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Biologic versus abiotic models of cometary grains

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Summary. The infrared spectral feature around 3.4 μm observed in comet Halley is indicative of organic material, as shown to lowest order by transmission layer calculations. The detailed profile of the waveband emitted by grains of dust depends, however, on their sizes and temperatures. Radiatively processed methane-ice shows a 3.4-μm feature as would be expected. But, contrary to a recent claim for the 'tholin' model, this differs significantly from the observed spectrum. New calculations for a size-distribution of realistic grains of biotic material give quite a close fit, confirming this is a good candidate for the complex organic material detected by the comet Halley probes.

Several authors have recognized, following Wickramasinghe & Allen (1986), that the infrared spectral feature around 3.4 μm is indicative of solid grains of organic material in comet Halley. The feature corresponds to stretching vibrations of the CH bond, with details over 3.3–3.5 μm depending on neighbouring molecular bonds (Encrenaz *et al.* 1987). The biological model supposes this arises from cometary particulates and predicted the 2–4 μm waveband well ahead of the arrival of relevant cometary observations. The diagnostic utility of this waveband lies in the high strength of emissions from solid as opposed to gaseous material, and in its dominance relative to scattered 'continuum' including from the component of mineral grains. Also, various observers on different nights recorded data from comet Halley.

These data allowed testing of our initial prediction in the form of the solid curve of Fig. 1 (Wickramasinghe *et al.* 1986). Here the infrared flux for the bacterial model was calculated according to the transmission formula

$$F_\lambda = \alpha\tau(\lambda) B_\lambda(T) + \beta F_{\text{solar}}(\lambda), \tag{1}$$

where $B_\lambda(T)$ is the Planck function at the grain temperature T, $F_{\text{solar}}(\lambda)$ is the solar spectrum and $\tau(\lambda)$ are the optical depth values for a sample of desiccated bacteria read-off from a calibrated pen-chart obtained using a Perkin-Elmer spectrophotometer (Hoyle *et al.* 1982). The value of T was taken to be 320 K and the ratio $\alpha:\beta$ arbitrarily chosen so that F_λ matches the

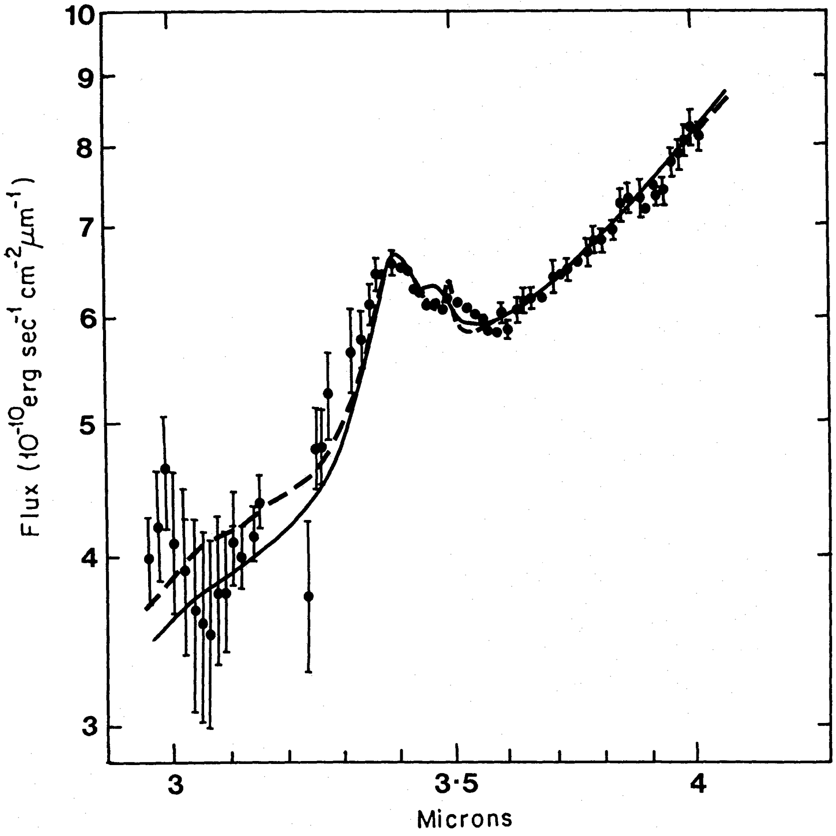

Figure 1. Observational data (points) for comet Halley on 1986 March 31 compared with calculations for the biological model. The solid curve is the prediction for a single temperature (transmission) model in the small particle limit; the dashed curve uses the distribution of grain sizes as detected by the Halley probes (McDonnell *et al.* 1987; Wallis *et al.* 1987b).

observational data at two prescribed wavelengths. The bacterial model is immediately seen (Fig. 1) to be satisfactory.

This simple model suffers from the arbitrarily chosen effective T and ignores the dependence on scattering angle for an optically thin distribution. The following refinements have therefore been made (Rabilizirov 1988; Wallis *et al.* 1987b):

(i) a distribution of grain-sizes adopted, as actually found in comet Halley by the Giotto probe, the grains being assumed spherical to allow use of Mie theory;

(ii) temperatures of bacterial grains as a function of grain-size at 1.17 AU, calculated using laboratory measurements to determine $n(\lambda)$, $k(\lambda)$ appropriate for this material and taking account of the effect of chromophores in the visual waveband;

(iii) the function $F_{\text{solar}}(\lambda)$ in (1) replaced by a scattered intensity function calculated for the bacterial grains at the appropriate scattering angle of 90° at 1.17 AU.

These refinements result in the dashed curve in Fig. 1. There is some improvement over the original agreement, particularly at 3.46–3.50 μm, through the more realistic modelling procedure. As is well known, the grain temperature varies substantially with size and composition; indeed, the new calculations show that the profile is sensitive to the distribution over grain sizes, proving that the early good agreement was contingent on the particular choice of effective temperature.

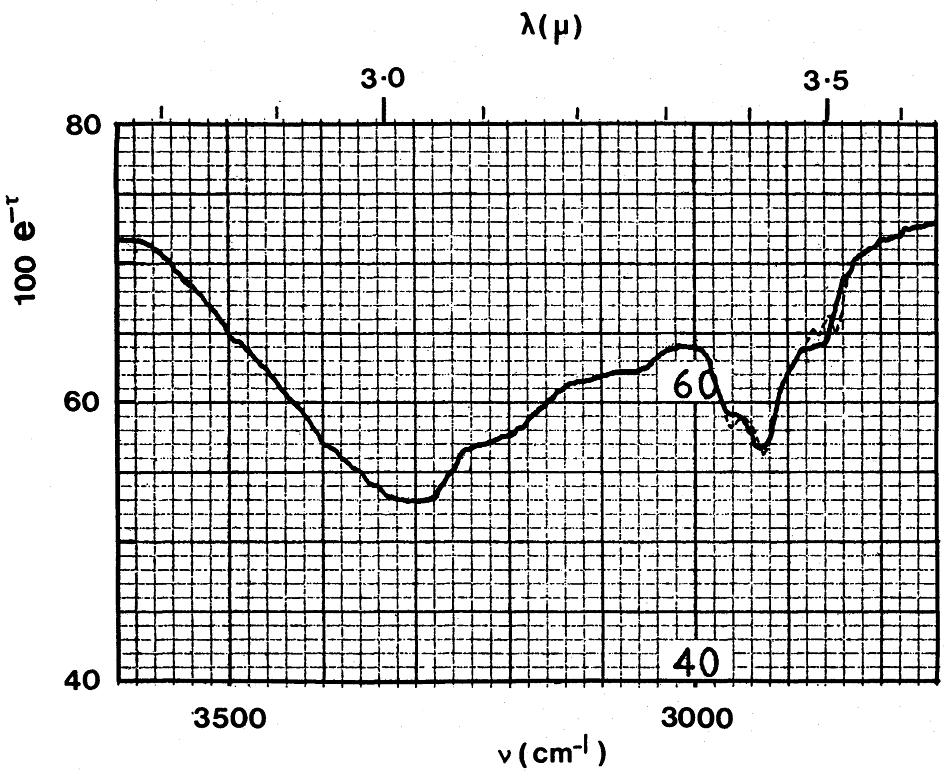

Figure 2. Laboratory transmittance data for sample of *E. coli* after heating to 350°C. The dashed segments near 3.4 μm correspond to transmittance values for a sample irradiated to 1.5 Mrad at 77 K (^{60}Co source, several hours duration) as an illustration of changes achievable via irradiation.

The agreement seen in Fig. 1 depends on the detailed absorption properties of bacteria as displayed in the pen-chart of Fig. 2. The 3.47 μm trough and 3.50 μm peak depend on the variations induced by irradiation (broken line in Fig. 2 — details in the caption). Similar structure can also be reproduced via inclusions of biological pigments (Rabilizirov 1988). Evidently, certain organic groups yet to be identified are responsible for such details. The structures within the 3.4-μm band arise essentially from the superposition of CH stretching modes within a distribution of functional groups that are, admittedly, common to a large number of organic molecules. The asymmetric stretch of methyl groups contributes at ~ 3.38 μm, so the shoulder in Fig. 1 at that position indicates a greater fraction of aliphatic side chains than in our sample. However, the claim that an appropriate mixture of functional groups could be found in abiotically produced organics is fraught with problems that seem to have been overlooked by recent critics (Chyba & Sagan 1987a, b, c).

If a mixture of inorganic ices (including CH_4) is exposed to large doses of non-thermodynamic energy, a flood of free radicals is generated; such radicals proceed to recombine through channels that inevitably include a wide range of complex organics. Amongst these organics are found substances that possess spectra with varying degrees of resemblance to that of Fig. 2. A class of materials referred to as 'tholins' produced in this way was considered earlier by Khare *et al.* (1984) to provide a plausible material for cometary grains. Our own examination of this claim has, however, led to the result that the data points of Fig. 1 cannot be matched within the observational uncertainties: indeed the refractive index given for tholin leads to the poorest fit of all proposed organic constituents (Rabilizirov 1988).

Since the Halley data became available, Chyba & Sagan (1987a, b) have used yet another candidate material. They consider a residue formed by irradiating a "methane clathrate with a

200:1 H_2O:CH_4 occupancy ratio". The conversion efficiency into organics is reported to be ~ 10 per cent of C, thus implying that any organic residue formed in such a process cannot exceed 10^{-3} of the H_2O content. While clathrate-ice models in which a small fraction of guest molecules occupy holes in the ice lattice have been popular in the past, they cannot account for the 15–30 per cent CO and abundant CH and C seen in Halley's coma gases. Moreover the fraction of organic material produced in this manner fails by two orders of magnitude to account for the substantial fraction of organic grains detected in comet Halley, with mass fraction *at least* a few per cent of the gas (McDonnell *et al.* 1987).

The total flux of keV solar wind protons from the Sun intercepted by comet Halley in the course of a single orbit between 5 AU and aphelion is calculated at 4×10^{17} eV cm^{-2} [Chyba & Sagan (1987c), corrected by a factor of π], roughly 4×10^{22} eV cm^{-3} to the outer 0.1 μm-skin. Such a radiation dose delivered to the laboratory methane clathrate is found to transform and darken the material. However, a layer several 10^5 times thicker is lost from the surface each apparition. So Chyba & Sagan proceed to argue for the operation of irradiation processes in the early history of the solar system. Cosmic rays could transform the material to depths of some 10–30 m (Johnson, Cooper & Lanzerotti 1986), but it is accepted that comet Halley has lost much deeper surface layers during its many perihelion passages. If the irradiation hypothesis is to hold up, they are left with interior radio-nuclides or processing of the grains prior to accretion, both rather uncertain.

The presence of a strong 3.4-μm feature in comet Wilson discovered by Allen & Wickramasinghe (1987), which is similar to that of comet Halley, could also be used as an argument against the production of organics through cosmic ray or solar wind processing after the comet's accretion. For comet Wilson is a 'new' comet, entering the solar wind region for the first time along a near-parabolic orbit.

Notwithstanding these problems, the laboratory organic sample could of course be tested in relation to the data of Fig. 1 and compared with our own biological model. The solid curve in Fig. 3 is the 'best fit' found for tholin (Chyba & Sagan 1987b), but we note conspicuous deficiencies. First, the detailed fit to the observational curve near the 3.4–3.5-μm feature and also at 3.0–3.2 μm is considerably worse than for our bacterial model (Fig. 1). The jump at 3.50 μm reproduced by biological pigments or by irradiated *E. coli* is in the wrong sense in Fig. 3. The 3.40-μm peak of Fig. 3 is too high and worse placed than our 3.39-μm peak. Its profile fits badly to data at another date (Baas *et al.* 1986) when a peak near 3.36 μm appeared stronger. Neither model reproduces the shoulder at 3.26–3.30 μm, which could be separate emission from the C–H stretch mode in gaseous aromatics (Encrenaz *et al.* 1987).

Secondly, Chyba & Sagan have several arbitrary fitting parameters. Instead of the distribution of precisely calculated grain temperatures for the empirically observed grain-size distribution, they assume a single temperature of about 500 K. The total flux of radiation in their model comprises three components: (i) solar scattered radiation assuming the smooth guestimate of Wickramasinghe & Allen (1986) rather than detailed wavelength-dependence, (ii) a 350 K blackbody emission continuum unconnected with the 3.4 μm emission, much hotter than a physically real blackbody and (iii) the emission from the laboratory-type synthetic organic residue at 500 K. The Chyba–Sagan model does indeed appear to suffer from "an extravagant departure from Occam's razor" (Chyba & Sagan 1987a). Thirdly, the time variability of the 3.4-μm feature's relative strength may reflect variable organic to inorganic dust components (Wickramasinghe *et al.* 1986). Alternatively, to accord with changes in the shape of the feature (peak at 3.36 μm mentioned above) and our inference of evolving grains in other comets (Hoyle, Wickramasinghe & Wallis 1985), we prefer to interpret time variability as due to thermal processing of grains (Wallis *et al.* 1987a, b). The 0.1-μm grains with temperatures above 500 K (at 1.17 AU) lose some of their hydroxyl content while the C–H emission

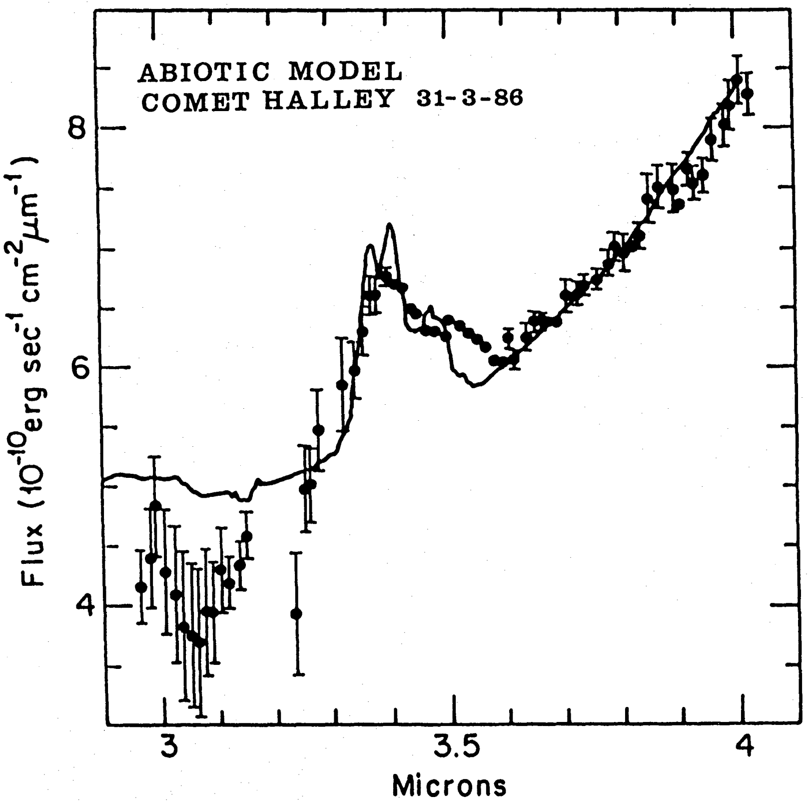

Figure 3. Calculations for the Chyba–Sagan organic residue plus additions of approximate components for background thermal emission and for scattering. The observational points are the same as for Fig. 1. The deviation below 3.2 μm is supposedly (Chyba & Sagan 1987b) due to OH absorption, though the gas coma is largely optically thin.

strengthens (Rouxhet, Villey & Oberlin 1979), but also move out of the coma more quickly following a burst.

At longer IR wavelengths, our organic material shows no strong features before the 9–10 μm ‘silicate’ peak, similar to the observational data. Fitting to the spectrum over the whole 3–30 μm region depends rather strongly on temperatures and on contributions of different grain types. Herter, Campins & Gull (1987) have produced a fit using an empirical interstellar spectral profile, but use of real material would be feasible and more useful.

Our final comment is that even if one could overlook the substantial fraction of N-compounds in comet Halley’s gas and dust (Clark, Mason & Kissel 1986), the existence of adequate quantities of the particular processed methane-ice on a cosmic scale must be in grave doubt. To find 10^{28} g of this rather specific organic mixture in the Solar System and 10^{40} g in the Galaxy stretches credibility. On the other hand, from our viewpoint material derived from bacteria would be as ‘common as muck’. As sure as life exists, its chemical material would also be present everywhere and in generally reproducible proportions with regard to the distribution of functional groups.

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