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CONSTITUENTS OF A REMOTE PACIFIC MARINE AEROSOL: A TEM STUDY

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Abstract—Marine aerosol particles from the Equatorial Pacific were studied using transmission electron microscopy. Sea-salt aggregates consist largely of NaCl and Na–Ca sulfate crystals. Variations in the composition of sea-salt aggregates occur, and these may reflect the effects of relative humidity. There are several species of submicron, S-bearing particles, presumably including ammonium sulfate and strong acids. Diatom fragments are common, and sparse kaolinite and rutile crystals are the mineral component of this marine aerosol. The samples we studied appeared to be free of obvious anthropogenic effects.

Key word index: Marine aerosol particles, Equatorial Pacific, FeLINE-I cruise, transmission electron microscopy, selected-area electron-diffraction, energy-dispersive X-ray spectrometry.

INTRODUCTION

Marine aerosols affect climate by scattering and absorbing radiation and by influencing cloud formation. Oceanic particles also play an important role in the global S and N cycle (Fitzgerald, 1991; Charlson *et al.*, 1987). Although the bulk composition of the aerosol in remote oceanic areas has been studied extensively, there are gaps in our knowledge of the chemical and structural properties of individual aerosol particles. In order to understand the processes that form marine aerosols it is necessary to know the principal particle species in the atmosphere.

Transmission electron microscopy (TEM) is uniquely well-suited for determining the nature of ultra-fine particles, since it is possible to obtain chemical, structural, and morphological data on the submicron scale (Buseck, 1992). It has proved useful for morphological characterization of marine aerosol particles (Mészáros and Vissy, 1974) and for identifying particles by their chemical reactions with thin reagent films (Bigg, 1980; Gras and Ayers, 1983). Electron diffraction has mainly been used in aerosol research to distinguish between crystalline and amorphous materials (Sheridan and Musselman, 1985; Mamane and Dzubay, 1986; Sheridan, 1989) and to recognize sheet silicates (Gaudichet *et al.*, 1986). Buseck and Bradley (1982) showed that high-resolution images can be useful for characterizing aerosol particles.

We used TEM imaging, selected-area electron-diffraction (SAED), and energy-dispersive X-ray spectrometry (EDS) to identify individual particles in samples collected in the Equatorial Pacific during the 1990 FeLINE-I cruise (Tindale, 1992). Particles occurring in the samples fall into three broad categories: (1) primary particles emitted by the ocean (sea-salt and biogenic material), (2) particles of secondary origin, and (3) crustal material. Our goal was to obtain information about particle transport and reactions through the identification of individual aerosol species.

In this study we characterize individual species in sea-salt aggregates and point out differences between the properties of sea salts collected under different meteorological conditions. TEM images help us understand the properties of submicron, S-bearing particles, thereby providing information about cloud condensation nuclei. The little crustal material our samples contained is identified.

EXPERIMENTAL

Aerosol samples were collected in the Equatorial Pacific (0°, 140°W) during the 1990 FeLINE-I cruise. Particles were collected both on stacked Nuclepore filters and directly onto TEM grids. Details of the sampling conditions and results of the microprobe analyses of the filter samples are given by Shattuck *et al.* (1994).

For the particle substrates we used Cu TEM grids coated with a C-reinforced holey formvar film. The grids were placed on top of coarse-fraction (8- μm pore size) Nuclepore filters. Nine samples were collected on grids between 3 and 14 July; sampling times varied from 14 to 39 h. Although particle loading is light on most grids, seven of the nine grids could still be used for TEM investigations. Both submicron and supermicron particles occur on the grids; the size distribution is probably not characteristic of the aerosol. There were practically no particles on two of the grids, even though they were exposed to similar collection conditions as the others. They effectively served as blanks and indicate that contamination of the samples was minimal.

The samples were studied with a JEOL 2000FX electron microscope operated at 200-KV accelerating voltage. Crystalline phases were identified using a double-tilt ($\pm 60^\circ$ about x , $\pm 40^\circ$ about y) specimen stage. Images (electron micrographs) of the particles were obtained at magnifications ranging from 100 to 500,000 times. We acquired energy-dispersive X-ray spectra using an ultra-thin-window KEVEX detector that allowed the detection of signals from elements heavier than boron.

Crystal structures were identified on the basis of several diffraction patterns obtained from a particular crystal. We found that quantitative analyses of EDS spectra of sea-salt and sulfates yielded unreliable results because volatile elements were lost during spectra acquisition; also, the thicknesses of individual particles in aggregates varied and neither the thin-film nor the ZAF quantification routine was applicable for the analysis of whole aggregates. Therefore, EDS analyses of volatile particles are only regarded as semi-quantitative. However, EDS data in combination with structural measurements commonly provided reliable particle identification.

RESULTS

Filter samples from the 1990 FeLINE cruise were analysed with an automated electron microprobe by Shattuck *et al.* (1994). Statistical evaluation of the microprobe data provides a picture of day-to-day changes of the aerosol, while our TEM study supplies complementary information about individual particles. Based on our analyses, we found it useful to group the particles into four classes.

Sea-salt aggregates and diatom fragments

Two of the nine samples contain a large number of both sea-salt and S-bearing particles. We shall refer to the sea-salt particles on the 6 July sample as "eu-hedral" sea-salts and those on the 9–11 July sample as "anhedral". Both types are aggregates with diameters in the 1- to 2- μm size range. By choosing a suitable selected-area aperture it is possible to obtain SAED patterns from individual crystals within an aggregate. EDS analyses can also be performed on individual crystals without having contributions to the spectrum from other members of the aggregate.

"Euhedral" sea-salt aggregates consist of NaCl crystals and sulfates of Na, Ca, Mg, and K (Fig. 1). Ca-bearing sulfate particles tend to form in characteristic rod shapes, whereas pure Na-sulfate forms crystals with smaller aspect ratios, although both have the same crystal structure. From the many known Na, Ca, and mixed-cation sulfate compounds, we identified a

monoclinic structure with $a = 5.34$, $b = 9.25$, $c = 7.13$ Å, $\beta = 91.37^\circ$ (space group Cc), having the composition $(\text{Na}_{0.8}\text{Ca}_{0.1})_2\text{SO}_4$ in the X-ray powder diffraction database (Powder Diffraction Files, 1991; No. 29-1196). Our semi-quantitative EDS analyses show that the material having this structure can accommodate even more Ca than is given in the chemical formula. Although the crystallinity of sulfate rods degrades in the electron beam, phase changes were not observed. We were intrigued that the sulfates associated with NaCl form with this structure instead of crystallizing as more common hydrated sulfates such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), or hydroglauberite ($\text{Na}_{10}\text{Ca}_3(\text{SO}_4)_8 \cdot 6\text{H}_2\text{O}$). There is a possibility that the sulfates were originally hydrated but lost water within the microscope.

The "anhedral" sea-salts look like featureless, circular spots with darker areas in them (Fig. 2). The SAED patterns obtained show the dark spots to be NaCl, but the distinctive morphology of halite crystals is not preserved. Mixed-cation Na–Ca–Mg sulfate rods are recognizable in many, but not all, "anhedral" sea-salt aggregates. These particles contain Cu, reflecting reaction with the TEM grid. Most likely HCl associated with "anhedral" sea-salt gave rise to the formation of Cl-bearing Cu-compounds when the hydrated particles contacted the collection surface. Individual Cu-bearing crystals were also observed on the grids, as is discussed in the next section.

Diatom fragments appear in every sample collected during the two-week cruise. No skeletal details are apparent in the large, irregularly shaped particles; their identification is based on their composition and amorphous character. Gaudichet *et al.* (1986) published pictures of similar-looking diatom fragments from Antarctic ice cores. EDS spectra from the fragments contain small peaks of Na, Ca, and Mg in addition to those of Si and O. Many NaCl, Na–Ca sulfate, and Na sulfate particles are commonly scattered around the diatom fragments and contribute to the halo surrounding the central particle (Fig. 3). Although they are much smaller, the sulfates nucleated on NaCl look similar to those occurring in "euhedral" sea-salt aggregates (Fig. 3b) and suggest that the seawater coating on the fragments was exposed to atmospheric S-compounds. The small NaCl and sulfate crystals formed on the collection surface from the water coating the diatom fragments.

HCl reaction products

Cl-bearing particles free of Na occur both as small grains ($d < 0.08$ μm) and in large ($d \sim 2$ μm), drop-like forms. Their EDS spectra and diffraction patterns indicate that they are $\text{Cu}_2\text{Cl}(\text{OH})_3$ (atacamite) crystals. Since we know from microprobe data that Cu was only present in the aerosol as a trace element during the 1990 FeLINE cruise, we conclude that the atacamite crystals are products of reactions that involved the aerosol and the TEM grid. Our studies of synthetic samples show that both HCl and NH_4Cl

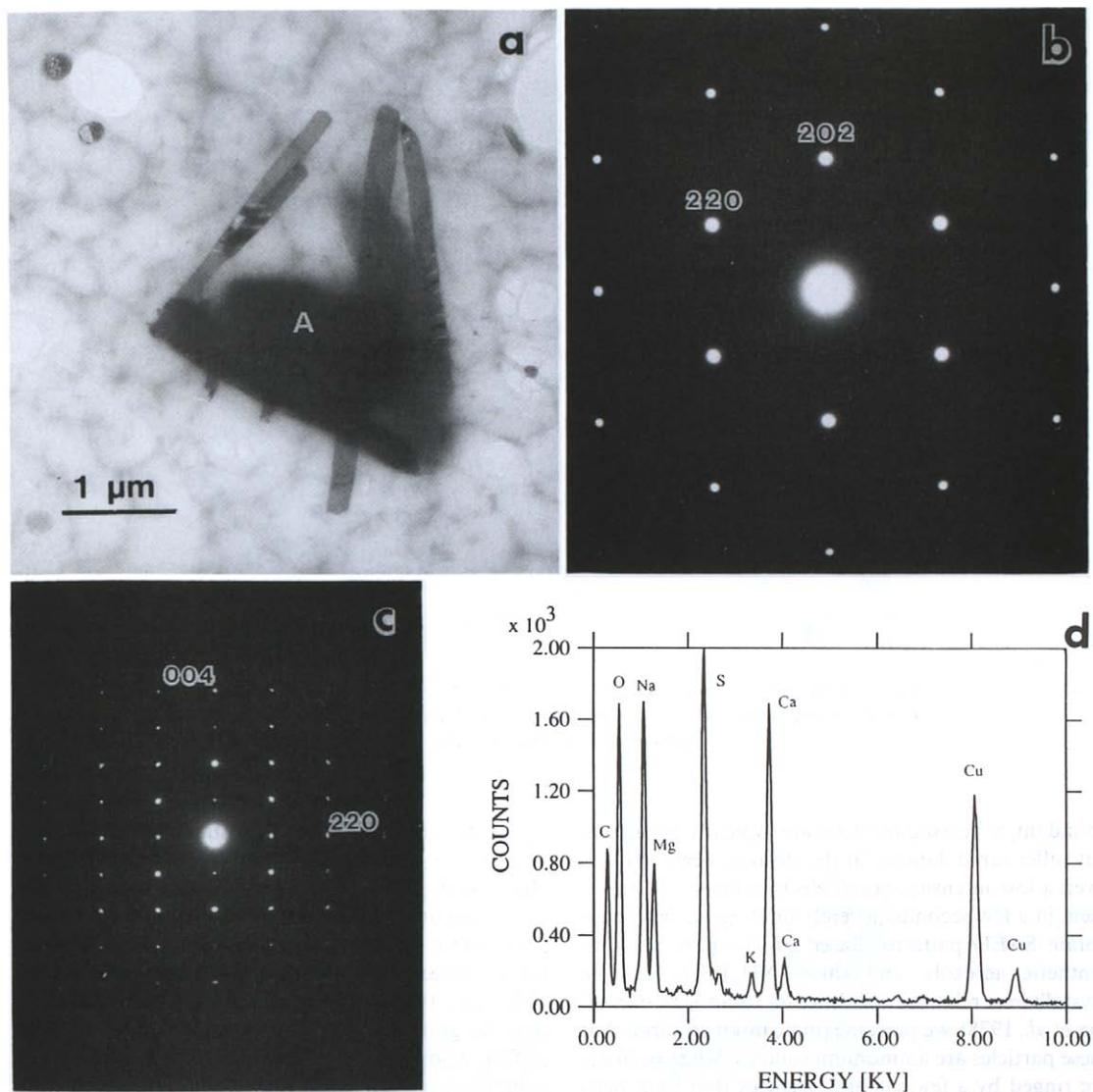


Fig. 1. (a) Micrograph of a "euhedral" sea-salt aggregate. (b) SAED pattern from the NaCl crystal marked A in the micrograph. (c) SAED pattern from one of the sulfate rods in the image, and (d) EDS spectrum from the same sulfate crystal. The Cu signal results from stray radiation from the grid. The formvar supporting film produces the C peak and contributes to the O peak.

aerosols can produce atacamite on such grids. Since the reaction with NH_4Cl implies that NH_4Cl first dissociates into HCl and NH_3 (Pio and Harrison, 1987) and then HCl reacts with Cu, atacamite crystals are referred to in the following as reaction products of HCl.

Scattered, submicron crystals of atacamite occur exclusively along the Cu bars of the TEM grid, with their numbers decreasing towards the center of the mesh. In some samples 10- to 12- μm wide bands, heavily loaded with $\text{Cu}_2\text{Cl}(\text{OH})_3$ crystals, frame the meshes of the grid. We interpret these crystals as formed from gas-phase HCl that was probably released from sea-salt. In one sample hundreds of sub-

micron ($d \sim 0.05 \mu\text{m}$) $\text{Cu}_2\text{Cl}(\text{OH})_3$ crystals occur in a circular feature around a slightly larger central grain (Fig. 4). The central and surrounding particles have the same composition and structure. Presumably these bunches of particles formed from large ($\sim 1\text{--}2 \mu\text{m}$) droplets that contained HCl. They only occur within $\sim 10 \mu\text{m}$ from the Cu bars of the grid.

Submicron, S-bearing particles

Several types of submicron, S-bearing particles are common in this class of marine aerosols. They are typically ringed by a halo of smaller particles, and their sizes are rather uniform, with typical diameters of about $0.2 \mu\text{m}$. On a day when "euhedral" sea-salts are

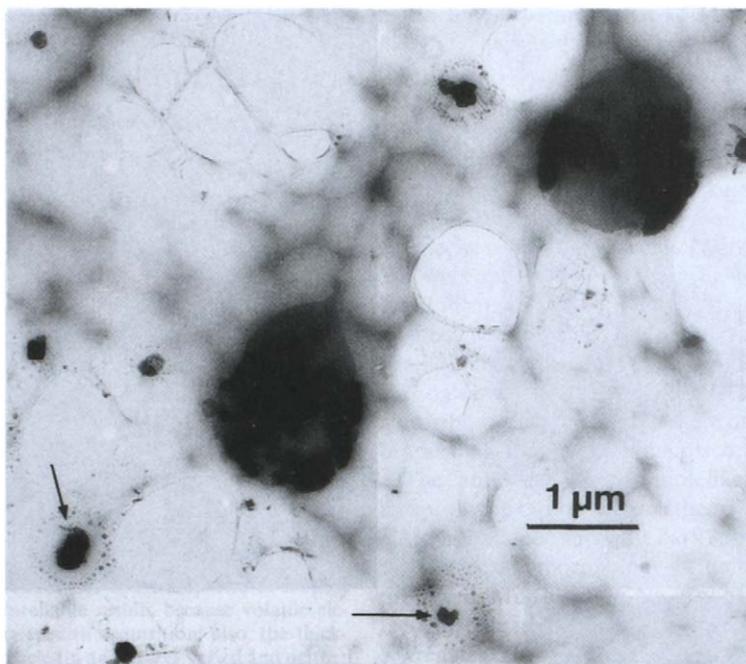


Fig. 2. "Anhedral" sea-salt aggregates containing NaCl (dark spots) and artifacts formed by the reaction of HCl with the Cu TEM grid. The arrows point to submicron, S-bearing particles.

abundant, S-bearing particles are typically crystalline but suffer rapid damage in the electron beam (Fig. 5). Even a low-intensity, broad electron beam volatilizes them in a few seconds, severely limiting our efforts to obtain SAED patterns. Based on comparisons with synthetic aerosols, and since $(\text{NH}_4)_2\text{SO}_4$ can be crystalline at relative humidities less than 81% (Charlson *et al.*, 1978), we presume (but cannot confirm) that these particles are ammonium sulfates. Some particles are ringed by a few satellite particles that have been considered signs of acidic sulfates (Gras and Ayers, 1983; Mamane and Dzubay, 1986). Since NH_4HSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ can exist in marine aerosols (Charlson *et al.*, 1978), it is possible that acidic ammonium salts are also present in this sample. Lack of the N peak in EDS spectra obtained from both natural particles and synthetic ammonium sulfate is attributable to the rapid deterioration of the material and to the low intensity of X-rays emitted by light elements.

Another type of small S-bearing particle in our samples is less beam-sensitive, and its spectrum typically contains large Cu peaks in addition to that of S, indicating reaction with the grid (Fig. 6). Halos around such particles consist of many more individuals than those around the presumed ammonium sulfate particles. Some of these particles are amorphous and are decorated by small dark spots (Fig. 6b). Since we observed similar spots in synthetic H_2SO_4 particles, we believe that they may be residues of interactions involving the natural, strongly acidic particle and the collection surface.

On the same sample that contains the "anhedral" sea-salts, S-bearing particles exhibit a crystalline structure (Fig. 6a). The crystals are also artifacts formed by reaction of the aerosol droplet and the impact surface. Studies of synthetic aerosols and literature evidence (Bigg, 1980; Sheridan and Musselman, 1985; Ito, 1989) suggest that such particles arrived onto the grids as strongly acidic sulfates, most likely as sulfuric acid droplets. Clarke *et al.* (1987) reported the occurrence of acid sulfate, probably H_2SO_4 , in the aerosol above the central Pacific. However, methane sulfonic acid, MSA ($\text{CH}_3\text{SO}_3\text{H}$), is also present in the marine atmosphere (Saltzman *et al.*, 1983; Savoie and Prospero, 1989), but the methods we used cannot distinguish the acid sulfate species from one another.

Mineral dust

Particles of crustal origin are sparse in the FeLINE-I samples. The most abundant minerals in the samples are kaolinite and rutile. We also observed muscovite, K-feldspar, and a Mg-bearing layer silicate, probably serpentine. Kaolinite (Fig. 7) is a common aerosol component at low latitudes (Chester *et al.*, 1972). It is more surprising that the only other mineral occurring in most samples (although in small numbers) is rutile. It is typically twinned (Fig. 8), and many crystals had a sulfate coating when they arrived onto the grid. The rounded shapes of the crystals indicate that they were intensely processed, possibly by weathering prior to entering the aerosol or by reaction within the aerosol.

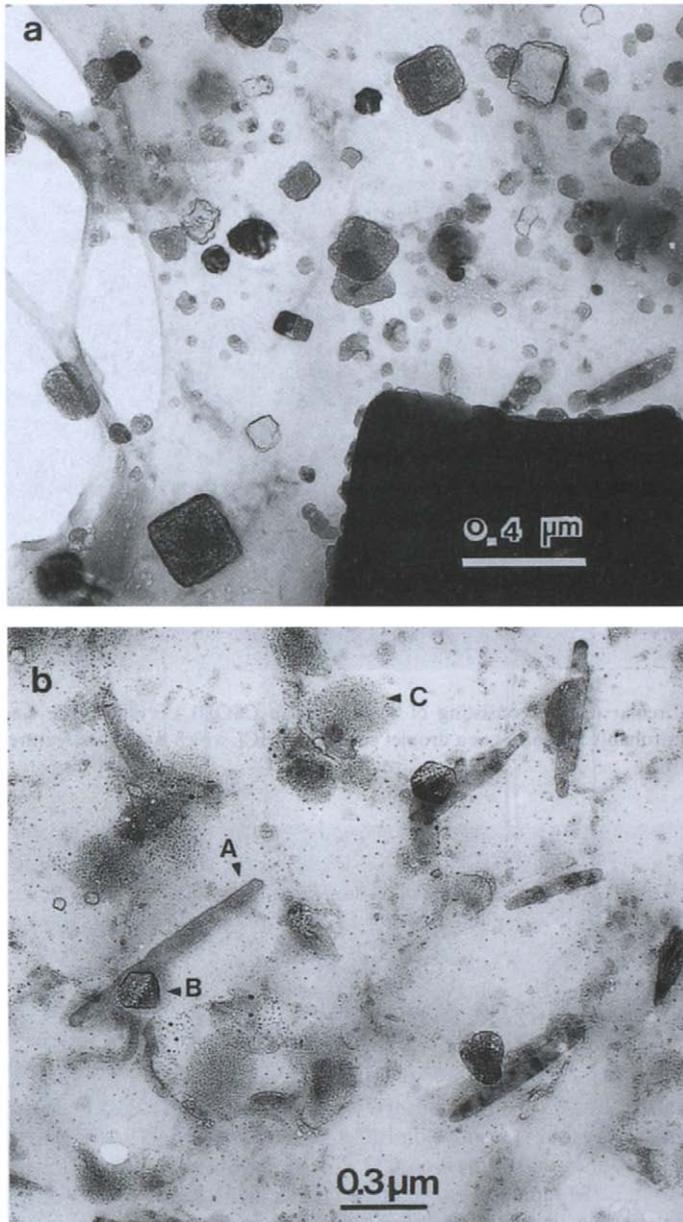


Fig. 3. Crystals scattered around a diatom fragment. (a) NaCl crystals. The black region in the lower part of the micrograph is the edge of the diatom fragment. (b) Ca-Na sulfate rods (marked A) with NaCl crystals (marked B); the small spots are Na sulfate (marked C).

DISCUSSION

It is important to know what, if any, changes occurred to the particles during and after sampling. When samples are stored, aerosol particles may lose water and other volatile materials. However, there are several examples in the present study where signs of a former liquid coating on the particle are still detectable. The small NaCl and sulfate particles around diatom fragments were probably dissolved in the

water coating the fragments, while they were in the aerosol; they presumably crystallized only after the water evaporated from the grid. We assume that if the sulfate crystals had formed on the grid from a coating on NaCl particles, then one would expect to see similar halos around sea-salt particles as occur around diatom fragments. Apparently the seeds of sulfate crystals formed in the atmosphere, and the rods grew further on the grid. It is difficult to estimate particle size changes that occur on the grid; loss of water

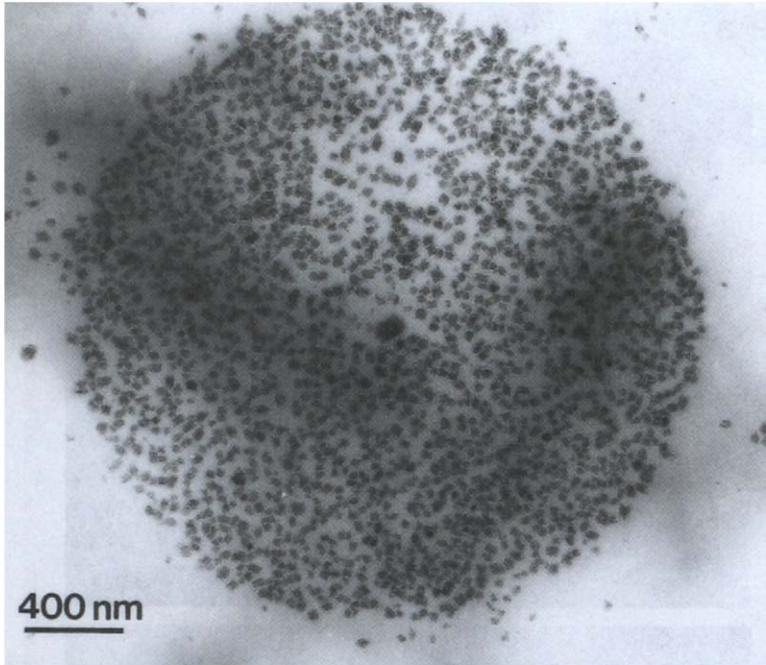


Fig. 4. Circular feature consisting of atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) crystals. The small particles probably formed from a droplet containing HCl, which is why the feature is round.

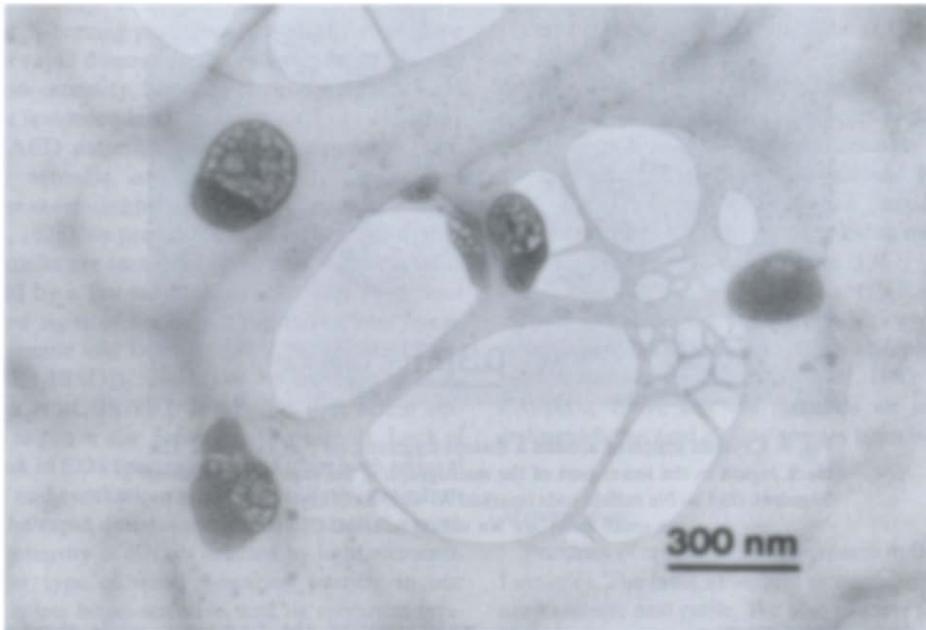


Fig. 5. Submicron S-bearing particles, presumably ammonium sulfates. The “bubbles” in the particles result from radiation effects from the electron beam.

decreases the size, while post-sampling crystallization probably increases the apparent particle diameter. Another post-sampling process occurs when particles react with the material of the collection surface. The

reaction products of HCl provide examples of this artifact.

Particle aggregates containing sea-salt and sulfates presumably formed by atmospheric reactions and

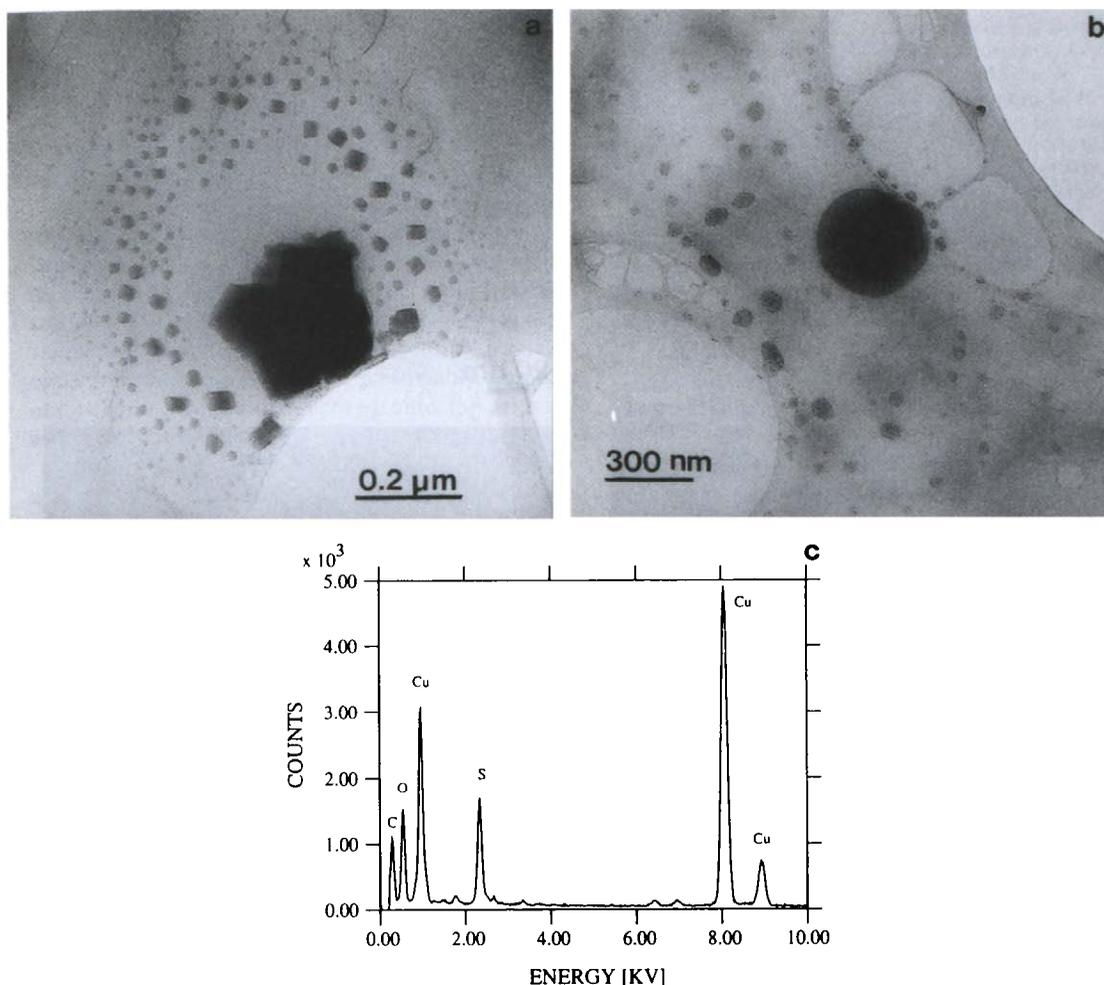


Fig. 6. S-bearing particles. These are reaction products of acidic sulfates having (a) crystalline and (b) amorphous structures. (c) A typical EDS spectrum of S-bearing particles.

agglomeration; low particle densities on the collection surfaces make it unlikely that the aggregates formed by impaction on the filters. NaCl aerosol reacts with H_2SO_4 (Hitchcock *et al.*, 1980) and HNO_3 (Martens *et al.*, 1973), and HCl is released. Sievering *et al.* (1992) suggested that SO_2 is oxidized by ozone in aqueous sea-salt droplets to form sulfates. This mechanism provides an important pathway for the removal of S from the marine atmosphere, and it would produce particle associations such as the “euhedral” sea-salt aggregates in the FeLINE samples. Andreae *et al.* (1986) speculated that Ca excess observed in massive aerosols (Maenhaut *et al.*, 1983) results from the reaction of SO_2 or H_2SO_4 with coccoliths (that consist of CaCO_3). We confirm that Na–Ca sulfate particles are major constituents of this oceanic aerosol, while no CaCO_3 crystals were observed in sea-salt aggregates in the same samples. The same reactions take place in the seawater coating the diatom (SiO_2) fragments as in sea-salt drops.

The ratio of Cl in gaseous and in particulate form varies inversely with relative humidity (Berg and

Winchester, 1977). Model calculations by Clegg and Brimblecombe (1985) predicted that 90% of the initial H^+ concentration is lost from droplets at relative humidities less than 97%, but under extremely humid conditions HCl will not be depleted from the larger droplets. The abundance of HCl reaction products on 9–11 July suggests that the relative humidity was high, which could slow the degassing of HCl from aqueous sea-salt droplets, resulting in the formation of “an-hedral” sea-salt aggregates. The increased humidity may also be responsible for the switch from gas-phase to aerosol HCl that produced the swarms of Cu-bearing artifact crystals on the grids.

Submicron S-bearing particles in the FeLINE samples include at least three different species. Although we were unable to unambiguously identify specific compounds, our TEM observations suggest that compositions could include $(\text{NH}_4)_2\text{SO}_4$ and strong acidic sulfates. These results are consistent with the report by Clarke *et al.* (1987) about the aerosol in the Equatorial Pacific. Defining the crystalline and molecular forms of aerosol sulfate compounds is of great importance,

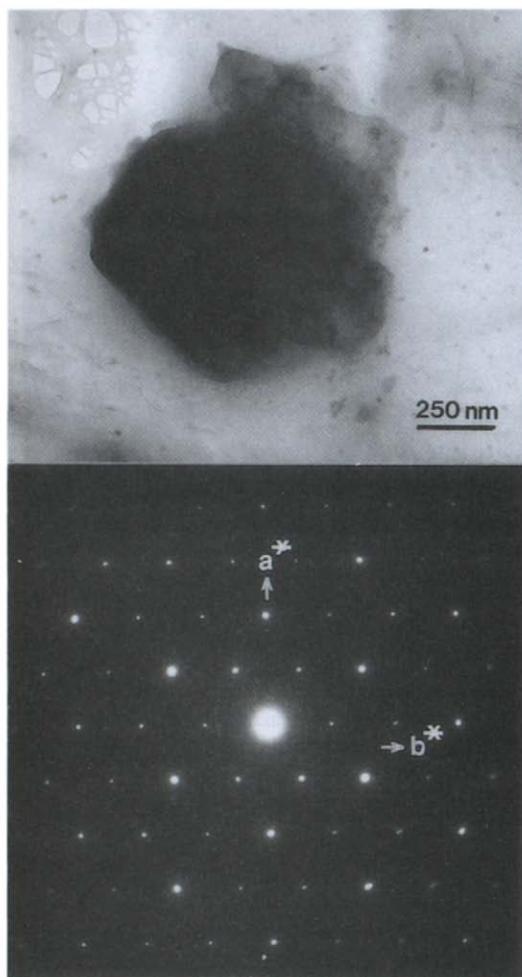


Fig. 7. A kaolinite crystal ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and its $[001]$ zone-axis SAED pattern.

because physical properties such as the hygroscopic nature and refractive index of these particles are governed by their molecular form (Charlson *et al.*, 1978). Also, knowledge of specific chemical species would help determine the natural or anthropogenic origin of S compounds (Prospero *et al.*, 1985) that play such an important role in climatic processes (Bates *et al.*, 1987; Charlson *et al.*, 1987). However, no current method seems able to solve this problem. The combination of TEM studies with X-ray diffraction analyses of high-volume samples (Sturges *et al.*, 1989) would possibly reveal the identity of crystalline materials. For the detection of N and organic C, electron energy-loss spectroscopy (EELS) seems promising (Katrinak *et al.*, 1992).

Correlation of TEM results with data from microprobe analyses of individual particles (Shattuck *et al.*, 1994) show the two methods to be complementary. Since the TEM grids were placed onto the coarse-fraction filters, many of the fine particles observed with the microprobe were not effectively collected on

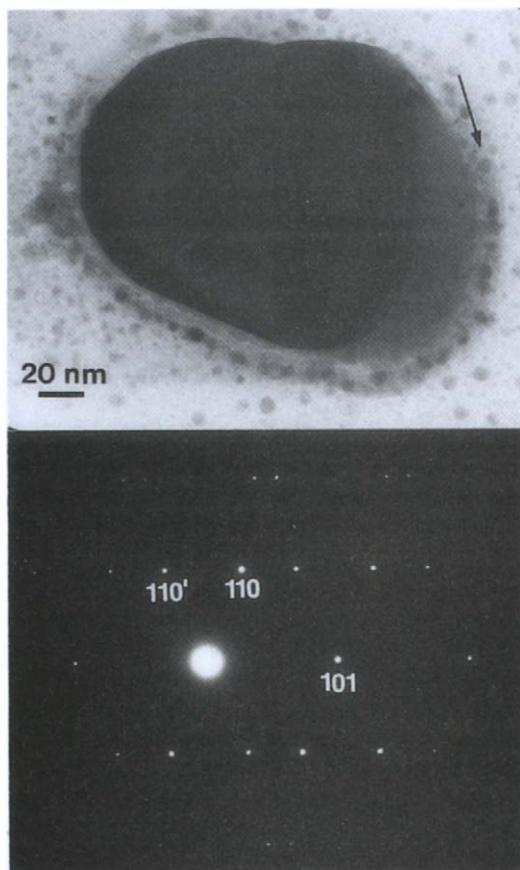


Fig. 8. Twinned rutile (TiO_2) with sulfate coating (marked by the arrow). Double reflections in the diffraction pattern (110 and $110'$) indicate twinning.

the grids. In spite of this limitation, differences are evident between the samples collected on 6 July and on 9–12 July. In the first sample all sea-salts are of the “euhedral” type, and the majority of submicron S-bearing particles are presumably ammonium sulfates. In the other sample, however, sea-salts are associated with HCl reaction products, and Cu–S-bearing particles are probably residues of strongly acidic sulfates. The microprobe data suggest that little anthropogenic S reached the samples. However, meteorological data show different atmospheric conditions for 6 July and 9–12 July; there was a strong subsidence in the airstream on 10–11 July that made particle deposition likely. Therefore, there is a possibility that the increased acidity of S-bearing particles sampled during this time is associated with the transport of air masses that originated from areas with high DMS production.

CONCLUSIONS

Using transmission and analytical electron microscopy we identified individual crystalline components

in sea-salt aggregates. Sulfates of Na and Ca with minor Mg and K form on NaCl particles.

Diatom fragments are common constituents of this marine aerosol. A halo of small NaCl and sulfate crystals typically formed on the grid from the water coating these biogenic particles.

Scattered $\text{Cu}_2\text{Cl}(\text{OH})_3$ (atacamite) crystals occurring along the Cu bars of the TEM grids and drop-like swarms of particles of the same material are artifacts that confirm the presence of HCl in this marine aerosol.

Different types of submicron, S-bearing particles occur in the samples; some are presumably ammonium sulfates, while others arrived onto the grids as acidic sulfates.

The most abundant crustal particles are kaolinite and rutile.

Matching our TEM results with data from microprobe analysis of individual particles collected on the same cruise indicates a correlation between the changes of particle properties and long-range transport of air masses. The results of this study show that it is possible to utilize the capabilities of TEM to good advantage in the study of marine aerosols.

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