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Molecular state of sulfate aerosols in the remote Everest highlands

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ABSTRACT

For the selective detection of the sulfuric acid component in individual submicron atmospheric aerosol particles, a new *in situ* approach using a vapor-deposited calcium thin film as a reactive aerosol-collecting surface has been tested in field observations carried out in the remote Everest highlands.

It is found that in the remote Everest highlands, atmospheric aerosol particles in the submicron size range are mostly sulfate-containing particles in the form of a hydrated sulfuric acid droplet and/or in the form of a supersaturated acidic sulfate solution droplet at ambient relative humidity less than 15%. While the results to date are preliminary and indicative in nature, it would appear that there is a vertical stratification in the acidity of sulfate-containing aerosols in the troposphere.

1. Introduction

Studies of atmospheric aerosol chemistry by direct sampling and examination of aerosol particles individually with a transmission electron microscope (TEM) in conjunction with a vapor-deposited thin film of barium chloride have confirmed that sulfate is the dominant component of submicron tropospheric aerosols even in areas remote from sources of man-made pollutants such as the Nepal Himalayas (Ikegami et al., 1978, 1980), Antarctica (Bigg, 1980; Ono et al., 1981a) and over the oceans (Ono et al., 1979, 1981a).

Atmospheric sulfate-containing aerosols in the submicron size range are thought to be formed from the oxidation of sulfur-bearing gases in the atmosphere by gas-to-particle conversion; the primary molecular state of sulfate is hydrated sulfuric acid, which in turn is neutralized in part or wholly by atmospheric ammonia. Therefore, knowledge of the molecular state of sulfate aerosols in their airborne state, either hydrated sulfuric acid or its products in part or wholly neutralized by atmospheric trace ammonia, is important to understand the growth patterns and chemical evolution of sulfate aerosols that occur in the atmospheric portion of the sulfur cycle, and the environmental effects of them such as health effects of air pollution, atmospheric optics and acid rain.

Despite its widespread presence in the troposphere, the determination of the actual molecular state of sulfate contained in individual aerosol particles is still poorly defined.

In December 1980, the Japan Winter Everest Expedition led by Naomi Uemura provided the opportunity to study the nature and origin of upper tropospheric aerosols in the remote Everest highlands. Since the aerosol studies had to be carried out along with the main efforts to reach the summit of Mt. Everest, all equipment had to be portable enough to be carried on the backs of porters. Under these circumstances, we used a simple hand-operated single-stage impactor for direct sampling of aerosol particles; concentrated efforts were made to obtain the actual molecular state of sulfate contained in individual aerosol particles as they exist in the air by applying a vapor-deposited thin film of calcium as an aerosol-collecting surface.

In this paper, we show how the *in situ* selective determination of the sulfuric acid component contained in individual submicron aerosol particles can be obtained by a simple technique using a calcium thin film, based on the different hygroscopic behavior of sulfuric acid as compared to its

ammonium salts, and present new evidence concerning the actual molecular state of sulfate aerosols in the remote Everest highlands.

2. Method of approach

2.1. *Reactive surface for the in situ selective determination of the sulfuric acid component in individual submicron aerosol particles*

Until now, the molecular state of sulfate contained in individual submicron aerosol particles has been studied mainly by morphological examination of aerosol particles collected on a surface with a transmission electron microscope (Frank and Lodge, 1967; Heard and Wiffen, 1969; Mészáros and Vissy, 1974), and recently in conjunction with a vapor-deposited thin film of barium chloride (Ikegami et al., 1978; Bigg, 1980; Ono et al., 1981a).

In most of the traditional aerosol sampling, however, aerosol particles collected *in situ* on a surface were not examined until some time after their collection. Then, the possibility of the reaction of the sulfuric acid component with ambient trace ammonia on a collected surface during sampling periods and/or subsequent sample handling periods cannot be completely dismissed. Sulfuric acid aerosol, for example, may be modified to ammonium sulfate, as pointed out by Gras and Ayers (1979) and Hayes et al. (1980),

To avoid possible chemical modification of aerosol particles on the collected surface, there is a need to develop a direct *in situ* technique (other than that of particle morphology) to detect the sulfuric acid component.

As is well-known, there is a marked difference in hygroscopic/deliquescent properties between sulfuric acid and its ammonium salts. Sulfuric acid is highly hydroscopic and always exists in the liquid state, but ammonium sulfate and acidic ammonium sulfate change their phases from the solid to liquid at an ambient relative humidity of about 80% and 35–39%, respectively (Charlson et al., 1974). The difference in hygroscopic properties between sulfuric acid and its ammonium salts will provide a possible base for the *in situ* selective determination of the molecular state of sulfate contained in individual submicron aerosol particles, if a suitably reactive aerosol-collecting surface is chosen and the ambient relative humidity is controlled before entering the impactor.

In the present aerosol studies, carried out in the remote Everest highlands, we used nitrocellulose-covered electron microscope grids precoated in vacuum with calcium as a reactive aerosol-collecting surface. From laboratory experiments, it is found that at low ambient relative humidity less than 20%, a vapor-deposited thin film of calcium is stable and upon impaction, hydrated sulfuric acid droplets etch calcium and leave concentric reaction products spread around the original particles; however, no reaction was observed in the case of ammonium sulfate produced from solution and dried to about 20% r.h. The specificity of a vapor-deposited calcium thin-film technique for the *in situ* detection of the sulfuric acid component contained in individual aerosol particles under controlled ambient relative humidity was established by an electron probe X-ray microanalysis (EPMA) of reaction products of aerosol particles on a calcium thin film, as will be described in the following section. The details of the technique will be published separately.

2.2. *Sampling of aerosol particles*

All aerosol samples from the remote Everest highlands were taken by one of the authors (M. Yoshida) while in the Everest area as a member of the expedition party.

Fig. 1 shows the aerosol sampling sites in the Khumbu Glacier and in the Western Cwm on the south flank of Mt. Everest in December 1980, during the post-monsoon winter season.

Sampling of aerosol particles was always carried out at least 10 m upwind of the camp to avoid contamination. Aerosol particles were collected simultaneously by impaction on a pair of nitrocellulose-covered electron microscope grids precoated in vacuum with calcium and carbon, respectively. The impactor was a single-stage rectangular jet (0.1 cm × 1.0 cm) drawing air by a hand-operated 100 ml syringe-type pump at a rate of about 6.0 litres/min. From sizing of individual aerosol particles collected on a carbon surface with a transmission electron microscope, it is found that the impactor collects aerosol particles efficiently down to 0.2 μm in diameter. The total sampled volume of air at each aerosol sampling was 20 litres at ambient pressure. After sampling, all aerosol samples were kept in a dry sealed plastic container and were brought to the laboratory for subsequent electron microscope analysis.

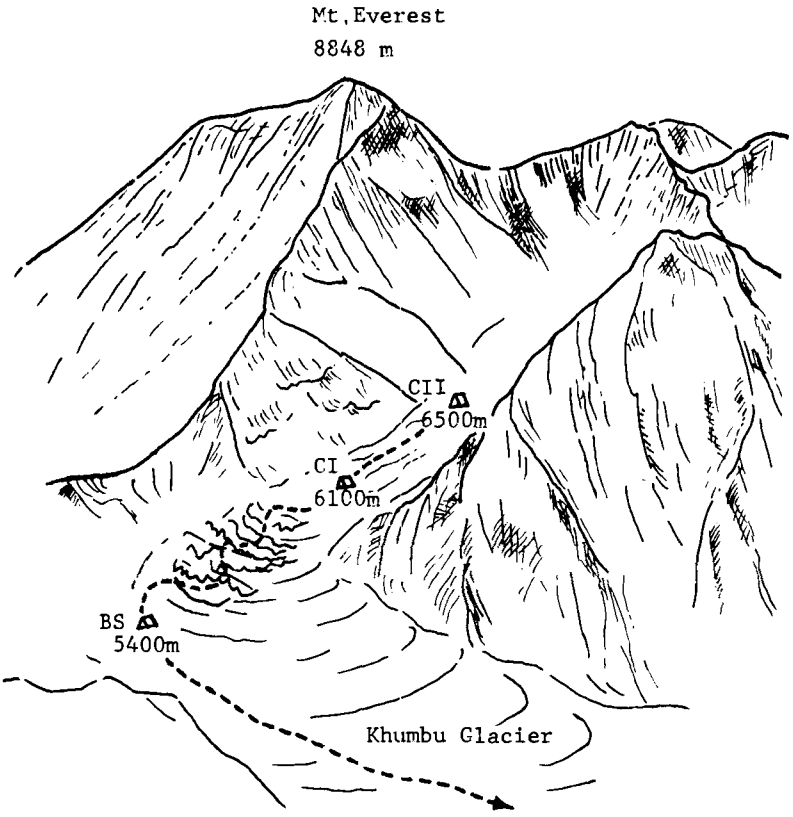

Fig. 1. Aerosol sampling sites in the Khumbu Glacier and in the Western Cwm on the south flank of Mt. Everest.

3. Results and discussion

3.1. *Molecular state of sulfate aerosols in the remote Everest highlands*

Fig. 2 is a typical electron micrograph of aerosol particles collected *in situ* on a reactive surface precoated in vacuum with calcium (the thickness of the calcium thin film was about 15 nm), which were collected on December 13, 1980, from 14.10 to 14.40 at the base camp (5400 meters above MSL) located in the Khumbu Glacier.

From Fig. 2, it is seen that more than 80% of the collected aerosol particles reacted with calcium and formed concentric reaction products spread around particles. This clearly indicates that the dominant aerosol particles were present in the liquid state as they existed in the air. The weather during the sampling period from 14.10 to 14.40 on December 13 was fine with downslope winds of 5–15 m s^{-1}. Air temperatures were about −4 to −5 °C and ambient relative humidities were 10 to 15%. At such low relative humidities, the most probable liquid which reacted directly with calcium upon impaction was therefore hydrated sulfuric acid.

In addition, in order to establish the specificity of a vapor-deposited calcium thin film technique for the detection of the sulfuric acid component in individual aerosol particles, we made an electron probe X-ray microanalysis of the reaction products of aerosol particles with calcium from the same sample as shown in Fig. 2.

A typical example of an electron probe X-ray microanalysis of the reaction products is shown in Figs. 3a–c. Fig. 3a shows an electron micrograph of the reaction products of aerosol particles with calcium and Figs. 3b, c show the distribution of sulfur and calcium in the same field of view as

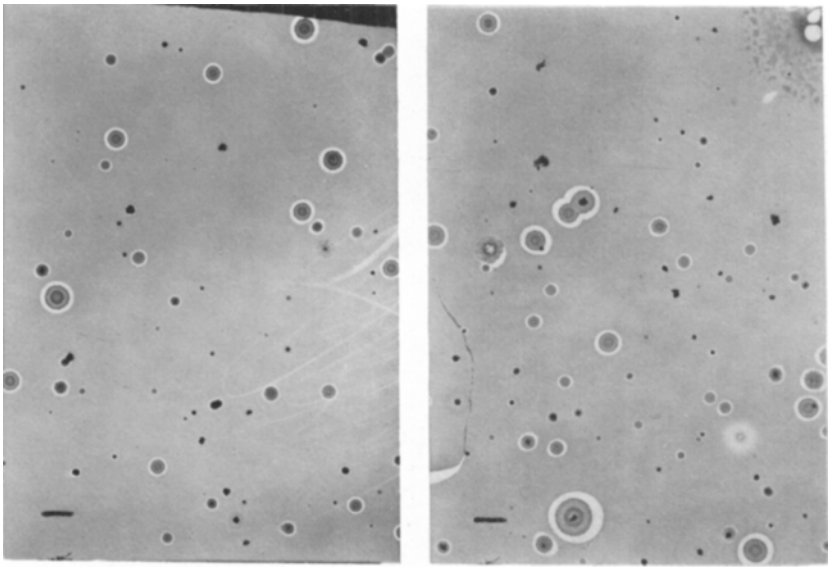

Fig. 2. Electron micrographs of aerosol particles collected on nitrocellulose-covered electron microscope grids precoated in vacuum with calcium, on December 13, 1980, from 14.10 to 14.40, at the base camp (5400 m MSL) located in the Khumbu Glacier. (Scale: 1 μm indicated in the lower left corner.)

shown in Fig. 3a. In Figs. 3b and c, each white dot indicates a pulse from the detector as a result of the detection of S-Kα and Ca-Kα X-rays, respectively.

From a comparison between Figs. 3a and b, it will be seen that the distribution of sulfur is superimposed exactly on the reaction products of aerosol particles with calcium. It will also be seen that the reaction of aerosol particles with calcium etched a calcium thin film, which resulted in the formation of a dark fringe around each reaction product, as shown in Fig. 3c. Thus, the X-ray data with the aid of an electron micrograph clearly indicate that all reaction products on a calcium thin film were composed of calcium sulfate as a result of the reaction between the sulfuric acid component contained in individual aerosol particles with calcium upon impaction.

As described above, the use of a reactive surface precoated in vacuum with calcium seems very promising for the *in situ* detection of the sulfuric acid component contained in individual submicron aerosol particles under controlled ambient relative humidities less than 15%.

However, the use of the impactor for the collection of aerosol particles raises some additional questions regarding the validity of this technique if condensation takes place on sulfate-containing aerosol particles other than sulfuric acid, as a consequence of the adiabatic expansion of the air in the jet. Depending upon the increase of the relative humidity in the jet compared to the relative humidity of the air entering the impactor, even ammonium sulfate-containing aerosol particles could undergo a phase change from the solid to the liquid state and could react with calcium upon impaction.

In the case of a single-stage rectangular jet (0.1 cm $\times$ 1.0 cm) impactor used in the present measurements, an estimate similar to that described by Hochrainer and Zebel (1981) indicates that no such effects are likely to occur: the temperature drop of the air before and after the expansion in the jet is negligible (less than 0.005 K) because of the low air velocity of about 10 m s^{-1} in the jet and the short residence time of air in the jet. Thus, the increase of the relative humidity of the air in the jet compared to the relative humidity of the ambient air (less than 15%) is not high enough for a phase change of ammonium sulfate.

Therefore, in the present aerosol measurements carried out in the remote Everest highlands, the collection of aerosol particles in the liquid state by impaction under such a low relative humidity of less than 15% was not due to the expansion

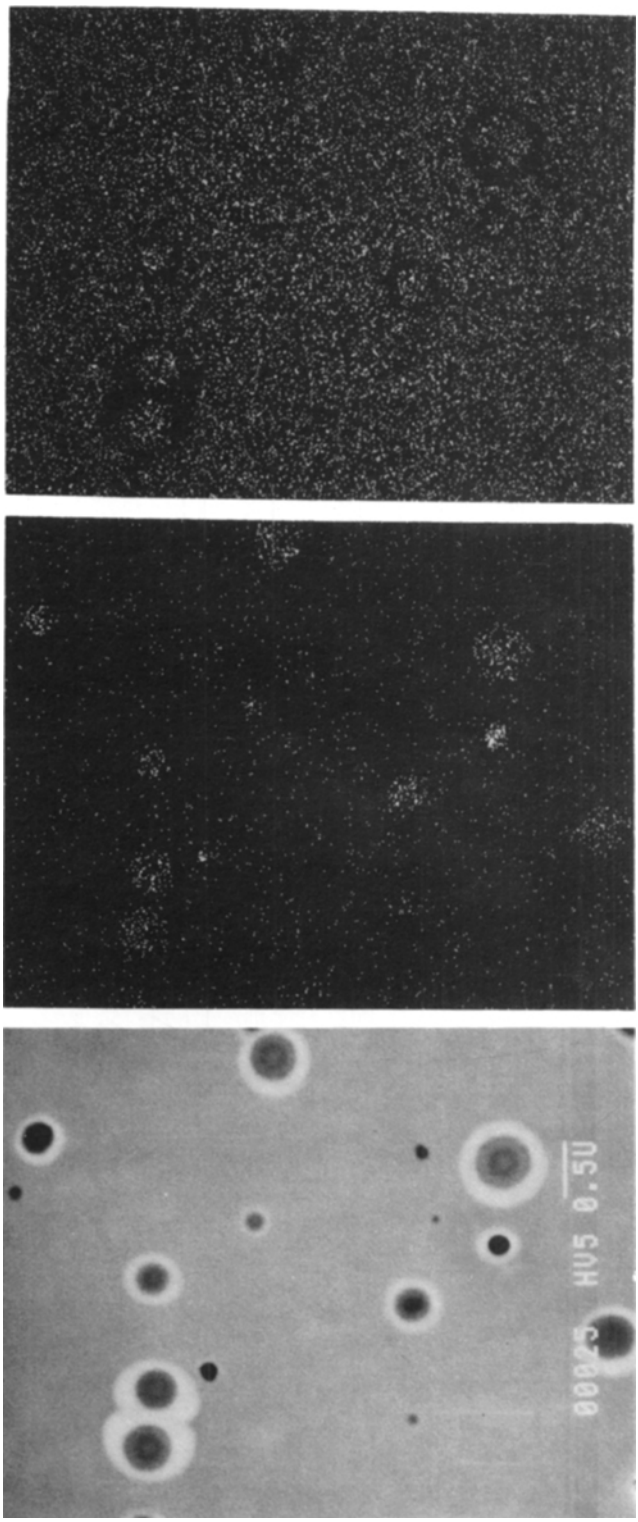

Fig. 3. Electron probe X-ray microanalysis of the reaction products of aerosol particles, from the same sample shown in Fig. 2. All figures have the same magnification (scale: 1 μm). (a) Electron micrograph of the reaction products of aerosol particles with calcium. (b) Scanning picture of sulfur distribution of the same sample as (a). White dots indicate the detection of S-Kα X-ray. (c) Scanning picture of calcium distribution from the same sample as (a). White dots indicate the detection of Ca-Kα X-ray.

humidity of the air in the jet, but because they already existed in the air in the liquid state before entering the impactor.

However, it should be mentioned here that our present vapor-deposited calcium thin-film technique does not prove the absence of ammonium ion. Therefore, as the probable liquid which reacted directly with calcium upon impaction at low relative humidities, less than 15%, we cannot dismiss the acidic sulfates, intermediates between sulfuric acid and ammonium sulfate, in the form of supersaturated droplets because of some uncertainty in the deliquescent/efflourescent properties of the acidic sulfate (Charlson et al., 1974).

With this proviso, it can be stated that in the remote Everest highlands, the majority of aerosol particles were sulfate-containing aerosols, the dominant ones being present in the form of a hydrated sulfuric acid and/or in the form of a supersaturated acidic sulfate droplet. Similar results were obtained for aerosol particles collected at 6000 m altitude above MSL (CI) in the Western Cwm as shown in Fig. 4. The aerosol sampling at an altitude of 6500 m above MSL (CII) was unsuccessful because of damage to the nitrocellulose film on the electron microscope grids.

It is significant to note that the existence (or at least the tentative existence) of sulfate aerosols in the form of a hydrated sulfuric acid/supersaturated acidic sulfate droplets, strongly indicates that they are not remnants of sulfate aerosols originating in a near-surface air with abundant ammonia, but are formed in air with a very low concentration of ammonia (Huntzicket et al., 1980), presumably in the upper troposphere or transported from the lower stratosphere. Although from our present limited data we cannot make a broad generalization concerning the origin of sulfuric acid/acidic sulfate in the upper troposphere, it is indicative that there is a vertical stratification in the acidity of sulfate-containing aerosols in the troposphere: ammonium sulfate in the lower troposphere and sulfuric acid/acidic sulfate aerosols in the upper troposphere, as suggested by Ono (1978) and Ikegami et al. (1980).

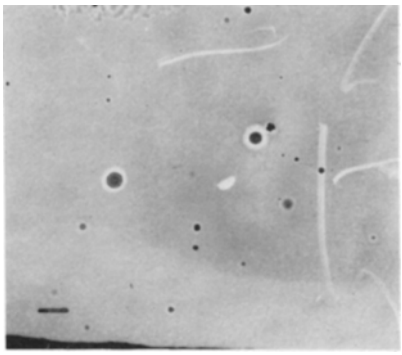

Fig. 4. Electron micrograph of aerosol particles collected on a reactive surface precoated in vacuum with calcium, collected on December 15, 1980, at an altitude of 6000 m MSL (CI). (Scale: 1 μm, indicated in the lower left corner.)

3.2. *On the validity of the morphological identification of the molecular state of sulfate-containing aerosols with electron microscopy*

The possible presence of hydrated sulfuric acid aerosols was evident from examining the *in situ* measurements of aerosol particles collected on a reactive surface precoated in vacuum with calcium as described above (see Fig. 2); however, from the morphology of aerosol particles collected on a carbon thin film and examined individually with the electron microscope later in the laboratory after shadowing with Au/Pd, no trace of a hydrated sulfuric acid-like appearance characterized with small satellite particles surrounding a central particle (Frank and Lodge, 1967) was observed, as shown in Fig. 5a.

These hemispherical aerosol particles were very unstable in the electron beam and evaporated to leave a thin cracked shell. Fig. 5b shows the results of sulfate tests applied to the samples of the same sampling as shown in Fig. 5a. When these aerosol particles were post-coated in vacuum with barium chloride and exposed to octanol atmosphere in the laboratory, they reacted with barium chloride and formed characteristic reaction products of barium sulfate spread around the original particles, as shown in Fig. 5b, indicating the presence of sulfate ion in individual aerosol particles (Ono et al., 1981b). These aerosol particles as shown in Fig. 5a were therefore identified as ammonium sulfate through a combination of their heat-sensitive nature and positive results of the sulfate test with a thin film of barium chloride (Bigg et al., 1974).

This obvious change in the molecular state of the aerosol particles collected on an inert surface precoated in vacuum with carbon from that obtained *in situ* measurements applying a vapor-deposited thin film of calcium, can only be

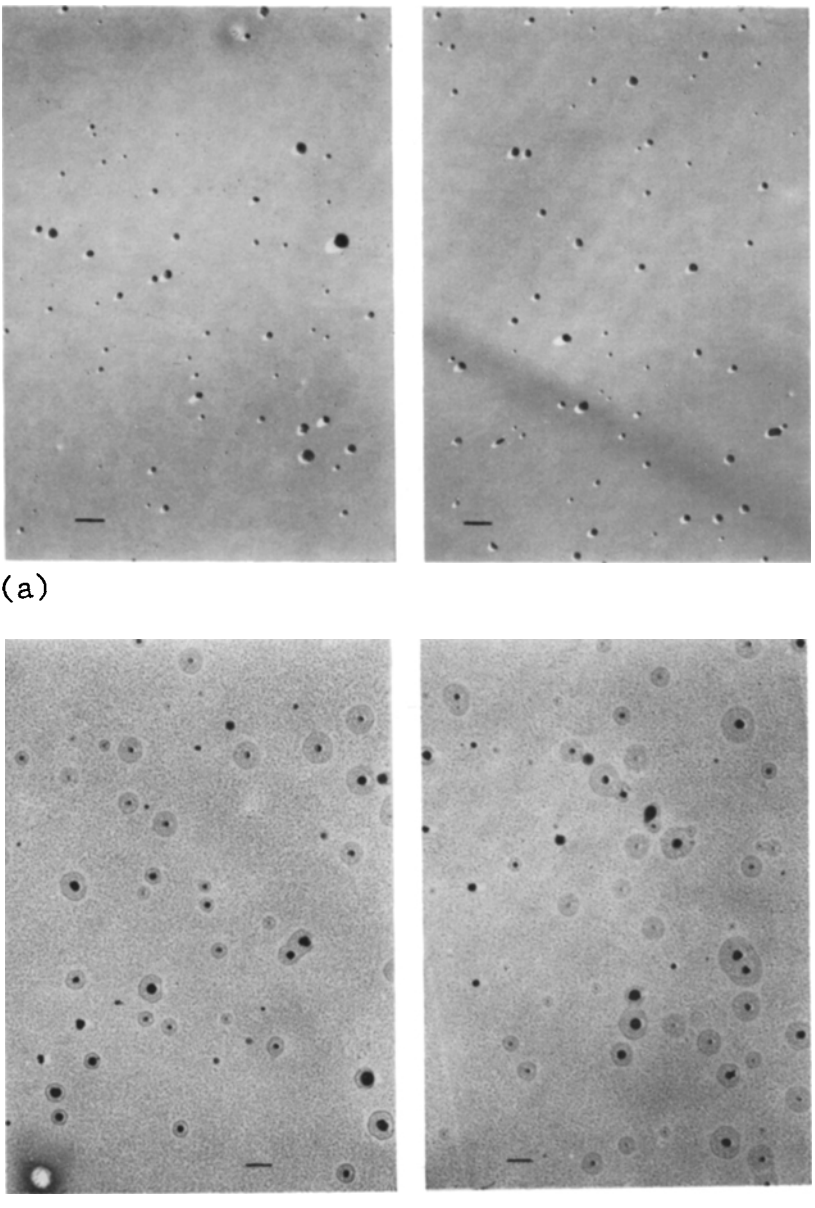

Fig. 5. Electron micrographs of aerosol particles collected by impaction on December 13, 1980, at the base camp. (Scale: 1 μm indicated in the lower left corner.) (a) Collected on a carbon surface and shadowed later in vacuum with Au/Pd. (b) Post-coated in vacuum with barium chloride and exposed to an atmosphere of octanol.

explained as due to the reaction of the sulfuric acid/acidic sulfate component in the original aerosol particles with atmospheric trace ammonia on the collecting surface after sampling, as pointed out by Hayes et al. (1980), who clearly demonstrated that the sulfuric acid component in aerosol particles reacts easily with trace ammonia in the laboratory air, especially on possible exposure to

the breath of a person handling the aerosol samples (Larson et al., 1977) and is converted to ammonium sulfate.

In our case, considerable time elapsed between collection of aerosol particles on a carbon surface and their examination; in addition, the samples were opened in the laboratory for shadowing in vacuum with Au/Pd before electron microscopy without special precautions being taken to exclude possible ammonia contamination, so that the reaction of the surface acid/acidic sulfate component in the original aerosol particles with ambient trace ammonia is very likely.

In summary, this study shows that the morphological identification of aerosol particles with electron microscopy does not always reflect the actual molecular state of sulfate aerosols in their airborne state, unless every precaution is taken to protect the samples from ammonia contamination, as described by Hayes et al. (1980). It should again be emphasized that this important conclusion emerged from the *in situ* selective determination of the sulfuric acid/supersaturated acidic sulfate component in individual aerosol particles collected on a reactive surface precoated in vacuum with calcium under the low ambient relative humidity of less than 15%.

4. Conclusion

The following form the main conclusions of this study. With the successful application of a reactive surface precoated in vacuum with calcium as an aerosol collecting surface, it is found that the upper troposphere aerosols in the remote Everest highlands are mostly sulfate in the form of hydrated sulfuric acid/supersaturated acidic sulfate solution droplets. Furthermore, it is confirmed that the morphology of aerosol particles collected on a carbon surface and later examined individually with the electron microscope, does not always reflect the actual molecular state of sulfate-containing aerosol particles because of the possible reaction of the sulfuric acid component contained in aerosol particles with ambient ammonia on a collected surface during and/or after sampling.

Plans are under way to make a further investigation of the upper tropospheric aerosols in order to see whether the existence of hydrated sulfuric acid/supersaturated acidic sulfate aerosols is globally representative of the upper troposphere.

5. Acknowledgements

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