Aerosols at altitudes between 20 and 37 km

By E. K. BIGG, A. ONO[1] and W. J. THOMPSON, *Division of Radiophysics, C.S.I.R.O., Sydney, Australia*

(Manuscript received February 10, 1970)

ABSTRACT

The physical appearance, size distributions and concentrations of particles impacted on electron microscope grids at altitudes between 20 and 37 km in the course of 17 flights extending over 14 months are described. It is concluded that many of the particles consist of sulphuric acid with varying degrees of ammoniation, which is least at the lower levels. Many particles at the higher levels had liquid or semi-liquid coatings and contained inclusions which are probably micrometeoritic. It is concluded that the coatings arise from reactions near the mesopause. There was little variation of median diameter with altitude in the range investigated, equivalent sphere diameters being estimated at 0.1 to 0.4 μ. Concentrations, expressed in numbers per cubic centimetre reduced to sea level pressure and temperature, ranged from 2 to 8 (uncorrected for collection efficiency) in the height interval 27 to 37 km, but were significantly less between 24 and 27 km and much more variable below 24 km. There is evidence of the loss of volatile constituents which may have led to an underestimate of particle diameters or concentrations.

Introduction

The existence of a relatively high concentration of large particles in the lower stratosphere was first demonstrated by direct collection by Junge, Chagnon and Manson (1961) and Chagnon and Junge (1961). The predominant detectable element which they found in particles collected by impaction during the ascent of balloons was sulphur. They assumed it was present in the form of sulphate and speculated that ammonium or sodium were the most probable cations associated with it. Further collections made from high-flying aircraft (18 km) and described by Junge & Manson (1961) confirmed the results and led them to suppose that ammonium sulphate was directly involved but that there was an excess of sulphate over ammonium. From the combined experiments they concluded that this stratospheric sulphate layer was world-wide and at much the same altitude everywhere and that maximum concentrations were very similar everywhere, about 100 l^{-1} of particles >0.1 μ diameter.

Friend (1961), Feely et al. (1963) and Friend (1966) reported further evidence of the composition of these particles showing that they were sometimes ammonium sulphate, sometimes ammonium persulphate and at other times mixtures of the two. Size distributions were slightly different from those given by Junge and his colleagues and concentrations were more varied, having a median value of 66 l^{-1} at about 18 km. This is equivalent to about 0.8 cm^{-3} at sea-level pressures.

Mossop (1963, 1965) using an aircraft flying at 20 km and fitted with probes like those used by the above authors, found similar concentrations of 40 to 90 l^{-1} in 1963 and 17 to 42 l^{-1} in 1965. These are equivalent to 0.7 to 1.6 cm^{-3} and 0.3 to 0.7 cm^{-3} at sea-level pressure. His electron microscope photographs showed far more detail than those in the earlier works and illustrated the curious, eroded appearance of some of the common particles. His most important contribution was to show that each sulphate particle contained one or more insoluble electron-dense inclusions. Size distributions obtained for the sulphate particles agreed with Friend's. In another paper Mossop (1964) described the very marked changes in the stratospheric aerosol which followed a major volcanic eruption in 1963. A year after the eruption predominantly liquid particles

[1] Present affiliation: Meteorological Research Institute, Tokyo, Japan.

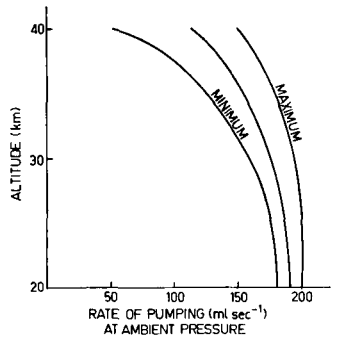

Fig. 1. Performance of pumps used for high-altitude sampling.

were collected instead of the squashy solids typical of the pre-eruption period.

Our aim in this paper is to present considerably more detail of the physical appearance as seen in an electron microscope of stratospheric particles collected from a wide range of high altitudes as a background for studies of their origin, growth, fallout and meteorological importance.

Equipment

The Australian Department of Supply releases balloons and retrieves their payloads on a regular basis for the Fallout Studies Branch of the Health and Safety Laboratories of the US Atomic Energy Commission, from Mildura in Australia (latitude 34° S, longitude 142° E). Through the generosity of these organizations we have been allowed to carry up to about 20 kg of equipment on these flights. Our first successful particle collections were made in March 1968 and are still continuing.

For particle collection we have used a simple impaction system in which air is drawn through a 1 mm diameter hole, 1 mm below which is located a 3 mm diameter electron microscope grid. A solenoid operated vaccum pump (the "Reciprotor") was used because of its excellent low pressure performance, high flow rate, light weight, robustness and modest power requirements (50 W). It was turned on only when the balloon reached its constant altitude level and was turned off again before the payload was cut down. The collection surface was protected by a series of baffle plates from accidental contamination, which is particularly likely when the payload lands. Large particles which might destroy the thin nitrocellulose and carbon film on the electron microscope grid are lost in traversing this baffle.

Auxiliary equipment included a half-frame 35 mm camera which photographed the horizon in colour at 500 m height intervals during ascent. Its purpose was to find the height of greatest aerosol concentration and to study qualitatively the vertical distribution of light-scattering material.

Performance of the pump and impactor

The type of pump used achieves an approximately constant volume per second to an altitude of at least 25 km. Direct measurement of flow rates at atmospheric pressure is easy, but at very low ambient pressures is difficult. They were calculated instead from a knowledge of the differential pressure produced by the vacuum pump across the impactor at appropriate environmental pressures and the flow rate measured at atmospheric pressure of an air leak required to produce the same differential pressure across it at the same absolute pressure. Several pumps were used in these experiments and their performances at low temperatures may have been slightly different from those in laboratory tests. Fig. 1 shows the expected range of flow rates, for a 1 mm impactor aperture.

The impactor's collection efficiency may be estimated from the formulae given by Ranz & Wong (1952) for this type of sampler and verified experimentally by them. They give curves for collection efficiency in terms of a dimensionless inertial parameter:

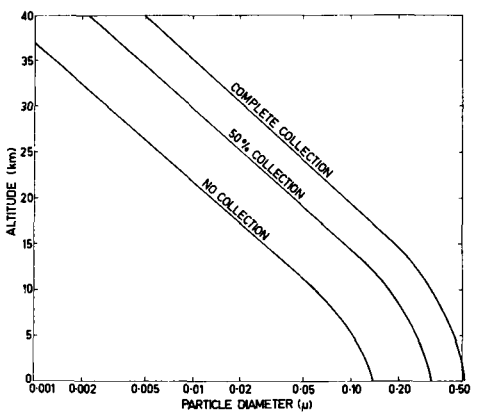

Fig. 2a. Collection efficiencies for particles of different diameters as a function of altitude.

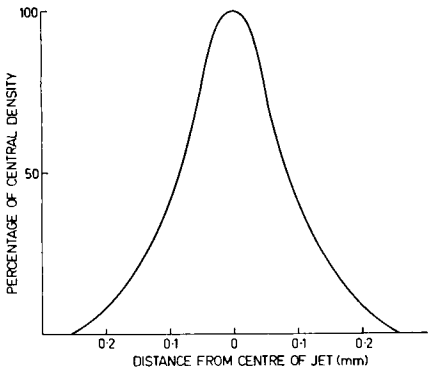

Fig. 2b. Distribution of particles larger than 0.1 μ diameter impacted at an altitude of 20 km.

$$\psi = C\,\varrho_p\,v_0\,D_p^2/18\,\mu\,D_c$$

where ϱ_p, D_p are particle density and diameter respectively, v_0 is the velocity of the air jet, μ is the viscosity of the air and D_c the diameter of the impactor's aperture. C is a factor dependent on particle diameter and mean free path, which assumes considerable importance at the altitudes in which we are interested.

$$C = 1 + \frac{2\,l}{D_p}\left[\left(1.23 + 0.41\,\exp\left(-0.44\,\frac{D_p}{l}\right)\right)\right]$$

where l is the mean free path.

Fig. 2*a* shows as a function of altitude the particle sizes which escape collection entirely, have a 50% chance of collection, or are completely collected.

The calculation is based on the assumption that the air velocity is simply the flow rate divided by the cross-sectional area. In fact, central velocities will be higher and peripheral ones lower leading to a broader spectrum of particle sizes for which there will be some capture.

Fig. 2*b* shows the way in which particles of diameter $\geqslant 0.1$ μ are distributed beneath the aperture. There is considerable size differentiation, the larger particles being found closer to the centre. This means that size distributions cannot be accurately estimated unless a cross-section through the impacted spot is taken. As we shall see, it is in any case rare in our experience for the particles to have a nature which allows much confidence in size distributions.

Photography of the Horizon

Photographs of the horizon taken at 500 m intervals as the balloon ascended showed that the light scattered from above the tropopause usually reached a maximum at about 16 km and at this altitude stratification of the aerosols in layers a few hundred metres thick was usually very clear. It was best observed with the camera looking within about 30° of the sun. Contrast between neighbouring layers was often great, as shown in Fig. 3, which is quite typical, except that layering is visible to a greater height (25 km) than usual. This photograph was taken at latitude 23° S on 11 November 1968 from an altitude of 30.6 km. Intense scattering between 13 and 17 km and in

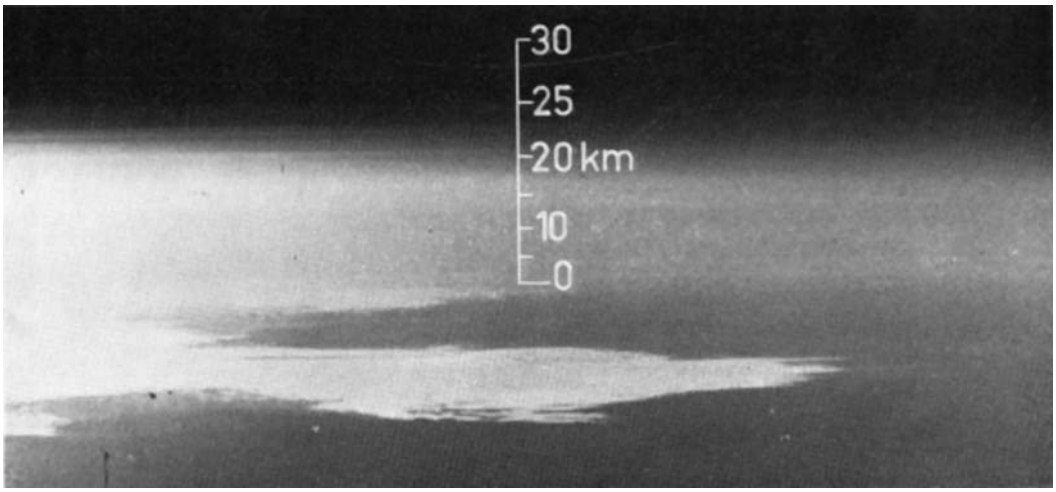

Fig. 3. Light-scattering layers photographed from an altitude of 30.6 km on 11 November 1968.

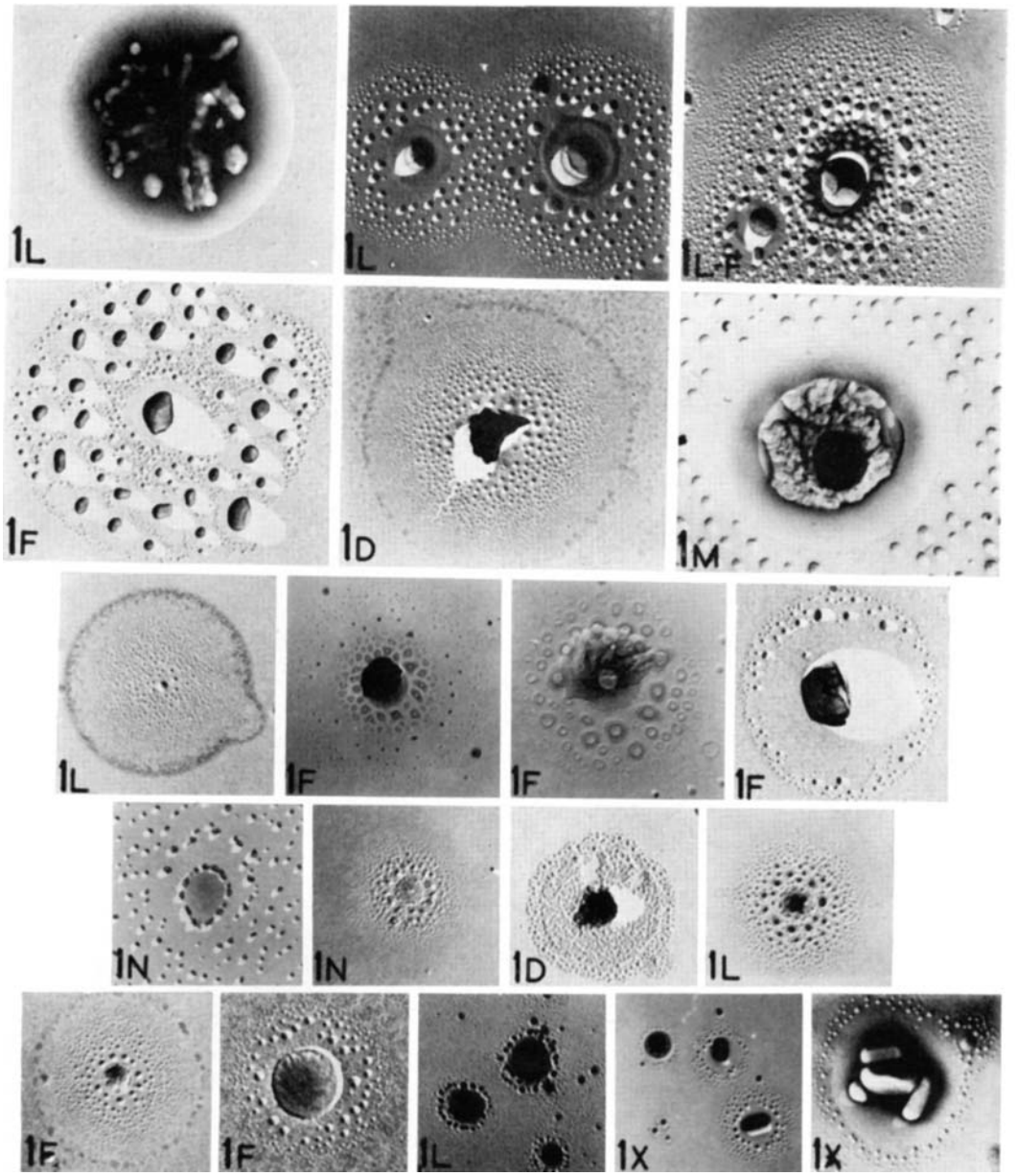

Fig. 4. Type 1: A circular group of small discrete satellites surrounding a central particle. Electron-dense areas appear black.

a thin layer at 21 km is readily visible on the colour original together with much fine detail.

The immediate lesson to be learned is that concentrations, size distributions or possibly even types of aerosols at any one level may be quite unrepresentative of the stratosphere as a whole. At altitudes above about 24 km, the lower absolute concentration of particles causes scattering to be barely detectable with the exposures we have used, but the different na-

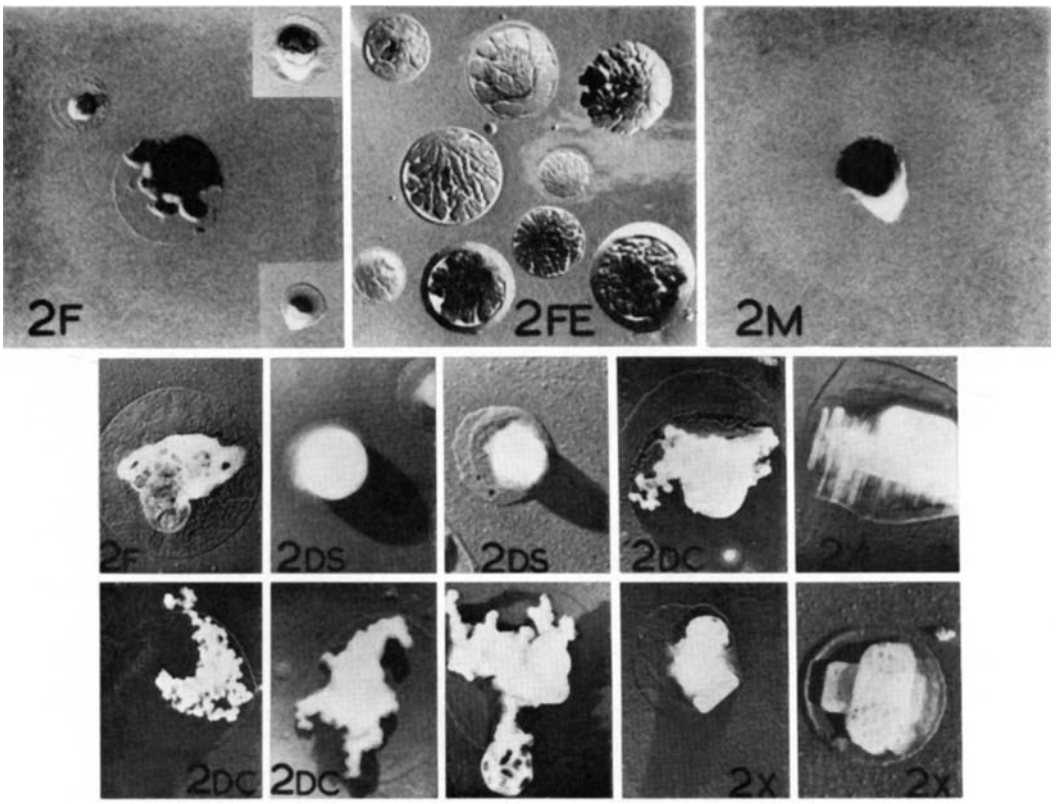

Fig. 5. Type 2: A central particle (or group of particles) surrounded by a continuous ring or stain. The smaller photographs have been reversed to make electron-dense areas appear white.

tures, sizes and concentrations of particles obtained on different occasions suggests that the conclusion is generally applicable.

Classification of Particles

In order to describe simply the nature of the particles collected, it is necessary to have some system of classification. Ideally this should be based on composition but, as this is not yet possible, we have based it on physical appearance in an electron microscopic examination. A carbon-coated nitrocellulose film on a copper mesh 3 mm in diameter formed the substrate for the particles. After exposure it was placed in a vacuum chamber in which a gold-palladium alloy was evaporated to form a thin film on it. The evaporated atoms arrived at an angle of 30° to the plane of the grid, so that elevated particles cast a "shadow" allowing their heights to be estimated.

Since much of the material collected was liquid or semi-liquid, its appearance was undoubtedly modified by impaction, storage, "shadowing" and examination.

Particles are classified into three types:

Type 1: A central particle surrounded by a circular group of smaller discrete satellites.
Type 2: A central particle surrounded by a nearly circular ring or stain but without discrete satellites.
Type 3: Simple particles without ring, stain or satellites.

The variety observed in types 1, 2, and 3 can be seen in Figs. 4, 5, and 6, in which overall particle diameters are of the order of 1 μ. Clearly a further subdivision is necessary and this is based on the appearance of the central particle. *L* denotes a liquid central particle (not applicable to type 2), *F* a flattened one, sug-

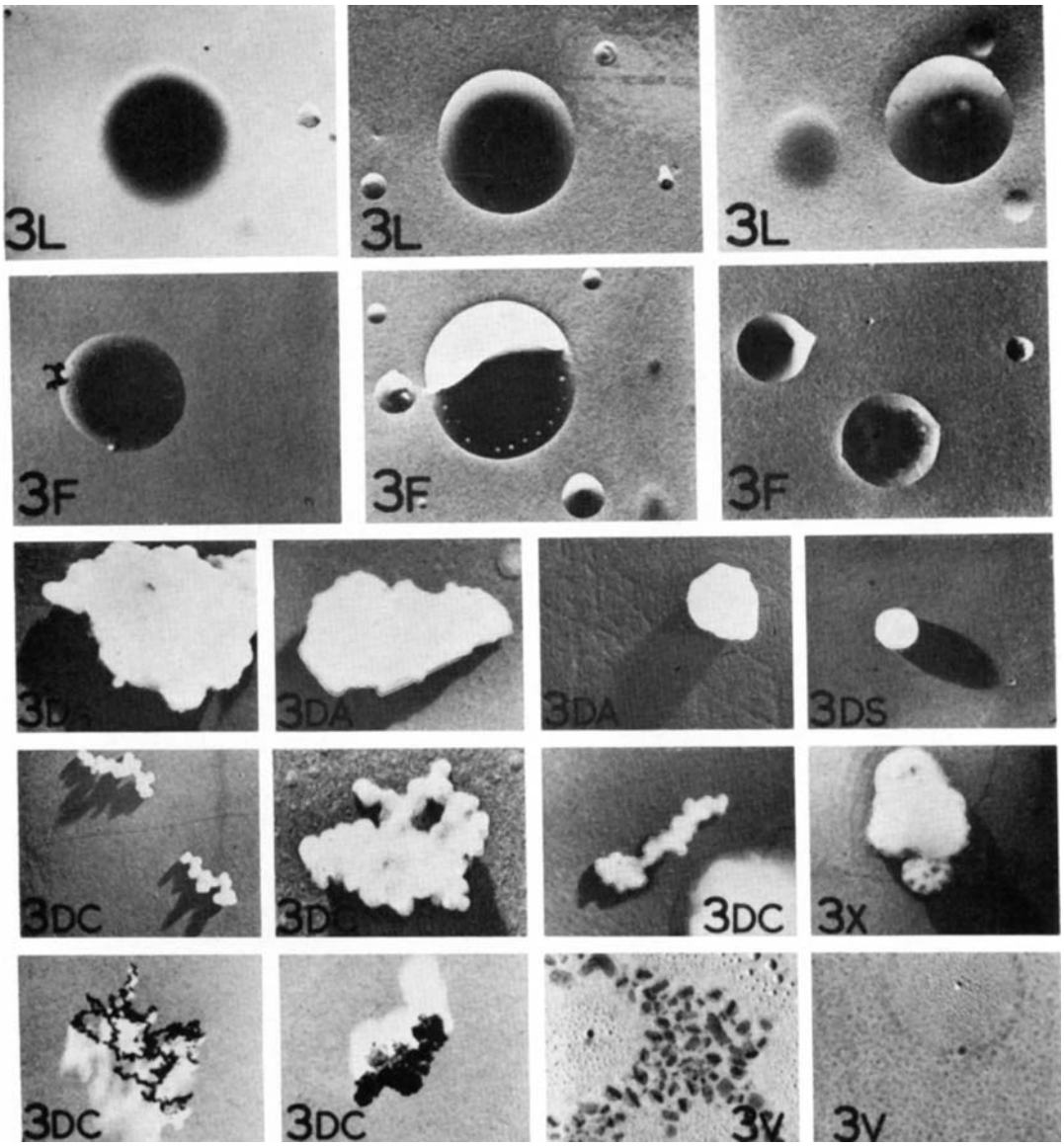

Fig. 6. Type 3: Particles which show no satellites, rings or stains. In the third and fourth rows electron-dense areas are white while in the remainder they are black.

gesting a squashy solid, and D an electron-dense nature, together with an appreciable vertical extent. (Some of the apparently liquid types which wet the surface are electron-dense so that this qualification is added.) M is applied to mixed central particles (not applicable to type 3). Special cases are: *no* central particle but a circular ring of satellites—type $1N$, a stain with no particle ($2N$) and a crystalline centre, types $1X$ or $2X$. A special and rather common variety of type $2F$ consisting of a flattened particle looking like an *eroded* landscape neatly framed in a smooth circular ring has been given the title $2FE$. Type $3D$ also needs further subdivision because of its three common and very different types. *Chains* of

small spheres are called $3DC$, single spheres, $3DS$, and *angular* irregular lumps, $3DA$. Often type $2D$ has so little liquid material that the nature of the central particle can be seen and the same subdivisions can be applied.

Volatile components

As well as the numerous particles with satellite rings, there are many indications of volatile components which condense on parts of the grid not occupied by captured particles, or on the perimeters of type 1 particles.

A common form, shown in Fig. 6 and called type $3V$, has a semi-crystalline appearance and because it is sometimes found in greater numbers after electron beam examination of nearby areas, it is assumed to be due to recondensation of material evaporated in the electron beam. On the other hand some of these marks could be the residue of particles collected at altitude which have subsequently evaporated. They have never been found to cast a shadow. Another common form is a series of electron-dense dots around the perimesters of type 1 particles and an example can be seen in Fig. 4, row 3 column 1, and row 2 column 2. Sometimes these dots completely fill the spaces between particles suggesting the recondensation of an important constituent. None has ever been observed to leave a shadow, so that it is not clear when they were actually deposited. Occasionally more electron-dense patches are observed in type 1 satellite rings in a pattern reminiscent of electron diffraction spots. Their origin is also unknown.

Some of the stains observed with type 2 particles are faint but extensive, suggesting the spreading of some chemical which either reacted with the carbon substrate or altered its response to being shadowed with metals.

These observations imply that we may be considerably underestimating the number and sizes of the actual stratospheric residents. Some method of fixing the deposit as soon as it is captured is obviously desirable.

Contamination problems

Impaction on a small spot has one great advantage—material collected during the flight is concentrated almost exclusively on 10% of the total area of the electron microscope grid, so that particles outside the impaction spot give a good indication of what has been collected during handling, impact of the payload, or its recovery. Of course, there are always a few particles collected in flight and deposited outside the control spot by turbulence but they are always small compared to those in the centre. In none of the flights to be described has the central density been so low that the impaction area has been hard to find, although sometimes it has been too densely populated for accurate counting.

In-flight collection does not automatically mean that the particles are stratospheric in origin, since it is possible for the balloon and equipment above the sampler to shed particles collected elsewhere. We have on occasions, for example, found a few large spheres, and on one occasion with a leaking balloon, large numbers of them, which were electron-dense, had no rings or satellites and appeared transparent under an optical microscope. They were found to be polythene spheres used for lubrication of the balloon. On occasions when these were collected other type 3 particles must also be regarded with suspicion, but did not in fact appear to have been more numerous than usual. Any of the liquid or semi-liquid particles collected by the balloon or associated equipment are most unlikely to be released subsequently since their small sizes will ensure tenacious adhesion to the surface. The most probable forms of contaminant are therefore types $3DC$, $3DS$ and particularly $3DA$ which includes most terrestrial dusts. However, when type 3 particles are present which closely resemble the centres of simultaneously collected types 1 and 2 then it is a reasonable assumption that the former were also collected in the stratosphere.

Relation to previous work and identification

Electron microscope photographs of particles in the publications of Junge and his colleagues did not reproduce well so that classification of their particles within our scheme is difficult. The particles in Fig. 5, Junge & Manson (1961) appear to be mostly type $1L$. However, Friend showed recognizable type $1L$ and $1F$, $3DC$ and $3DA$ particles. Mossop's excellent pictures are mainly type $2FE$ (1963 and 1965) with one type $2M$. An illustration of the particles collected shortly after the Bali eruption showed type $2FE$, $1DA$ and $2DA$, while those collected a year later were almost exclusively type $1L$.

The nature of type $1L$ particles such as that

Table 1

Date	Altitude (km)	Types	%	Maximum diameter, μ		Median diameter, μ		Total concentration l^{-1}	
				Group	Sphere	Group	Sphere	Ambient pressure	760 mm pressure
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
13 March 1969	36.2	2*F*	60	2	0.7	1	0.3		
		2*FE*	15	2	0.7	0.9	0.3		
		2*D*	11	2	1.5	0.8	0.4		
		3*L*	5	3	0.8	1.1	0.3		
		2*X*	5	3	0.9	1.1	0.4	20	4 000
		3*DC*	2	4	0.8	1.5	0.4		
		3*DS*	1	0.5	0.5	0.4	0.4		
		3*DA*	1	4	3.5	2	1.5		
		3*F*	<1	—	—	—	—		
21 March 1968	36.0	3*V*	90	0.9	—	0.3	—	Excluded	
		2*F*	10	0.8	0.2	0.4	0.1		
		2*D*	1	6.0	1.5	0.5	0.2	40	8 000
		3*DA*	1	1.2	1	0.5	0.4		
		1*D*, 3*S*	<1	—	—	—	—		
11 Nov. 1968 (Lat. 23° S)	32.2	1*L*	100	1.5	0.3	1	0.2	40	5 000
21 May 1969	32.1	1*M*	70	2.5	0.4	1.2	0.2		
		1*D*	20	2	0.3	1.2	0.2	20	2 500
		1*L*	10	1.5	0.2	0.7	0.1		
14 Aug. 1968	31.9	2*D*	100	>4	—	>1.5	—	>20	>2 000
								Too dense in centre	
28 Mar. 1968	31.6	2*F*	50	2	0.7	0.4	0.1		
		2*FE*	30	2	0.7	0.7	0.2		
		2*D*	10	1.5	0.5	0.6	0.2		
		3*DA*	8	2	1.5	0.5	0.3	40	4 500
		3*DC*	<1	2					
		3*DS*	<1	0.4	0.4				
		1*D*	<1	1	0.4				
26 Mar. 1969	31.3	2*F*	50	0.8	0.2	0.3	<0.1		
		2*FE*	32	1.3	0.3	0.6	0.2		
		2*D*	6	0.7	0.2	0.6	0.2	45	5 500
		3*DC*	5	1.0	0.1	0.5	<0.1		
		1*N*	5	0.8	<0.1	0.5	<0.1		
		1*F*	2	0.8	0.1	0.5	<0.1		
5 Mar. 1969	27.2	1*F*	95	4	0.8	1.5	0.3	70	4 000
		1*X*	5	4	0.6	1.5	0.3		
17 Mar. 1968	26.7	3*V*	98	0.4	—	0.2	—	Excluded	
		2*D*	2	0.5	0.2	0.2	<0.1	>2	>100
		1*D*	<1	0.4	0.1	0.1	—	(centre torn)	
29 Nov. 1968	26.3	1*L*	97	4	0.7	2	0.3		
		1*F*	2	—	—	—	—	10	500
		1*X*	1	—	—	—	—		
1 Apr. 1969	24.7	1*D*	30	1.5	0.4	0.5	0.2		
		3*DA*	30	0.4	0.3	0.2	0.2		
		1*L*	20	1.3	0.3	0.5	0.2	10	400
		2*D*	15	0.5	0.3	0.3	0.2		
		2*X*	4	0.6	0.3	0.3	0.2		
		3*DS*	41	0.4	0.4				

Table 1 (*continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
8 Aug. 1968	24.2	1*L*	65	7	1	0.5	0.1		
(lat. 23° S)		1*D*	25	4	1	0.5	0.2	>150	>5 000
		1*X*	5	5	1	0.5	0.1	Too dense	
		3*DA*	5	1	0.8	0.2	0.1		
14 Nov. 1968	24.2	1*L*	60	2.5	0.2	1	0.1		
(Lat. 23° S)		1*F*	30	2.5	0.2	1	0.1	10	250
		3*F*	10	0.5	0.2	0.3	0.1		
6 Mar. 1969	24.1	1*F*	100	3	1.5	0.5	0.2	6	100
19 Sept. 1968	23.8	1*D*	30	1	0.4	Insufficient particles photographed			
		3*DA*	20	0.4	0.3	for reliable estimates			
		2*N*	20	1.5	—				
		2*D*	20	1.0	0.3				
		1*F*	10	0.3	0.4				
12 Aug. 1968	22.7	3*DA*	90	0.7	0.6	0.2	0.2	400	10 000
(Lat. 23° S)		1*D*	10	1.7	0.4	1	0.2		
7 Dec. 1968	20.3	1*L*	99	3	0.6	1.2	0.3	150	3 000
		1*X*	1	3	0.6	—	—		

in Fig. 4, row 1 column 2, has been well established in the literature as sulphuric acid, which is relatively common in polluted atmospheres. Frank & Lodge (1967) discuss this identification and an excellent photograph is also given by Lawther, Ellison & Waller [1968). Type 1*L*, 1*F* and 1*X* collected in the Antarctic atmosphere have been illustrated by Cadle, Fischer, Frank & Lodge (1968) and assumed by them to be sulphuric acid with varying degrees of ammoniation.

In recent flights we have exposed 4 grids simultaneously, and on one occasion when particle type 1*L* was common, one of the duplicate grids was kept in an ammonia atmosphere for 24 hours. There was a complete transition to type 1*F* of both central particle and satellites. This makes it fairly certain that the distinction between the two types is only the extent to which free sulphuric acid has reacted with ammonia. It also shows that the satellites are on the grid *before* vacuum shadowing.

Friend has commented on type 3*DC* which he has likened to a "bunch of grapes". Particles with a similar appearance are typical of combustion products (Lawther et al. show some good examples) and are frequently found at ground level in high concentrations. Many of those which we have caught at altitudes as high as 36 km are surrounded by liquid rings and have clearly acted as nuclei in the sulphating process. It therefore seems probable that products of meteor ablation or recombination assume this form, for if they were instead of tropospheric origin we would expect to find considerably greater concentrations of the flat, angular clay particles which are in general much more common in the troposphere.

Concentrations and size distributions

In estimating concentrations, we have assumed that in particle groups such as those of type 1 only one primary particle was responsible for the entire group. Type 3*DC* aggregates are also considered as only one particle. The volume sampled is known within reasonable limits from Fig. 1 as are sampling times, which are known accurately. An estimate of concentration may then be made from photographs of the central part of the deposit, using Fig. 2*b*. No correction has been made for collection efficiency.

Size distributions are much more difficult to assess. Friend assumed that all his flattened particles with diameters >0.4 μ had heights of 0.2 μ, while Mossop assumed that they were discs with heights one-seventh of their diameter. Ours were generally less well behaved and many of them were too flat to cast measurable shadows, even with low angle shadowing. Those which did, resembled spherical caps rather than discs. Because our grids were rarely flat the shadowing angle was variable and a measurement of height required the presence

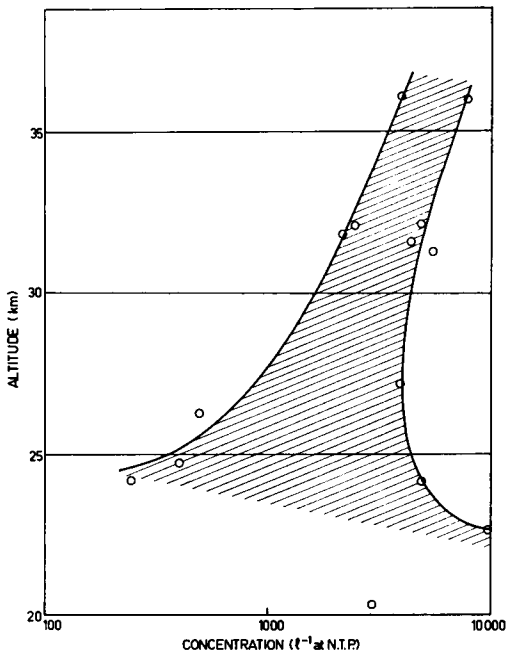

Fig. 7. Particle concentrations estimated on each flight. The apparent increase with altitude is partly due to the improved collection efficiency of the impactor.

of spherical or nearly spherical particles in the vicinity. For particles of the common type, $2FE$, the height was found to be typically one-tenth of the diameter. Assuming a spherical cap the diameter is then three times that of the equivalent sphere. This conversion factor is twice that used by Mossop, but because of the large spread in flattening that we have found and the fact that our impaction velocities and collection altitudes were higher, there is not necessarily any inconsistency here.

A conversion factor was guessed for particles whose heights could not be measured, by comparison with the most similar particles whose heights had been measured. Obviously there is scope for an error of a factor of two in the estimate of the equivalent sphere's diameter.

For particles of type 1 it was assumed that all the satellites were originally part of the central particle and the possibility of evaporation ignored.

Results of Particle Collections

In Table 1 the local dates of each flight and the mean altitude of collection (usually there was very little variation during sampling) are given. The types of particle according to our classification scheme and a rough estimate of the percentages of each are then given. Two measures of maximum and median diameters are then given; the latter is calculated by ignoring particles for which the collection efficiency of the equivalent sphere is less than 50 %. The first measure gives the diameter of satellite ring (type 1) or stain (type 2) or long dimension (type 3) and the second the diameter of the equivalent sphere as described above. Concentrations (number per litre) are given for ambient pressure and temperature and also sea-level pressure and temperature. The latter is more useful for comparing concentrations at different levels, and for comparison with previous work.

Discussion of Table 1

The median concentrations which we have found are quite similar to those reported by others at 20 km but their variability is greater. Since our samples were collected at constant altitude following almost the same parcel of air while the others were made from aircraft over long flight paths, this result is to be expected in view of the observed complex stratification. To make the results clearer, the concentrations (normalized to sea-level conditions) are plotted in Fig. 7, where each flight is represented by a point. Rough limits of concentrations are indicated by the shaded region. The apparent concentration increase with altitude can be partially accounted for by the increasing efficiency of collection of small particles with increasing altitude. Note the apparent decrease in variability of concentrations with increasing altitude.

Free sulphuric acid appears to have been more common at lower altitudes. Of the eight collections obtained from below 26.5 km type 1 particles formed the majority in seven, while of the nine higher samples they dominated in only three and were virtually absent in the two highest flights. There is a possibility of seasonal bias in this result, since six of the nine highest flights were in the month of March.

Perhaps the most important collection was that of 13 March 1969 obtained at an altitude of 36.2 km. It contained not only the most diverse set of particles that we have obtained

but included many liquid particles in which the electron-dense nucleus could be clearly seen. Examples are included in Fig. 5, rows 2 and 3 and Fig. 6, rows 3 and 4. It is almost certain that these particles were collected at altitude for there were none away from the impaction spot and no indication of contamination from the balloon. Because of their relatively large size and the altitude it is also almost certain that they did not diffuse upwards from some lower altitude. We are therefore looking at either the material of which micrometeors are made, or the ablation or recondensation products of large meteors. In a few cases the electron-dense inclusions are crystalline and these might instead be reaction products.

Now these particles and their liquid or semi-liquid coatings, some of which by analogy with Mossop's identifications are ammonium sulphate, pose new problems. At what levels did the coatings originate? Because the temperature increases quite rapidly between 36 km and 50 km, the mixing ratio of any substance with an appreciable vapour pressure and near saturation would have to be unreasonably high to allow direct condensation. The main possibilities appear to be: (1) adsorption of sulphur trioxide followed by reaction with ammonia; (2) a meteoric input of ammonium sulphate, or its constituents. In the first case, residence times increase rapidly with decreasing altitude so that most of the coatings would be expected to occur near the level of collection. However, there is little evidence of a diminution in coating thickness with increasing altitude in the collections described, which would be a necessary consequence of this hypothesis.

Nature and Origin of the Particles

Existing theories of their origin

Junge, Chagnon & Manson (1961) suggested that oxidation of sulphur-bearing gases diffusing upwards from the ground formed sulphur trioxide and the intervention of water vapour and ammonia led to the observed ammonium sulphate particles. Martell (1966) produced a different interpretation, supposing instead that the sulphate formation took place in the troposphere and that the particles were then carried into the stratosphere by air interchange. They were trapped in this region, in just the same way as is debris from nuclear explosions, by the lack of efficient removal mechanisms.

The occurrence at all altitudes up to 36.2 km of similar particles to those found at 20 km is strong evidence against Martell's theory, for appreciable upward transport is unlikely in this region and a normalized concentration such as we have found which is at least stationary and possibly increasing with altitude is quite impossible for a source at lower levels. We shall therefore consider exclusively the possible chemical reactions which may be involved, although recognizing that Martell's theory may account for part of the aerosol below the heights where we have collected our samples.

Chemical reactions in the stratosphere

Reactions which do not involve atomic oxygen or ozone, such as those between sulphur dioxide and ammonia as considered by Scott, Lamb & Duffy (1969), are more likely to occur in the temperature minimum nearest the source of the gases—that is, near the tropopause, than in the higher stratosphere and are therefore probably irrelevant to particle formation in the altitude range which we have considered here.

The wide range of particle types which we have found, and Friend's identification of ammonium persulphate as a major constituent of the aerosol, suggests however that Junge, Chagnon & Manson's theory needs some further elaboration.

Cadle & Powers (1966) showed that the reaction of sulphur dioxide to sulphur trioxide would occur with ground state atomic oxygen rather than with ozone as Junge had assumed. They suggested that the balance between increasing amounts of atomic oxygen and decreasing amounts of sulphur dioxide as the height increased might be one cause of the observed stratification of the particles.

While the concentration of sulphur dioxide in the stratosphere is unknown, it is unlikely that the mixing ratio will be very much higher than in the troposphere, where on an average it appears to be much less than one part per million. Vapour saturation requires a minimum SO_3 concentration of about 100 ppm. Thus particle formation must take place through adsorption on existing particles, reaction with adsorbed water vapour to form sulphuric acid

and further adsorption. The vapour pressure of sulphuric acid has not been recorded at low temperatures, but by extrapolation will be considerably less than that of ice, so that in its cooler regions the atmosphere may be saturated with sulphuric acid vapour. Probably the existence of free sulphuric acid to an altitude of 32 km suggests near-saturation at the appropriate temperature (about $-35°$).

Consequences of the presence of persulphate

Friend's identification of ammonium persulphate (also known as peroxydisulphate) as the main constituent of the collected aerosol on several occasions complicates very considerably the range of chemicals which may be important. If its formation proceeds by way of persulphuric acid, then the reversible reaction products, peroxymonosulphuric acid (Caro's acid, H_2SO_5) and hydrogen peroxide, are also likely to be present. The ammonium compound itself is subject to hydrolysis, particularly in the presence of metallic ions, and possible products include ammonium bisulphate (NH_4HSO_4), hydrogen peroxide, ammonium peroxymonosulphate ($(NH_4)_2HSO_4$), ammonium sulphate, nitric and sulphuric acids. It is interesting to note that Murcray et al. (1968) claim to have identified nitric acid by a spectral feature at an altitude of 30 km.

All of the compounds mentioned should be stable at stratospheric temperatures (except perhaps to photolysis) and with the possible exceptions of nitric acid and hydrogen peroxide to have low enough vapour pressures to exist in particulate form for appreciable times.

Although early literature claims that sulphur tetroxide could readily be formed in a glow discharge in a sulphur dioxide–oxygen mixture, Wannagat & Schwarz (1956) have shown that it can exist only in polymer form. They also state that the properties usually quoted for the tetroxide are in fact the properties of a mixture of this polymer and dinitrosyl disulphate ($(NO)_2S_2O_7$) which is formed when a trace of nitrogen is present. The ionic and atomic species expected in a glow discharge are not all present in the lower stratosphere but may be found in the lower ionosphere. If this compound should indeed be formed in the higher atmosphere, the various possible nitrosylsulphuric acids will complicate the chemistry even further.

RELATED OBSERVATIONS

Two types of cloud are observed in the stratosphere. Both are seen only when the atmosphere below them is dark and both are relatively rare. The majority of reports have come from high northern latitudes but a few from high southern latitudes suggest that this may be due to the distribution of observers.

Noctilucent clouds

The higher of the two types, noctilucent clouds, occur almost exclusively in the polar summers near an altitude of 80 km. Their relatively rapid formation suggests condensation, and since the temperature at 80 km in the polar summer is often lower than anywhere else in the atmosphere at any other time, condensation of water vapour has remained a popular (though not the only) explanation.

Hemenway, Soberman & Witt (1964) have published photographs of particles actually captured with the help of a rocket in a noctilucent cloud display, which show rings of satellite particles which they originally attributed to water. However, the photographs on pages 98, 101, and 108 of this reference are quite clearly indistinguishable from some of our type 1*D*, 1*M* and 3*D* particles respectively. Skrivanek (1966) has already come to the conclusion that sulphuric acid is probably involved, both because of the appearance of the particles and the fact that sulphur was the only detectable element in a direct analysis of these particles.

This suggests that the particles which we have observed above about 25 km could have received their coatings at the mesopause. Such particles are probably present there all the time but exceptional circumstances are required for them to become large enough or numerous enough to form a visible cloud.

Mother-of-pearl, or nacreous, clouds

According to Hesstvedt (1957) these wave clouds, which show brilliant iridescence and occur only in the late winter at high latitudes are formed only in the altitude range 17 to 30 km, with a most frequent height of just over 20 km. They must therefore incorporate the type of particles which we have described. Some excellent colour photographs have appeared in the journal *Weather* (*19*, 117, 1964), and Hallett (1967) has attempted an explana-

tion in terms of the condensation of sulphur trioxide and its conversion to sulphuric acid droplets. Since this is precisely the altitude range in which we find free sulphuric acid his theory is supported by our collections. However, as we have pointed out, the direct condensation of sulphur trioxide from a saturated vapour would require an improbably high concentration and a combined adsorption–reaction process seems more likely. The windward edges of some of the clouds are so sharply defined that it is hard to imagine that direct condensation is not involved. Perhaps some of the unknown relatively volatile substances which we have collected are responsible.

Meteorological Importance of Stratospheric Particles

This work was initiated because there was some evidence that a significant proportion of ice nuclei (i.e. particles having the property of producing ice crystals in a supercooled cloud) was of stratospheric origin, as described by Bigg & Miles (1962). We have since found the ice nucleus concentrations in the stratosphere to be highly variable, probably because of the extent to which the particles have been involved in chemical reactions. However, the possibility is still open that air interchange between stratosphere and troposphere leads to natural cloud seeding.

The free acid and sulphate particles, too, could play a part in cloud microphysics under special conditions since they should be very active condensation nuclei. Their contribution is probably outweighed by aerosols of tropospheric origin except near regions of air interchange.

Water vapour measurements in the stratosphere

Measurements of water vapour in the stratosphere made by keeping a deposit of frost in equilibrium on a cooled substrate make the assumption that there are no other condensible vapours which might interfere with the result. The existence of free sulphuric acid on particles up to about 30 km shows this to be a dubious proposition, for the acid has a measurable vapour pressure and would presumably evaporate from the particles if the atmosphere was not saturated with its vapour. Even sulphur trioxide is probably present in sufficient concentrations to condense at temperatures 20° below ambient, up to 25 km.

These considerations may account for the rather surprising increase in humidity from just above the tropopause to an altitude of about 25 km found by Sissenwine, Grantham & Salmela (1968).

Future Research

The obvious deficiencies in our work are: (1) a complete cross-section in altitude of particle types and concentrations would be far more informative than the fixed altitude collections which we have made; (2) identification of the chemical composition of the particles is lacking in most cases; (3) we have failed to ensure that volatile components have not been lost.

Starting early in 1969 we have rectified the first defect by installing an impactor in which electron microscope grids rotate beneath the impaction hole thus producing a continuous record of particles as a function of altitude. It is quite clear from the first results that very much larger particles are found just below the lowest collection level described here. Results will be presented in a later paper when sufficient have been accumulated.

The remaining problems still await solution but will have to be solved before a complete understanding of the nature and origin of the particles can be reached.

Acknowledgements

This work was only made possible through the wonderful cooperation of the "Hibal" balloon-launching team (then under the leadership of Mr Eric Curwood) and their sponsors, the Fallout Studies Branch of the Health and Safety Laboratories of the US Atomic Energy Commission and the Australian Department of Supply.

We would also like to thank Mr Cedric Shorey of the Sydney University Electron Microscope section, whose skill and interest in this project has resulted in so many excellent electron microscope photographs.

REFERENCES

Bigg, E. K. & Miles, G. T. 1963. Stratospheric ice nucleus measurements from balloons. *Tellus 15*, 162–166.

Bigg, E. K. & Thompson, W. J. 1969. Daytime photograph of a group of meteor trails. *Nature 222*, 156–157.

Cadle, R. D., Fischer, W. H., Frank, E. R. & Lodge, J. P., Jr. 1968. Particles in the Antarctic atmosphere. *J. Atmos. Sci. 25*, 100–103.

Cadle, R. D. & Powers, J. W. 1966. Some aspects of atmospheric chemical reactions of atomic oxygen. *Tellus 18*, 176–185.

Chagnon, C. W. & Junge, C. E. 1961. Stratospheric aerosols. *J. Met. 18*, 81–108.

Feely, H. W., Davidson, B., Friend, J. P., Lagomarsino, R. J. & Leo, M. W. M. 1963. Ninth quarterly report on "Project Star Dust". Isotopes Inc. D.A.S.A. 1309, Chapter 3.

Frank, E. R. & Lodge, J. P., Jr. 1967. Morphological identification of airborne particles with the electron microscope. *J. Microscopie 6*, 449–456.

Friend, J. P. (ed.). 1961. Final report D.A.S.A. 1300, Vol. 5.

Friend, J. P. 1966. Properties of the stratospheric aerosol. *Tellus 18*, 465–473.

Hallet, J. & Lewis, R. E. J. 1967. Mother-of-pearl clouds. *Weather 22*, 56–65.

Hemenway, C. L., Soberman, R. K. & Witt, G. 1964. Investigation of noctilucent cloud particles. *Tellus 16*, 84–117.

Hesstvedt, E. 1959. Mother of pearl clouds. *Geofys. Publik 20*, 1–29.

Junge, C. E., Chagnon, C. W. & Manson, J. E. 1961. Stratospheric aerosols. *J. Meteor. 18*, 81–108.

Junge, C. E. & Manson, J. E. 1961. Stratospheric aerosol studies. *J. Geophys. Res. 66*, 2163–2182.

Lawther, P. J., Ellison, J. McK. & Waller, R. E. 1968. Some medical aspects of aerosol research. *Proc. Roy. Soc. A 307*, 223–234.

Mossop, S. C. 1963. Stratospheric particles at 20 km. *Nature 199*, 325–326.

— 1964. Volcanic dust collected at an altitude of 20 km. *Nature 203*, 824–827.

— 1965. Stratospheric particles at 20 km altitude. *Geochim et cosmoch acta 29*, 201–207.

Murcray, D. G., Kyle, T. G., Murcray, F. H. & Williams, W. J. 1968. Nitric acid and nitric oxide in the lower stratosphere. *Nature 218*, 78–79.

Ranz, W. E. & Wong, J. B. 1952. Jet impactors for determining the particle size distribution of aerosols. *Arch. Ind. Hygiene and Occup. Med. 5*, 464–477.

Rosen, J. 1968. Simultaneous dust and ozone soundings over North and Central America. *J. Geophys. Res. 73*, 479–486.

Scott, W. D., Lamb, D. & Duffy, D. 1969. The stratospheric aerosol layer and anhydrous reactions between ammonia and sulfur dioxide. *J. Atmos. Sci. 26*, 727–733.

Sissenwine, N., Granthem, D. D. & Salmela, H. A. 1968. Mid-latitude humidity to 32 km. *J. Atmos. Sci. 25*, 1129–1140.

Skrivanek, R. S. 1967. Chemical composition of noctilucent cloud particles. "*Noctilucent clouds*", *International Symposium, Tallinn 1966*, pp. 135–139. Moscow.

Wannagat, U. & Schwartz, R. 1956. Zur Existenz eines monomeren Schwefeltetroxyds. *Z. anorg. Chem. 286*, 180–192.

АЭРОЗОЛЬ НА ВЫСОТАХ МЕЖДУ 20 И 37 КМ

Описываются вид, распределение по размерам и концентрации частиц, уловленных на решетку электронного микроскопа на высотах между 20 и 37 *км* во время 17 полетов, происходивших в течение 14 месяцев. Делается вывод, что многие частицы состоят из серной кислоты с различной степенью примеси аммиака, которая наименьшая на нижних уровнях. Многие частицы на верхних уровнях имеют жидкие или полужидкие оболочки и содержат включения, вероятно, микрометеоритного происхождения. Представляется, что эти оболочки возникают благодаря реакциям вблизи мезопаузы. Наблюдались лишь небольшие вариации медианного диаметра частиц с высотой в исследуемом интервале, причем пределы диаметров эквивалентных сфер оцениваются от 0,1 до 0,4 *мкм*. Концентрации, выраженные в числе частиц на $см^3$, приведенные к давлению и температуре на уровне поверхности моря, меняются от 2 до 8 (без поправок на эффективность сбора частиц) в интервале высот 27–37 *км*, но значительно меньше для высот 24–27 *км* и выявляют существенно бóльшие вариации ниже 24 *км*. Имеются указания на утери испаряющихся компонент, что может привести к недооценке диаметров частиц или их концентраций.