

General Discussion after Session III

G. W. Wetherill, A. H. Delsemme, C. T. Pillinger, P. Pellas, M. K. Wallis, R. N. Clayton, E. Jessberger, H. Wanke, S. Chang, R. Hutchison, D. W. G. Sears, M. E. Lipschutz, J. T. Wasson, G. C. McVittie and D. Clayton

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General discussion after session III

G. W. WETHERILL. Much has happened in the years since I started on isotope measurements, over 50 years ago. It was a struggle to make even elementary measurements in the early days and 1 % accuracy or so was considered good; now they worry about fractions of a δ unit. Work in this area and in many areas illustrates the important role industry has played in recent years in making instruments available. When I used to work on these things we had to build our own instruments but now through the availability of instruments of all kinds, not only mass spectrometers, the field has opened to many other people. Many other talents can enter the field, which is why we have seen this enormous progress in the field in recent years. However, I was curious that in Professor Delsemme's talk he said nothing about daughter elements or daughter molecules, in the way that they used to be talked about.

A. H. DELSEMME. I avoided talking about the traditional approach because we are so much farther into the field we do not now need to speak about the possible parent molecules of radicals that we observe in spectra. We still observe comets by traditional means of course, but the new results with the mass spectrometer on comet Halley are so outstanding that we are way beyond the traditional methods.

G. W. WETHERILL. I have a question for Dr Pillinger about the nitrogen in iron meteorites. In what form is the nitrogen?

C. T. PILLINGER. At the risk of pre-empting the contribution of one of my colleagues this is an area in which we are trying to find out information by performing experiments on acid residues from the iron meteorites and although we can identify concentrations of nitrogen we haven't yet identified the phases which we have recovered.

G. W. WETHERILL. I was worried about what it did to the isotopes; if you had to do a lot of chemical manipulations in making these precise measurements then what might this do to the results?

C. T. PILLINGER. Well we try and work out mass balances at the end of the exercise, obviously to make sure we have not done anything improper.

P. PELLAS (*Museum Histoire Naturelle, Paris, France*). Have we now more information to establish whether carbonaceous chondrites have come from comets?

A. H. DELSEMME. Paul Pellas asks whether comets become close to CI carbonaceous chondrites after they have lost their water. My answer can be found in tables 4 and 5. Comets are 15 times as rich in hydrogen, 12 times as rich in carbon, 28 times as rich in nitrogen, twice as rich in oxygen as the CI chondrites; all other elements are consistent with chondritic abundances. Of course, the H, C, N, O excess lies mostly in volatile molecules; the abundances of H, C, N, O in the residual dust comes indeed very close to those in CI chondrites. Of course, it is too early

to compare fine chemical or mineralogical details; for this purpose, we need a rendezvous mission of the CRAF type.

M. K. WALLIS (*Department of Applied Mathematics and Astronomy, University College, Cardiff, U.K.*). I would take issue on four points. The studies of Comet Halley have revolutionized our understanding of comets, but Professor Delsemme seems to have missed the fundamental changes.

1. The *vaporization analysis* is faulty, as pointed out several times in published work, for it assumes a uniformly heated comet surface. Lebovsky (1975) said that realistic solar heating gives vaporization changing far differently with heliocentric distance r . Calculations of a rotating ice ball show that gas production is close to the stationary case for plausible values of thermal conductivity and rotation period. I showed (Wallis 1982) that this means a source function with equivalent scale distance r_0 (where 2.5% incident energy is used for sublimation) is close to twice Professor Delsemme's value; i.e. for H_2O ice $r_0 = 3.2\text{--}8$ AU with typical value 5 AU not the 2.5 AU given. The IUE data on many comets show that their gas production varies much more steeply (Festou 1986), contradicting the hypothesis that H_2O -ice sublimation controls their emission. Only Comet Halley – the extreme datum on Professor Delsemme's figure – has scale r_0 compatible with H_2O , and Encke lies far away. But Halley is not a good example, for its gas strength profile deviates in general shape and it was in fact cited by Professor Delsemme as an unsuitable candidate (Delsemme 1985). He can no longer argue that Encke is different because just some 10% of its surface is active, for that is the very characteristic discovered for Halley.

2. Much of Halley's gas was *emitted by grains* composed of *organic* material. This was shown

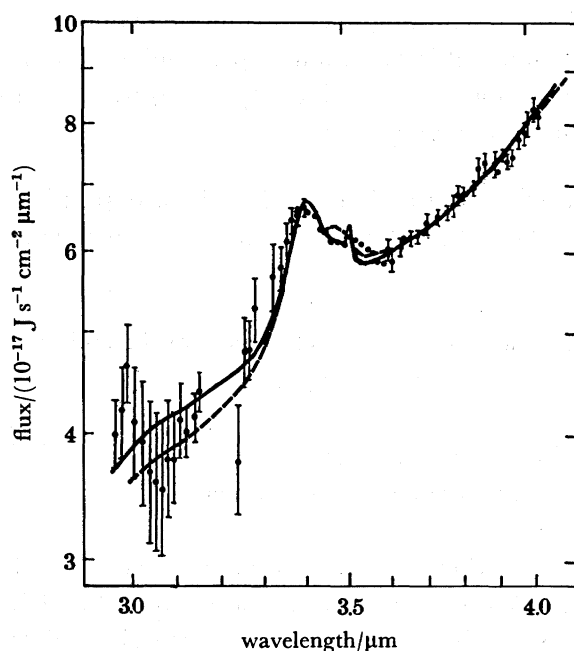


FIGURE D1. Infrared fluxes measured with the Anglo-Australian Telescope (Wickramasinghe & Allen 1986) on 31 March 1986 together with our optimal fit for a distribution of organic grains of sizes compatible with the comet-probe's measurements (Wallis *et al.* 1987). The broken line is the earlier fit of Wickramasinghe *et al.* (1986).

by the comet-probe measurements of carbon-containing gas and of dust-grain compositions, by jets of CN associated with the dust, and by spectra in the infrared 3–4 μm region. Figure D1 shows AAT data with the CH feature peaking at 3.4 μm fit with two theoretical curves. The original broken curve corresponds to thermal emission for a thin layer of organic material, while our newest results shown by the continuous line results for grains at particular temperatures appropriate to free space conditions and with a size distribution compatible with the Halley probe measurements. The submicrometre organic grains heated to 400–800 K or more doubtless emit gas, but cannot be modelled by any sublimating ‘ice’ with single binding energy. Our group at Cardiff has interpreted the behaviour of other comets (specifically *Bowell* and *Crommelin*) as showing gas emission from grains before Halley’s incontrovertible demonstration. The proposal for organic composition (H_2CO polymers) dates from 1975 (*Vanysek & Wickramasinghe 1975*).

3. *Organic polymers* of high molecular mass are implied by *Giotto*’s positive-ion analyser (*Mitchell et al. 1986*). Broad peaks in heavy ion mass numbers up to 130 were observed at a spacing of 14–15 u around 10^4 km from Halley’s nucleus. These could not be H_2O -cluster ions as foreseen by the experimenters (spacing 18 u), but probably linear hydrocarbons with CH_3 and CN sidechains.

4. *Absence of phosphorus*, or even an upper limit of 10^{-6} (*Kissell & Krueger 1987*) if true, would weigh against biological material. However, there are problems with the interpretation of the dust-grain mass-analysis data (e.g. detection of zero for some of the Si Mg-rich grains implies strong binding in molecular form) and mass-31 is evident in some specimens at the 10^{-3} level (e.g. the C-rich particle 53499 encountered by PUMA-1).

In summary, ices of H_2O and other simple gases do not dominate comets’ composition; rather many of the volatiles arise from simple and complex organic solids with a wide range of attachment energies. The question of biological or non-biological material is still open.

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A. H. DELSEMME. Dr Wallis expresses doubts about the prevalence of water in the icy conglomerate of the cometary nucleus; he does not like my use of light curves as an indication that water drives the vaporization of the nucleus. He claims rightly that the heliocentric distance r_0 which separates the radiative régime from the vaporization régime, depends on several parameters, including the sophistication of the model used. My argument is that r_0 is much more sensitive to the chemical nature of the major constituent than to any of the other physical parameters. I have shown (*Delsemme 1985*) that provided the range in heliocentric distances is large enough, many light curves can be used for this purpose. To make my point easy to understand I have used here the simplest possible model, which admittedly hides all the

unknown parameters behind a fictitious albedo, but the results are not fundamentally changed with more sophisticated models. Of course, many other arguments are also in favour of the prevalence of water; as an example, the two velocity components for the hydrogen atoms observed in the Ly- α halo are consistent with the two energy-balance sheets of the two photodissociations $\text{H}_2\text{O} = \text{OH} + \text{H}$ and $\text{OH} = \text{O} + \text{H}$, themselves consistent with 80% of water in the coma. If Dr Wallis does not accept this interpretation of the two velocity components, he should at least propose other photodissociations of another abundant parent molecules that would explain the two velocities of 20 km s^{-1} and 8 km s^{-1} of the hydrogen atoms.

Reference

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R. N. CLAYTON. I noticed that Dr Pillinger avoided mentioning any connection between the nitrogen isotope ratio in the Earth to that in the meteorites. Does he have some thoughts on that?

C. T. PILLINGER. When we started analysing diamonds we felt we were going to find out something about this parameter, the nitrogen isotopic composition of the deep Earth. It seems that there is a very large spread in nitrogen composition in diamonds; we have something like 200 measurements now, many more than anybody else. We do not yet see a pattern which would allow us to predict what is going on in the deep Earth. One of my reasons for worrying about this number is that I think that nitrogen is able to undergo some quite large fractionations during the production of diamond.

P. PELLAS. I ask Professor Delsemme that, if we accept that there is 80% of water in comets, then by subtracting a given amount of water is it possible to obtain a C1 chondrite from comets according to what we have learnt since *Giotto*?

A. H. DELSEMME. Dr Pellas asks whether comets become close to C1 carbonaceous chondrites after they have lost their water. The answer can be found in tables 4 and 5 in my paper in this symposium. Comets are 15 times as rich in hydrogen, 12 times as rich in carbon, 28 times as rich in nitrogen and twice as rich in oxygen as the C1 chondrites; all other elements are consistent with chondritic abundances. Of course, the H, C, N, O excess lies mostly in volatile molecules; the abundances of H, C, N, O in the residual dust comes indeed very close to those in C1 chondrites. Of course, it is too early to compare fine chemical or mineralogical details; for this purpose, we need a rendezvous mission of the CRAF type.

P. PELLAS. I have a second comment about nitrogen isotopes. I am a little bit surprised that Dr Pillinger finds in Nakhla such a beautiful signature when he does not find the same signature in other Nakhrites. They are very similar, so it is strange that the carbonates are in Nakhla but not in the other Nakhrites.

C. T. PILLINGER. It is not possible to say that because we have never done an acid dissolution experiment on the other Nakhrites, which would be a much more definitive way of recognizing

whether or not there was carbonate in them. The two other Nakhla samples that have been measured for bulk carbon abundance and isotopic compositions are probably so heavily terrestrially contaminated that the carbonate, if it is a small amount, will not show up by the combustion technique that we have used.

P. PELLAS. So one is subtracting in Nakhla something that is called possible magmatic carbon? And something that is close to the martian atmosphere is obtained?

C. T. PILLINGER. I think that Dr Pellas confused two things I have said there. We were talking about 79001 where we subtracted magmatic carbon from the very highest temperature carbon dioxide release to look at what we thought was a martian atmospheric component which is released about the same temperature as are the noble gases and nitrogen. Now in Nakhla we do not see a martian atmospheric component; what we see is something which we believe is a carbonate: it has the properties of a carbonate, it combusts and it pyrolyses at approximately the correct temperature and it dissolves in phosphoric acid to give CO_2 . Its isotopic composition seems to match very well the value that we measured for the atmospheric CO_2 in 79001, so we are using circumstantial evidence to suggest that there is weathering on the martian surface.

E. JESSBERGER (*Max-Planck-Institut für Kernphysik, F.R.G.*). I have a comment on Professor Delsemme's talk. I do not wish to question the identification of organic molecules by Kessel & Kruger. However, I would like to sound a note of caution because these molecules constitute about 1 per mille at most of the ion abundance of the CNOH which mostly have been measured as atomic ions with others as molecular ions. We have no idea in what state they are except that these elements are grouped together and that they have to be refractory otherwise they would not have reached the spacecraft. Again, there is a question about the $^{12}\text{C}:^{13}\text{C}$ ratio. In the dust at least, the range is from 12 or 13 to 1 to about 4000. I cannot give any explanation for that although there are models that predict ratios of about 4 or so and also ratios of 4000. I would be very cautious about using these elements.

H. WÄNKE. Just a word of caution to Dr Pillinger about the Nakhla result. The two Nakhla samples we worked with are very heavily contaminated with halogens, namely chlorine and bromine, which is why we think they fell somewhere in terrestrial brine waters in Egypt. The sodium is 1200–1800 p.p.m. and it is water soluble at room temperatures so the carbonate may also have a similar connection. I cannot say that this is so, but just mention it as a word of caution.

C. T. PILLINGER. It is a problem we are well aware of but let me give two reasons why I think it is not a problem in this particular instance. Firstly, Nakhla and 79001, the two samples in which we have found carbonates, were found very far apart, one in Egypt and the other on Antarctica. The two samples have very close carbon and oxygen isotopic compositions. It is difficult to believe that you can contaminate two samples that far apart in the world with the same kind of terrestrial carbonate. I think that it is a martian carbonate that we have found.

H. WÄNKE. I now have two comments on Professor Delsemme's contribution. I do not quite understand why he stresses phosphorus so much. The phosphorus value in C1 meteorites is low and we have no reason to believe that this should be different in a comet. The second point is that he said that the water of the comet has the same isotopic HD ratio as do the terrestrial oceans. He did not raise the argument that the Earth's water was formed by comets which others do. The cometary community and astrophysicists should understand that the Earth is very dry; carbonaceous chondrites have much more water. The question about water on Earth was put the wrong way. It is not so much a question of where the water comes from it is rather a question of why do Earth and Mars, especially Mars, have so little water. I do not think there is a real connection with comets; comets should have delivered water to Mars in approximately the same quantities as to the Earth but the abundance of water is very different on the two planets.

S. CHANG. I have a question for Dr Pillinger. Many people believe that most of the carbon coming out of the surface of the Earth now is coming out of spreading centres. Carbon has been measured isotopically by a number of workers and typically the average of those numbers is the order of -5 to -6 per mille. The question I ask is, why should diamonds, which represent such a small proportion of the carbon inventory of the Earth, be used as a better gauge of what is the internal isotopic composition of the whole Earth rather than the carbon that is coming out of mid-ocean regions?

C. T. PILLINGER. I agree that one should be using what comes out of the ocean spreading centres and, as you are aware, my group is one which has made measurements to try to refine the isotopic composition of deep ocean basalts. In the first paper that we published on this subject, we looked at the kind of gases that were coming from spreading centres and we found in those samples clear evidence that there was a component added to that gas which had a recycled sedimentary isotopic composition.

R. HUTCHISON. I have a comment on a previous question. There is a 1975 paper by John Ashworth and me, where we showed that Nakhla, which is of course an igneous rock, underwent partial hydrothermal alterations since there is Iddingsite in it that looks like part of the fabric of the rock and quite possibly there is indigenous carbonate there too. I am sure that it was not immersion in a brine pool that produced the Iddingsite.

D. W. G. SEARS (*Department of Earth Sciences, The Open University, U.K.*). Probably the most significant point concerning chondrite origins is that although their bulk compositions are all close to cosmic, as Dr Wasson described, there are subtle but significant compositional differences which are recognized in the nine classes of chondrite meteorite. Chondrule formation cannot account for these chemical classes. Although chondrules experienced a great many diverse processes, as described by Dr Hutchison and Dr Kurat, some of which affected their individual compositions, these processes produced only local effects because chondrites of a given class have remarkably constant composition. Oxygen isotope patterns produce the same classes as elemental composition, and because the patterns involve non-mass-dependent fractionations, it is clear that the nine classes reflect processes involving the precursor dust from which chondrules formed, and not the chondrule-forming process itself. Equilibrium

thermodynamic models provide a most successful means of understanding the processes responsible for chondrite classes (through the removal of high-temperature condensates, separation of metal and silicates and low-temperature oxidation and sulphurization) as well as many detailed observations, but such models have become unpopular because isotopic heterogeneities and astrophysical models indicate that the nebula was never universally 'hot' (at least 2000 K). Astrophysical models have undergone major developments in the past few years, and, although based on a variety of assumptions and uncertain in several respects, are remarkably consistent concerning predicted temperature gradients, with temperatures of a few thousand kelvin at *ca.* 0.2 AU and a few hundred kelvin at *ca.* 3 AU. The astrophysical models also indicate considerable radial transport and turbulence, the latter being important in redistributing angular momentum. These models provide a most plausible means of understanding the chemical and physical processes responsible for the chondrite classes in terms of equilibrium reactions occurring at a variety of nebula temperatures and solar distances with considerable radial transport of material, a point discussed in several papers by G. E. Morfill and his colleagues.

R. N. CLAYTON. In Professor Wänke's models where are the components mixed to explain the abundances of, for example, potassium? One component has returned all its potassium and the other has not and I would expect from that to see no difference between stable potassium isotopes in chondritic material Earth or Mars. However, as we reported at Houston last March we are beginning to get potassium isotope data on chondrites, on Earth and on one Nakhilite, and we do appear to see potassium isotopic fractionation effects that look as if the potassium depleted bodies have an enrichment of ^{41}K , as if they are residuals of vaporization. When we have more data we shall be providing an interesting test of your two-component model.

H. WÄNKE. In our papers we always say that this is the simplified scenario. The two components can only be regarded as end members. If, say, component A is depleted by up to 95% in potassium there will be isotopic fractionation which can then mix with undepleted material. The data does not exclude two major components, perhaps component A highly depleted in all volatiles and B not depleted, with mixtures of the two giving the result.

M. E. LIPSCHUTZ. In his discussion, Professor Wasson has described the belief of many of us that the chemical compositions of chondritic groups essentially reflect nebular conditions during formation at different distances from the proto-sun. In this light, would he comment on the fact that unequilibrated ordinary chondrites (H, L and LL3 chondrites) more closely resemble each other in their volatile element contents, oxygen isotopic composition, etc. than they resemble their equilibrated brethren? In many respects, an L3 is more like an LL3 than it is an L4.

J. T. WASSON. The differences between type-3 and type-4 chondrites are important, but they are relatively small and probably understandable in terms of differing degrees of preservation of nebular heterogeneities. There is no consistent demarcation in any of the common taxonomic parameters (e.g. volatile element contents) between 'low' type-4 and 'high' type-3 members of the well-studied L group. The O-isotope data published by Clayton and Mayeda show extensive overlap between the L4-6 and L3 fields, and cannot be used to assign the type of an

L chondrite. Published O-isotope data on LL3 chondrites show ^{18}O contents significantly higher than LL4–6 only in Allan Hills A76004, Chainpur and Semarkona; some A76004 values are normal, and Chainpur differs from L4 Cynthiana by only 0.2‰ in $\delta^{18}\text{O}$. This leaves only Semarkona, for which $\delta^{17}\text{O}$ is *ca.* 0.2‰ and $\delta^{18}\text{O}$ is *ca.* 0.8‰ higher than the edge of the LL4–6 field. Semarkona has hydrated minerals and its O-isotope composition is displaced away from the LL4–6 field in the direction of CI chondrites. If the labile O lost during metamorphism is similar to that in CI chondrites, loss of about 6% of the total O, or about 1% H_2O would move it back to the LL field.

R. HUTCHISON. Chondrites are a paradox. They are composed of chondrules that have highly variable refractory element ratios. Calcium aluminium can vary by a factor of 20 from one to another as can aluminium:scandium and calcium:scandium. They also appear to have formed from the same oxygen isotopic reservoir. The bulk chondrites are uniform within each chemical group, as Professor Wasson showed. They might be produced by fragmenting and recombining a differentiated planet but how does one produce them in a nebula that has uniform oxygen isotopes and highly fractionated lithophile elements in the chondrules?

J. T. WASSON. I think that these fractionations that Dr Hutchison mention in the chondrules are not so apparent in the most unequilibrated meteorites. I would argue that oxygen isotopes in the solid matter that existed before the chondrules formed showed at least the same range that we now see within the chondrules. There clearly were inhomogeneities in the solid matter that was there.

D. W. G. SEARS. I think Professor Wasson raise a good point. The chondrules can be highly variable in their compositions, they have the most remarkable metal fractionations and yet if you take a bulk chondrite its composition is remarkably fixed. All H chondrites have remarkably well defined compositions, that tells us that the chondrule-forming process occurred on pre-existing dust which already had those chondritic class signatures in it.

G. C. McVITTIE. Professor Wasson used the term frequently ‘condensing out of the solar nebula’. I wondered whether it was anything like a hail shower. I can understand that water vapour in our atmosphere condenses to water – rain drops – and then with a further fall of temperature to bits of ice, but is this what is envisaged in the solar nebula? Do we have iron vapour which condenses into liquid iron and then turns into solid metal?

J. T. WASSON. At the low pressures present in the solar nebula the liquid field is not present, you go directly from the vapour field to the solid field, so in the calculations that are done, one does go directly to metallic grains without going through the liquid.

P. PELLAS. The A and B components mentioned by Professor Wänke are a purely phenomenological approach to the problem; in other words they do not solve the problem but just explain the composition. What we have to understand is how the components A, B and those in between were produced. An approach in which we attempt to understand why various processes occurred in the early Solar System is the most fundamental research we have to do. My second point concerns the martian soil. When Professor Wänke presents the data and

compares them with SNC meteorites, he subtracts the chlorine and sulphur because there is no agreement for these between SNC meteorites and the martian soil.

H. WÄNKE. Dr Pellas's first point is certainly important. There is very little certainty about such models as exist for events in the early Solar System which is why one is left with a phenomenological approach. I disagree with the second point. I know that he prefers not to have SNC meteorites from Mars. I said myself I do not want to stress too much the similarity of the Viking soil and the Shergotty meteorite; the only clear point is that chlorine and sulphur cannot be in a basalt because on Earth there are no primary basalts which contain a couple of percent of chlorine and sulphur. This is in the Viking aerolean soil. If the Earth's ocean were dried up then the ocean beds would have a lot of chlorine and in the early days of the earth there may also be a lot of sulphur in this dried up ocean bed, but these are not basalts. Basalts on any planet must come from lava flows and not from aerolean wind deposit fragments.

D. CLAYTON. Professor Wasson listed three alternatives about chemical fractionation. One was listed as a pre-solar fractionation and a second something like sedimentation or sorting according to grain sizes, thereby producing microscopic fractionations if I understood correctly. How does that solve the problem unless the large particles are different in composition from the small particles? If one is going to separate magnesium from silicon different magnesium:silicon ratios in the large and small particles are needed. And this takes one straight away back to pre-solar fractionation in preparing those fractionation differences between large and small particles.

J. T. WASSON. I agree that the materials in the different particle sizes have to be different in composition. To get a magnesium-silicon fractionation you need to have, say, one component which might be like olivine with an Mg:Si ratio of two and another one which might be more like SiO₂ or plagioclase which would have a very low Mg:Si ratio. It is not obvious that it is easier to do this in a pre-solar setting than in a solar setting; I think we have to keep both possibilities in mind.