Sources of particulates in the upper stratosphere

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Abstract

The dominant forms of particles collected at altitudes of 39, 42 and 45km during three balloon flights over Australia were aggregates having components with diameters typically 40 to 50nm. Their partial electron transparency suggested an organic composition and all were accompanied by a volatile liquid that could be stabilised by reaction with a thin copper film. They closely resembled particles called “fluffy micrometeorites” collected earlier in the mesosphere from rockets and their properties were consistent with those of particles collected from a comet by a recent spacecraft experiment. Particles in the upper stratosphere included some that resembled viruses and cocci, the latter being one of the organisms cultured from upper stratospheric air in a recent experiment. A plausible source of the stratospheric, mesospheric and cometary aggregates is consistent with the ”panspermia” theory, that microorganisms present in space at the birth of the solar system could have reproduced in water within comets and brought life to Earth.

1. Introduction

Junge and Manson (1961) were the first to show that the layer of particles at about 20km known to be responsible for the “purple glow of twilight” was dominated by sulphate particles in volcanically quiescent times. Mossop (1965) carried this work a stage further by demonstrating that the sulphate particles contained insoluble inclusions or small groups of them, the components having typical diameters of 40 to 50nm. No elements were detected by X-ray analysis and no recognizable diffraction patterns were found, suggesting that the particles were organic or amorphous carbon. The source of these apparently carbonaceous inclusions in sulphate particles was not obvious. Murphy et al. (2007) using laser mass spectrometry of individual particles in the stratosphere up to a maximum altitude of 19km found that the proportion of carbonaceous particles decreased rapidly in the first three km above the tropopause and then very slowly to 19km. A limitation of the instrument was the very low detection efficiency for particles <220nm diameter so it would only have detected carbonaceous particles within relatively large sulphate particles. The inclusions represented a very small proportion of the total mass.

From 1968 to 1974 collections of particles were made at considerably higher altitudes over Australia and parts of USA to delineate the vertical extent of the particles of the sulphate layer (Bigg, 1975, 1976, 1984). Particles were impacted directly onto transmission electron microscopy (TEM) grids using carbon coated nitrocellulose collecting surfaces. In addition some of these grids had vacuum deposited thin films of copper, silver, nickel, aluminium or gold to examine chemical reactions of the particles with those metals. Particles consisting mainly of sulphuric acid, ammonium sulphate or bisulphate dominated the aerosol between 15 and 27km, although inclusions having a different transparency to electrons were often visible within them. Above about 27km particle numbers decreased rapidly and sulphate particles were not usually found at all above 32km. The particles remaining above this altitude were remarkably similar to those found by recoverable sounding rockets, for example by Hemenway and Soberman (1962), Hemenway and Hallgren (1968), Hemenway et al. (1968), Soberman et al. (1968). The most comprehensive collection of TEM photographs was shown by Farlow et al. (1970). Much more recent collections of particles from the upper stratosphere have been described by the Cardiff group. Harris et al. (2002) and Wickramasinghe et al. (2003) provided evidence that some of the particles captured were actually organisms such as cocci. Very careful protection against contaminants was used in those flights.

In this paper properties will be described of particles captured in the Australian upper stratosphere collections between 39 and 45km, their relation to previously published work and the implications of these comparisons.

2. Properties of particles collected at 39, 42 and 45km altitude

From 50 to 80% of particles appearing on the TEM grids were chain aggregates. The components of most of them were partially electron-transparent, had diameters of 20 to 60nm (median 40-50nm) and often showed angular corners suggesting a pentagonal or hexagonal structure. Although the junction between individual parts sometimes appeared frail, very few shattered on impact. A uniform coating on members of the chain ranged from slight to thick enough to make them roughly spherical. Examples are shown in figure 1.

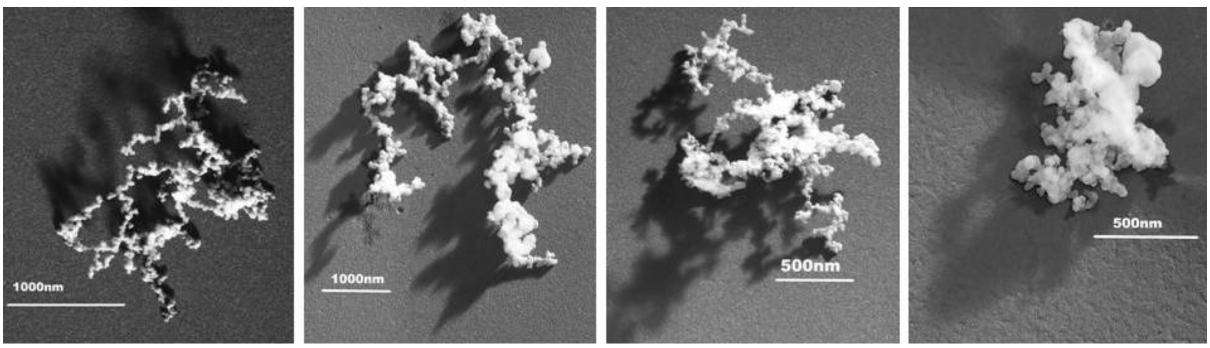

Figure 1. *Representative chain aggregates showing varying extents of coating material*.

In this and subsequent figures, electron dense areas appear bright. Application in a vacuum of a beam of gold/palladium alloy at an angle of about 26^{0} before examination yielded shadows twice as long as the height of the particles. In comparing particles found in these collections with those of the Cardiff group two factors have to be considered. The first is the method of collection; impaction was used in these samples and compact particles like that in the right panel could possibly spread out to appear as branched chains. Cryogenic sampling as used in the Cardiff collections would have disturbed the particles far less. The second difference is that the TEM representation is a shadowgraph while the SEM representation used in the Cardiff collections gave a three-dimensional picture of the particle.

The size distribution of the individual components of these aggregates is almost identical to that of the inclusions found within sulphate particles at 20km altitude by Mossop (1965). The implication is that many of the aggregates broke into smaller groups and acted as nuclei for the deposition of sulphate. Another apparent coincidence is that the size distribution of marine chain aggregates over oceans is also almost identical to it (Leck and Bigg, 2005).

In addition to particles like those of figure 1 there were small clusters or short chains of completely electron-dense particles, or individual spheres. These are likely to have been meteoric ablation products and will not be considered here. The morphology of the partially electron-transparent chains immediately raises the question of whether they were collected in the stratosphere or were inadvertent contaminants on the TEM grids. Whenever particles occur in high concentrations they aggregate into branched chains that may subsequently become folded into more compact forms. Soot particles derived from combustion in the form of chains, or balls of folded chains, are common in urban atmospheres or when forest fires are prevalent. Chain aggregates are also common in oceans and in the atmosphere over oceans (Bigg, 2007) and consist of viruses and cellular material from lysed bacteria. Those in the atmosphere have been carried aloft by bubbles bursting on the ocean surface. Their morphology and size distribution of the component particles more closely resemble those of the stratospheric chains than do those of soot particles. With these two sources of carbonaceous material in the lower atmosphere, there is certainly the potential for contamination of the TEM grids, even though these were loaded and unloaded in a cleanbench within a cleanroom. However, Wickramasinghe et al. (2003) using extreme precautions to avoid terrestrial contamination also found aggregates of carbonaceous particles collected at an altitude of 41km.

Within the sulphate layer a small proportion of particles was clearly of terrestrial origin, including large (mostly skeletal) rod-shaped bacteria and brochosomes (particles released by leaf-hoppers). No similar particles were found on the three highest flights, suggesting that air interchanges from the troposphere did not reach 39km. This is not surprising in view of the 50^{o}C temperature inversion between the sulphate layer and the stratopause at 50km.

There were two distinguishing features of the great majority of the upper stratospheric particles. One was the traces left of an associated volatile liquid that stained metallic collecting surfaces but left little impression on carbon surfaces. The other was the stabilisation of the associated liquid when collected on a thin film of copper. In every case a pool of liquid occurred where the chain touched the surface and often immersed it completely. Figure 2 shows three examples, the liquid being generally more extensive than the solid portions. The reaction with copper is quite different from the reaction noted with particles within the sulphate layer from about 15 to 25km altitude. There, circular holes in the copper resulted, leaving needle-shaped crytals of copper sulphate (or cuprammonium sulphate). In the high altitude collections, not only chain aggregates reacted in this way but all particles except those that were very electron dense (thought to be ablation products from meteors). Even particles smaller than 50nm diameter that would have been easily overlooked on a carbon surface usually had a similar liquid associated with them if collected on a copper surface .

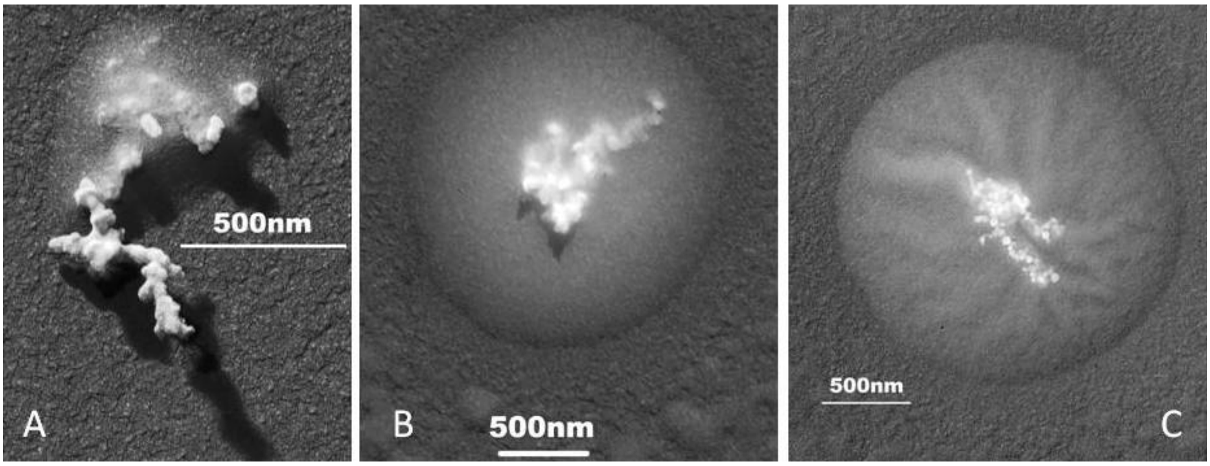

Figure 2. *Chain aggregates captured on a thin film of copper. The associated liquid was stabilised by reaction with the copper.*

Brownlee et al. (1968) described the formation of reaction areas on a much thicker (0.7µm) copper film by particles collected during a Gemini-12 manned space flight. The particles were far more numerous than those collected simultaneously on a gold surface and so were classed as some unknown massive contaminant. X-ray analysis of the reaction areas showed no elemental signatures other than copper and so were assumed to be copper oxide. They could equally well have been organic copper compounds. The similarity of reactions with copper of particles collected beyond the atmosphere to those collected in the upper stratosphere shows that the associated liquid had an extraterrestrial origin. It is possible that part of it evaporated on entry into the atmosphere and then recondensed at the mesopause.

In hindsight it would have been very useful to have made estimates of the absolute concentration of the chain aggregates. The very detailed examination of the TEM grids necessary to achieve this was carried out within the sulphate layer, but not at higher levels. At the time the much smaller number of particles found above the sulphate layer were not thought to be significant.

3. Comparison with particles collected in the mesosphere.

The mesospheric samples of particles obtained from rockets listed in the Introduction serve as a guide to whether particles in the upper stratosphere in the collections to be described were contaminants, came from below, or were falling in from the mesosphere. Farlow et al. (1970) provided the most comprehensive set of photographs of particles collected at altitudes above 60km. Since these were collected by impaction and examined with TEM they are completely comparable to those described here. Two types of particle were considered not to have been contaminants and they illustrated 30 examples of each. “Type 5” particles were aggregates having components of the order of 50nm diameter and were very similar to those described by Soberman (1961) as “fluffy micrometeorites” and also to those of figure 1. “Type 2” particles described by Farlow et al. fell within the range of particles other than semi-transparent chain aggregates found in the upper stratosphere samples considered here. Although morphology alone is not a reliable guide to properties, the remarkable similarity to those collected in the upper stratosphere makes it seem very likely that both have the same source.

4. Cometary dust and panspermia

Direct collection of dust from the comet 81P/Wild2 by the Stardust spacecraft has shown the presence of aggregates with a grain size that could not be resolved but was <100nm (Price et al. 2010). This is consistent with the predominantly 20-60nm grain size of the upper stratospheric or mesospheric aggregates. Complex organic compounds were also found in the Stardust samples (Clemett et al. 2010) as well as the amino acid glycine (Elsila et al. 2009). Amines react with copper in much the same way as ammonia or ammonium compounds to form stable complexes in the presence of water. If they are present in significant quantities in cometary dust, the reactions described here and in the Gemini-12 spacecraft collections (Brownlee et al., 1968) would be explained. The question of where the water and organic compounds might have come from and how compounds with low melting points, high vapour pressures or susceptibility to decomposition by ultraviolet light can survive in space or in the upper atmosphere will be considered in the next section.

Hoyle and Wickramasinghe (1981) proposed that microbes present in space at the birth of the solar system (“Panspermia”) could have reproduced in water trapped within comets and kept warm temporarily by the decay of radioactive isotopes. Comets could then have brought life to the Earth at an early stage of its history and may continue to provide an input of stored microorganisms through particles of insufficient mass to undergo significant heating. Wickramasinghe et al. (2003) were able to cultivate certain bacteria from the cryogenically sampled air. Providing that these had indeed fallen in from the mesosphere, the cometary source of life would be indicated. Their demonstration that viable cocci are present in the upper stratosphere suggests that these ought to have also been present in the Australian samples. Wherever bacteria exist, viruses are also present, so these should also be sought. One theory of the origin of oceans on the Earth is that the water was derived from comets (or protoplanets) in the early stages of the evolution of the solar system.

Marine viruses of the present day might therefore provide some insight into the morphology of those that could be present in cometary dust. Viruses in oceans are exceedingly numerous (about $10^{7}ml^{-1}$) and more numerous than bacteria by about a factor of ten. The most common forms of present day marine viruses have perimeters with hexagonal or pentagonal outlines, while the bacteriophage types have tails as well. An asymmetric hexagonal type is very distinctive, having two long sides in contact with a much smaller one and are therefore unlike inorganic crystals. Figures 3A, 3B show presumed airborne marine viruses collected near the surface over the Coral Sea. 3C, from the upper stratosphere samples has a very similar shape although coated with some semi-liquid material. Figure 3D is an enlargement of the components of the chain aggregate seen in figure 2C. The associated smooth coating has dispersed into a cloud around the chains and this has revealed the hexagonal and pentagonal shapes of some members of the chain. A reviewer has suggested that the particle of figure 3E has pili or flagellae and so is not viral. Experience with marine particulates suggests however that the protruberances are the tails of viruses embedded in a polysaccharide matrix. The strange particle in 3F resembles the top portion of a presumed microorganism described by Pflug (1984) in the Murchison meteorite (Type C).

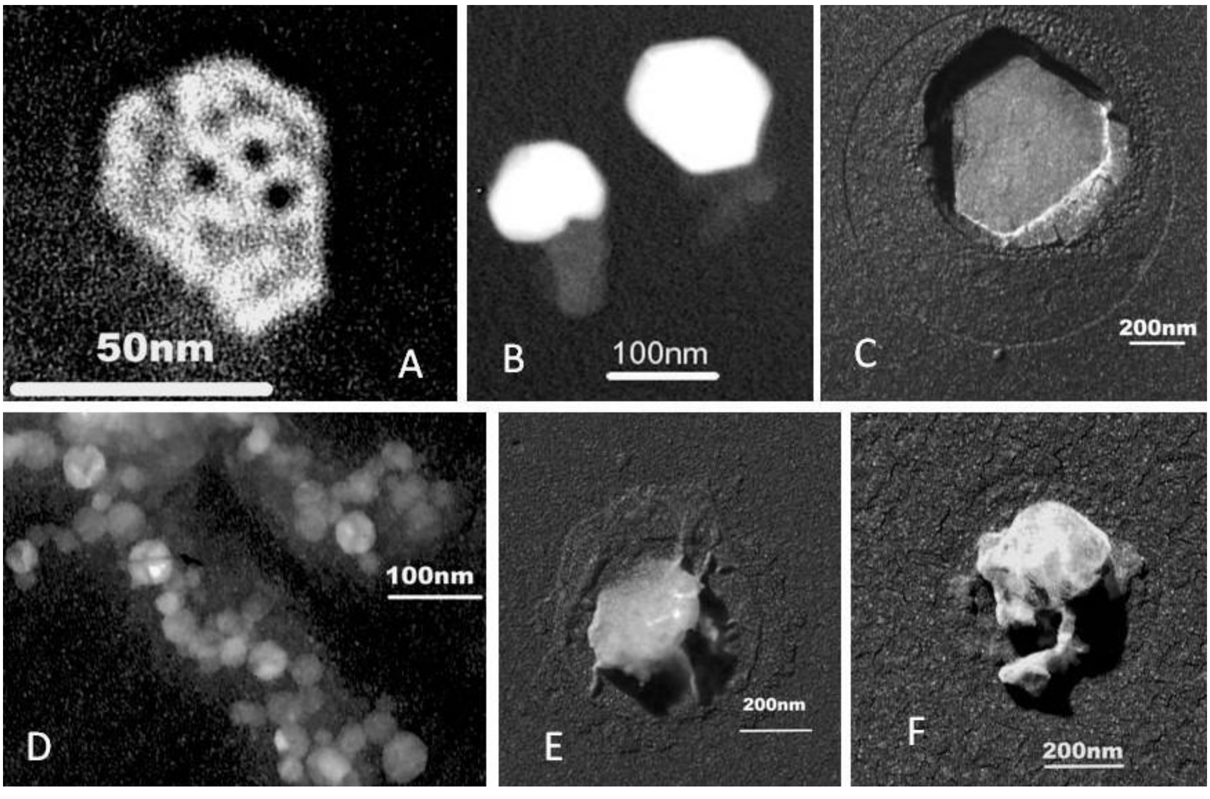

Figure 3. A, B: A*irborne present day viruses collected over the Coral Sea. C-E particles resembling viruses collected in the upper stratosphere*. F: *particle resembling the top portion of a suspected microorganism in the Murchison meteorite*

Bigg (1984, figure 7) showed a chain of egg-shaped or spherical particles captured in the upper part of the stratospheric sulphate layer that were surrounded by a small amount of liquid. It was suggested that they were cocci. As small proportions of tropospheric air are occasionally transported as high as that, there was a possibility that they were of terrestrial origin. This seems less likely following the work of Wickramasinghe et al. (2003). Farlow et al. (1970) also found apparently similar particles in the mesosphere (some of "Type 2"). Similar particles were obtained in the Australian flights at 39, 42 and 45km. Figure 4A shows a group of four, 4B a single nearly spherical particle having a hole in it. The particle of figure 4C has a hole in it that suggests it was a docking station for a virus resembling that of figure 3A. Holes like that in the particle of Figure 4B have been observed in TEM pictures of cocci and given the name "mesosomes" (Higgins and Daneo-Moore, 1972). They were subsequently suspected to be artefacts due to dehydration in the electron microscope but are nevertheless distinctive features not observed in other particles.

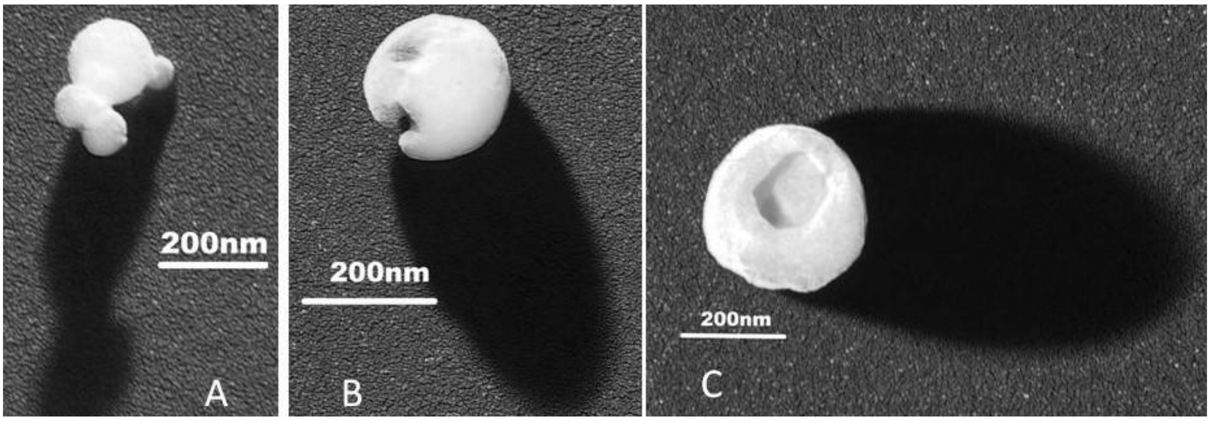

Figure 4. *Coccus-like particles collected above 39km*

It therefore seems likely that they were indeed cocci. Rod-shaped terrestrial bacteria are common in the troposphere and to a lesser extent in the sulphate layer of the lower stratosphere. Their absence on these high altitude flights reduces the possibility that the cocci were contaminants. Also forms like those in figure 4 appear to be greatly over-represented in the upper stratosphere samples compared to those in the troposphere.

5. Implications of the chain aggregate forms of extraterrestrial particles

The Stardust spacecraft collections have shown the presence of aggregates of small partly or wholly organic particles. The question then arises: how did these aggregates form within comets? Accepting the Hoyle and Wickramasinghe (1981) model of a comet having an originally warm watery interior in which microorganisms could replicate, consider what particulates would result. If bacteria were present, it is very likely that viruses would have been present in greater numbers. The latter would numerically dominate the particulates in the water, together with cellular material from the bacteria that they destroyed. When the concentration of small particulates in the water became sufficiently high they would aggregate in the form of branched chains that could fold to form more compact forms. Although the amount of water in any one comet would be far less than in a terrestrial ocean, this is irrelevant to the formation of aggregates – it is simply the concentration of particles within the water that is important. The aggregates should therefore closely resemble those found in present day biologically productive oceans and held together with bacterial exopolymers. Decho (1991) has described the remarkable properties of these exopolymers that consist mainly of polysaccharides. They are like sponges, consisting of 99% water which is not readily given up, often surviving in the vacuum of the electron microscope (Bigg, 2007). Another property is that they readily bind organic compounds such as proteins, peptides and amino acids.

Two examples of oceanic aggregates are shown in figure 5.

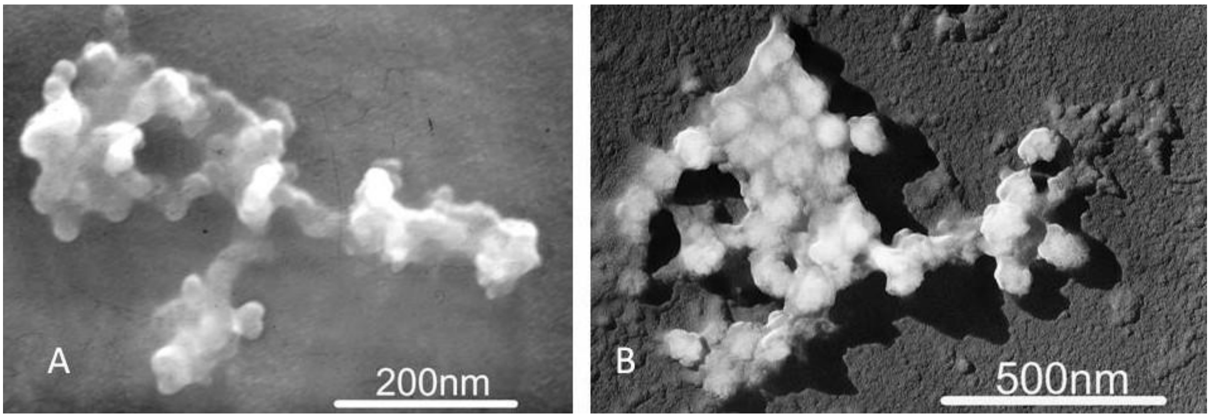

Figure 5. A: *A chain aggregate collected in air near the surface of the central Arctic Ocean in summer.* B: *A chain aggregate collected over the Southern Ocean in spring , surrounded by exopolymer material that has not lost its water.*

Disregarding the coating of exopolymer material, the median component diameters are very similar to those of the particles of figure 1. This is probably not just coincidence but due to the similar nature of the building blocks. Although subject to cleavage by ultraviolet light, exopolymers are otherwise very stable compounds and if protected within compact aggregates could survive exposure to UV and would provide a source of water for the observed reactions with copper. The complex organic compounds detected in the Stardust collections could be explained by their partial degradation.

6. Conclusions

The new observational feature of this work is the reaction with copper of particles in the upper stratosphere that indicates the presence of ammonium compounds or amines together with a source of water. The similar reaction observed by Brownlee et al. (1968) on a manned space flight provides an additional link between extraterrestrial particulates and those of the upper stratosphere. The hypothesis offered to explain the presence of particulate aggregates in cometary dust revealed by the Stardust spacecraft collections and their atmospheric counterparts invokes the Hoyle-Wickramasinghe (1981`) “panspermia theory”. It concludes that the morphology, size distribution of the component particles of the aggregates, the presence of bound water and complex organic compounds would be explained if they were derived from thriving bacterial and viral colonies in a watery medium within a comet as proposed by that theory.

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