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Ammonium compounds in stratospheric aerosols

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ABSTRACT

The circumstances under which morphological examination can provide a reliable guide to the composition of stratospheric particles are discussed. It is then shown that while stratospheric particles often consist largely of sulfuric acid, there are occasions when ammoniated aerosols are present. This would be expected theoretically, for tropospheric-stratospheric air interchanges are known to occur and must inject both ammoniated tropospheric aerosols and ammonia into the stratosphere.

1. Introduction

Hayes et al. (1980) have shown that in stratospheric particles sampled from altitudes of 12, 15 and 18 km over California, only sulfuric acid was present. It was not stated how many flights were made, or on how many days. It is important to know whether this result can be generalized, because interpretation of remote-sensing signals from stratospheric aerosols depends on their refractive index, and this is different for sulfuric-acid/water solutions and those containing ammonium compounds.

Russell and Hamill (1984) reviewed the literature recently and concluded that all stratospheric particles contain mainly sulfuric acid. The purpose of this note is to provide evidence that the statement is often but not always true. While methods exist for specific determination of ammonium ion in mixtures, they have not been applied either to individual particles or to stratospheric aerosols over long periods. The morphological identification method described here is simple and direct but generally considered to be unreliable, for reasons given by Hayes et al. (1980). The causes of the unreliability are largely overcome in the experiments to be described because particles were collected on one surface from a wide range of altitudes and subjected to the same variations in temperature, humidity and ammonia before being "shadowed" in a vacuum chamber, which fixes the morphology. Differences in appearance then reveal differences in original composition.

2. Morphology of sulfuric acid examined in the electron microscope

It has been known for more than 20 years that sulfuric acid particles examined with an electron microscope have such a distinctive appearance that they are readily distinguished from all other common atmospheric particles. A circle of droplets usually graded in size surrounds a central larger droplet, the size of which increases as the acid concentration diminishes. The droplet "halo" only forms if the acid is subjected to an appreciable humidity after collection (Fig. 1a). If care is taken to exclude both water vapour and ammonia by covering the collected particle immediately with a cover smeared with strong acid, no rings form (Fig. 1b). Exposed to excess ammonia and 60% relative humidity for 1 h, the central particle develops crystal facets but the droplet rings are still present (Fig. 1c). Exposure to the much lower ammonia concentrations of laboratory air for 1 h produces almost identical droplet rings (Fig. 1d).

From this, it is obvious that the droplet halo forms so rapidly in the presence of water vapour that the simultaneous presence of ammonia is of

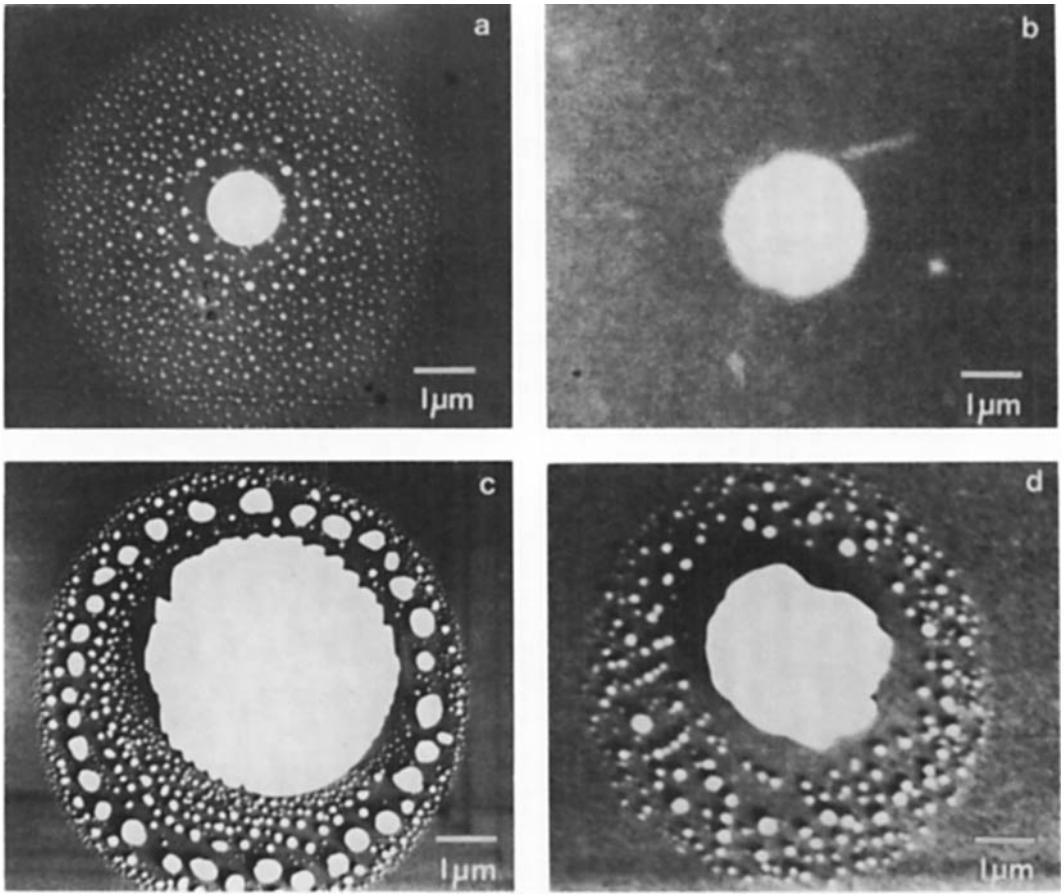

Fig. 1. (a) Sulfuric acid particle transferred rapidly from dry ammonia-free environment through laboratory air to vacuum chamber. (b) Similar particle transferred without exposure to water vapour or ammonia (c) Similar particle exposed to excess ammonia for 1 h before being transferred to vacuum chamber. (d) Similar particle exposed to laboratory air for 1 h before being transferred to vacuum chamber.

little consequence to the observed morphology. Thus, when incompletely sealed specimens collected in the stratosphere are returned to ground, the first encounter with tropospheric water vapour creates the halo. By the time they are examined, the central particle and all the droplets may have been completely converted to ammonium sulfate. While chemical analysis would have been highly misleading, the morphology still reveals the original composition.

Droplet rings are *not* formed when stratospheric sulfuric acid particles are present if: (1) the specimens are kept perfectly sealed until shadowed; or (2) the humidity rises above water saturation, causing the droplet rings to be engulfed, dissolved, and subsequently recrystallized. Particles without droplet rings can therefore only be used as a guide to original composition if there are also present some particles with them. This applies to 55 out of the 57 balloon flights made between 1968 and 1973 (Bigg, 1985).

The remaining indeterminacy is the possibility that outgassing of ammonia from the balloon, its payload or the impactor-housing influences the collected particles before water vapour is available to create the droplet haloes. Since in the great majority of flights, particles with small central particles and large droplet haloes were present on the same collecting surface, it is obvious that this is not an important inaccuracy.

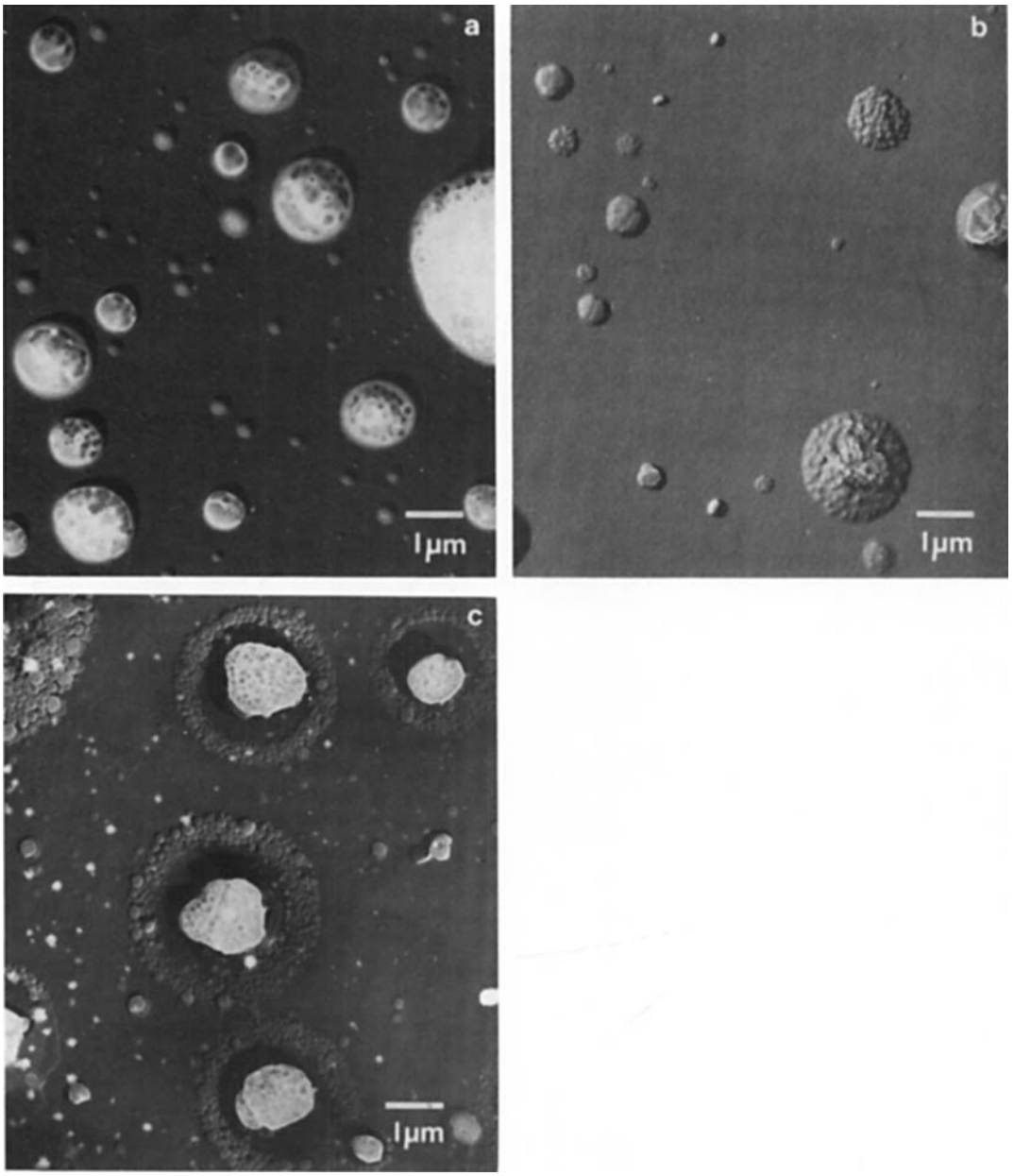

Fig. 2. Particles collected by sedimentation of evaporated droplets of solutions of: (a) ammonium sulfate; (b) ammonium bisulfate; (c) ammonium persulfate.

3. Morphology of ammonium compounds

Typical appearances of ammonium sulfate, bisulfate and persulfate particles prepared by impaction of atomized and evaporated droplets of solution are shown in Fig. 2. The sulfate particles are smooth and rounded, the bisulfate particles have an eroded appearance, while persulfate particles are surrounded by rings of flat disks around irregular flat central particles. Each is readily

destroyed by heating if the electron beam is intensified, giving the mottled appearance visible in Figs. 2a, c. The first two are quite frequently found in stratospheric collections while the third appears to be rare.

4. Results from 57 balloon-borne sampling missions over Australia, 1968–1973

In nearly all flights, the ratio of halo diameter to central particle diameter showed appreciable variations with altitude, indicating either a changing water content or a changing ammonia content. Two methods of examining the non-acid component of the particles were described by Bigg and Ono (1974) and by Bigg (1975). Toon et al. (1979) pointed out a discrepancy between them and, by claiming incorrectly that the methods and places of collection were the same, discounted both. There *is* a discrepancy; it was due to an inappropriate model used for calculating the mass of sulfuric acid involved in halo formation. Using the Gras and Ayers (1979) method for estimating it, we find that the two methods agree within the accuracy of the measurements.

At altitudes above 15 km, highly or completely ammoniated compounds were found at some altitude on 16 of the 57 flights. It is unlikely that the humidity at the collection level would have been high enough for the central particle to be simply very dilute sulfuric acid. In addition, of course, high humidity would normally be accompanied by high ammonia concentrations, since both originate in the troposphere.

5. Other records

Mossop's (1965) particles at 20 km (collected before the Mt. Agung volcanic eruption in 1963) were unequivocally ammonium bisulfate from their morphology, although on other later occasions typical acid particles were found. Friend (1966) also found particles with and without droplet rings. Junge et al. (1961) and Junge and Manson (1961), in the papers which first revealed the nature of stratospheric particles, also found particles with variable droplet rings. Gras (1978) described an event during which most stratospheric particles seemed to be ammonium sulfate.

These observations should now be given proper recognition. They do not represent varying amounts of contamination subsequent to collection of the particles but unequivocally illustrate the variable ammonia content of the stratosphere.

6. Discussion

This result should be no surprise. Tropospheric-stratospheric air interchanges are known to occur and tropospheric aerosols often consist wholly of ammonium sulfate. As the air is injected into the stratosphere during such air interchanges, both tropospheric particles and tropospheric ammonia will be added to the stratosphere. There will therefore be a patchy distribution of ammoniated and non-ammoniated aerosols, and this needs to be taken into account when interpreting optical signals that involve refractive index.

On the whole, my measurements support the concept of an aerosol often dominated by sulfuric acid, but Mossop's (1965) records from a period that appears to have been volcanically unusually quiescent, suggest that this may not always be the case. During future monitoring of the stratospheric aerosol by optical means, interpretation would be aided by direct collection of particles. While the methods used by Hayes et al. (1980) would be most suitable, they are also far more complex than those that I have used, and the latter may on occasions be more practical and the results unlikely to be misleading.

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