligible amounts. For this reason, for a total pressure of 10⁻⁴ atmosphere, we computed the condensates of those equilibria only, where each of these four compounds had simultaneously a partial pressure larger than 10⁻¹⁶ atmosphere. The rationale of this decision is based on order of magnitude assessments, implying that in a nebula of 1 solar mass, all comets have at least a total mass of 0.3 earth (10⁻⁶ sun), that they have at least 10% of their volatile fraction in the sum of the compounds H₂O, CO₂, HCN, CH₃CN, and that none of the four compounds should be less than 10⁻⁵ of the sum. The same type of reasoning was used for the other total pressures.

RESULTS

Table II gives the special range of each parameter that is requested to simultaneously condense enough of H₂O, CO₂, HCN and CH₃CN. The most restrictive

TABLE III
SPECIAL RANGE OF THE PARAMETERS REQUESTED TO
SIMULTANEOUSLY CONDENSE ENOUGH H₂O, CO₂, HCN AND CH₃CN

1. The H/O and C/O ratios of the primitive nebula must be linked by the relation:

$$H/O = 4.17 C/O - (4.12 \pm 0.08)$$
2. Graphite must not have time to form.
3. The gas temperature of the nebula must be between 550° and 650 °K.
4. Its gas pressure must be of the order of 10⁻⁴ atmosphere.
5. The grain temperature must be higher than 60 °K but below 100 °K.

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condition is the first; it implies that, when the C/O ratio is chosen, the H/O ratio is set by a linear relationship with not much leeway. In the C/O versus H/O plane, its domain is a narrow strip between the two straight lines:

$$H/O = 4.17 C/O - 4.04$$

$$H/O = 4.17 C/O - 4.20$$

Hence in particular, the lower limit of C/O = 0.97 (because H/O cannot be negative); and the upper limit of H/O = 3 (because from solar data, the *primitive* C/O ratio could not reasonably be higher than 1.7). Outside of the strip, for a given H/O ratio, H₂O diminishes for larger values of C/O, where HCN diminishes for smaller values of C/O.

Graphite condensation constitutes a sink for the carbon present in the gas phase; therefore, its appearance at thermal equilibrium suppresses quickly all possibility of making enough CO₂, HCN and CH₃CN to condense eventually; fortunately, it is known that graphite formation has a very slow kinetics.

The temperature range between 550 and 650 °K as well as the rather high pressure are a compromise required to make enough of the four compounds.

The missing carbon mainly remains in uncondensed CO within the primeval nebula.

Typical condensation temperatures, at partial pressure 10⁻⁶ atm, are about 200 °K for H₂O, 175 °K for CH₃CN, 140 °K for HCN and 105 °K for CO₂; therefore if the grain temperature varies in a range not much lower than 105°, a variable fraction of CO₂ might condense, whereas the bulk of the other three molecules will usually condense anyhow.

These results are illustrated in Table IV, where four condensates of the

TABLE IV
CONDENSATES OF A THERMAL EQUILIBRIUM AT 600 °K

H/O = C/O = 1.3, gas pressure 10 ⁻⁴ atm				
	A	B	C	D
Grain Temperature	85° K	93 °K	96 °K	98 °K
H ₂ O	10%	10%	78%	88%
CO ₂	89%	89%	21%	11%
HCN	0.4%	0.4%	0.8%	0.9%
CH ₃ CN	0.001%	0.001%	0.002%	0.002%
NH ₃	0.1%	0	0	0

600 °K equilibrium are shown, as a function of the grain temperature. They all are reminiscent of Model II, column C having about the right ratios for H₂O, CO₂ and HCN. Table IV also shows that the H₂O/CO₂ ratio is a sensitive function of grain temperature.

DISCUSSION

The model can explain the four probable major constituents identified so far in the volatile fraction of comets, by using a thermodynamic equilibrium near 600 °K, in the gaseous phase of the nebula, at a total pressure of 10⁻⁴ atmospheres, and its condensation onto cooler (silicate) grains at a temperature between 100° and 80 °K.

However, the conditions requested for the explanation are very narrow. Namely, they imply that:

a) the solar abundance of C/O (which of course is smaller than 1, since we know that the sun is not a carbon star) must be at least as large as 0.66 and probably larger than 0.7. More exactly, the primitive ratio must be around 1.3. Surprisingly, this is not excluded by recent data, as established in section 3.

b) the hydrogen of the primeval nebula should have been drastically depleted: in particular, any amount not bound in H, C, N, O molecules should have been lost earlier; again, this is not ruled out by recent evidence, since a 100 to 1 depletion is suggested by Uranus and Neptune (see section 4).

CONCLUSION

The price we have to pay for the explanation to hold, does not make it very attractive, although it came as a surprise that it is not inconsistent with any of the known data. The major difficulty probably comes from the HCN/CH₃CN ratio, which is much too high. The observed ratio is not well known, but seems to be within an order of magnitude of unity. Larger production rates of CH₃CN could be found in non-equilibrium situations, similar to the Fischer-Tropsch type reactions invoked by Anders to explain higher hydrocarbons in carbonaceous chondrites. Concentration mechanisms of CH₃CN by prior vaporization of the more volatile fraction could also be invoked. Production mechanisms in the coma (by charge-exchange reactions) do not seem very promising (Huebner 1977).

However, the drastic hydrogen depletion suggested by thermodynamic equilibrium, could be understood in an entirely different context. There is not much doubt that interstellar grains had to follow suit in the contraction of the primitive solar nebula. The inside of the nebula was obviously very much heated by its final contraction, therefore some of the grains were certainly processed by heat or even vaporized, but the *outer* rings of this nebula may not have been heated to temperatures much larger than 60 to 80 °K, where even their icy mantles could have been preserved. If comets were formed there from unprocessed interstellar grains, it is clear that the kinetics of the charge-exchange reactions, to be considered for their prior formation in the interstellar space, may have simulated the drastic hydrogen depletion suggested by our results. To put it in a simple way: thermodynamics is still valid in the interstellar space, it is just that hydrogen does not stick easily to grains, and the final results of the charge-exchange reactions could be not far away from a thermal equilibrium, simulated in particular by a large hydrogen deficiency.

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REFERENCES

- Anders, E. 1977, *Annual Review Astron. Astrophys.*, 9, 1.
 Cameron, A.G.W. 1973, *Space Sci. Reviews*, 15, 121.
 Delsemme, A. H. 1977, this volume.
 Grossman, L. 1977, this volume.
 Hoyle, F. 1963, p. 63, in *Origin of the Solar System*, edit. Jastrow and Cameron, publ. Academic Press, New York.
 Huebner, W. 1977, American Astron. Soc., Division Planet. Sci., 8th Meeting, Hawaii, Abstract 094-5, page 25.
 Kuiper, G. 1951, p. 357 in *Astrophysics: A topical Symposium*, edit. Hynek, publ. McGraw Hill, New York.
 Lambert, 1977, preprint.
 Larimer, J. W., and Anders, E. 1970, *Geochim. Cosmochim. Acta*, 34, 367.
 Levine, H. B. 1962, *J. Chem. Phys.*, 36, 3049.

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- Öpik, E. 1963, p. 73 in *Origin of the Solar System*, edit. Jastrow and Cameron, publ. Academic Press, New York.
- Owen, T., and Cess, R. D. 1975, *Astrophys. J. Letters*, 197, L37.
- Polodak, M. 1976, *Icarus*, 27, 473.
- Ross, J. E., and Aller, L. H. 1976, *Science*, 191, 1223.
- Whipple, F. L. 1950, *Astrophys. J.*, 111, 375.
- Whipple, F. L. 1951, *Astrophys. J.*, 113, 464.
- Whipple, F. L. 1964, *Proc. Nat. Acad. Sci.*, 51, 711, and 52, 565.
- White, W. B., Johnson, S. M., and Dantzig, G. B. 1958, *J. Chem. Phys.*, 28, 751.