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Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol

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ABSTRACT

Marine aerosol was collected in September 1998 and July 2005 on the upwind coast of an island at latitude 15°S, about 15 km downwind from the outer edge of the Great Barrier Reef, Australia, and examined by electron microscopy. Exopolymer gels, aggregates of organic particles, marine micro-organisms and fragments of marine life formed a substantial part of the accumulation mode aerosol. Differences in transparency, firmness of outlines and shape of gels and the influence of organic vapours on them, suggested progressive physical and chemical changes with atmospheric residence time. The organic aggregate components had a size distribution remarkably close to that found in similar particles over the central Arctic Ocean peaking at diameters of 30–40 nm. Single components or small groups of these aggregates were found within at least 75% of particles resembling ammonium sulphate in appearance, indicating that aggregates fragmented in the atmosphere. Sea salt was not detected in particles <200 nm diameter unlike many observations showing it to be a major component, a result that was entirely consistent with the Arctic findings. The deduced sequence of changes to particles entering the atmosphere from the ocean is also very similar to that found in the Arctic, suggesting that it is a common pattern over the oceans. That conclusion would require modification of the parametrization of the marine aerosol used in climate models and of possible climate feedback effects.

1. Introduction

Considerable efforts have been made in recent years to estimate accurately the effects of aerosols on cloud reflectivity, one of the major uncertainties in the global radiation budget (IPCC, 2007). To apply such an estimate to projections of global climatic change, potential climate feedback processes must also be identified. This requires knowledge of sources, physical and chemical properties of the aerosol and of atmospheric processes that alter those properties. The marine contribution to the global aerosol is large because about 70% of the world's surface is covered with oceans. In principle it is likely to be less complicated than continental aerosol and therefore a good starting point for evaluating the effect of aerosols on clouds.

Parametrizations of the marine aerosol used in models predicting the effects of cloud condensation nuclei (CCN) on clouds, radiation and climate have often in the past taken a fairly simple view of the nature of the marine aerosol. Sea salt production by bursting bubbles and sulphate formation from oxidation products of dimethyl sulphide (DMS) were considered the only important processes. Sea salt production results partly from fragments of the bubble film ('film drops') and partly from 'jet drops', the break up of the jet of water that shoots upwards when a bubble bursts (Blanchard, 1983). O'Dowd et al. (2004) have recently attempted to include the nature of the organic content of oceanic aerosols into models describing their effects on clouds. They showed that during phytoplankton blooms, the organic contribution can be as high as 63% and that the water-soluble portion contributes to CCN concentrations. A comparison of satellite-derived cloud properties and radiation over and near phytoplankton blooms in the Southern Ocean (Meskhidze and Nenes, 2006) found a doubling of cloud drop concentration over the blooms and 15 Wm^{-2} decrease in short-wave radiation flux at the top of the atmosphere, suggesting that CCN production in bloom regions was greatly enhanced. This illustrates the importance of correctly describing the origin of marine CCN.

Separation of the organic fraction of bulk aerosol into water-soluble and water-insoluble portions is an important step in calculating the effects of organic compounds on CCN concentrations and properties. However, the way in which the organic compounds are distributed in individual particles, resolved over size, whether the insoluble compounds are hydrophilic,

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hydrophobic or mixed with soluble organic compounds, and how that may change with atmospheric residence time all have to be known before models based on the information can be considered complete.

Wells and Goldberg (1991, 1993) were the first to note the presence of high concentrations in the surface ocean, typically of the order of 10^9 ml^{-1}, of particles predominantly <50 nm in diameter, which they called 'marine microcolloids'. Many of them appeared to be aggregates of particles as small as 2 nm. Wells (1998) attributed their production to 'a combination of cell exudation and lysis, microbial degradation of particulate organic matter and sloppy feeding and excretion by zooplankton'. Subsequent to their discovery they have been found at all sites that have been suitably sampled, from the Southern Ocean to the North Atlantic and in the Pacific (Wells and Goldberg, 1994; Benner et al., 1997). A 'mucus-like' or gel-like material was found to join the aggregated microcolloid particles (Wells and Goldberg, 1993). The huge amount of this gel material in the oceans and its ecological importance have been described by Verdugo et al. (2004).

Bigg et al. (2004) examined the morphology and chemical properties of individual particles in the surface microlayer of open water between ice floes at latitudes 88–89°N in August, 2001. Sizes, morphology and concentrations were very similar to those found by Wells and Goldberg at much lower latitudes, and the amorphous gel-like joining material was very obvious. At the same time and location Leck and Bigg (2005a) studied individual particles above the open leads of the semi-persistent pack ice area. All the main particle types of the microlayer samples were found to have corresponding airborne particles—aggregates of the microcolloid particles, amorphous gel, bacteria, virus-like particles and fragments of marine organisms. The amorphous gel-like material binding the particles in both the water and the air had properties (Decho, 1990; Verdugo et al., 2004) entirely consistent with those of exopolymer (EP) secretions (gels) of algae and bacteria. EP molecules are very surface active and consist of highly hydrated (99% water) polysaccharides, with high melting points, that bind amino acids proteins and peptides, (Decho, 1990). Divalent ions are thought to provide bridges between adjacent or different sugar chains to give the gel-like consistency (Chin et al., 1998). To distinguish the airborne aggregates from those in the water but to emphasize their origin, they will be referred to as 'airborne marine aggregates (AMA)'.

Accumulation mode AMA were found by Leck and Bigg (2005a,b) not only in the Arctic but over lower latitude oceans. Some remained intact and others fragmented when collected by impaction. In the Aitken particle range they found small groups and single components of these particles. In view of the sensitivity to ultraviolet light or acidification of the EP-gel material that were observed in the surface microlayer to bind the marine aggregates, it seemed reasonable to assume that aggregates become unstable during their atmospheric residence and their components separate into progressively smaller groups. The discovery that 50–90% of accumulation mode sulphate particles contained similar inclusions within them and having an almost identical size distribution to the components of larger aggregates reinforced this view. Particles of 40 nm diameter provide an energetically easy path for the deposition of even slightly supersaturated gases. This provides an obvious explanation for their presence within sulphate particles and leads to the supposition that their number concentrations may also control the concentrations of sulphate particles. Sulphate particles have usually been considered to grow to CCN size from nanometre-sized embryos, although the time required for this to happen is prohibitively long in a cloudy troposphere (Raes and van Dingenen, 1995). The presence of large nuclei provides a much more direct and faster path to CCN status. A recent model study by Lohmann and Leck (2005) has examined the hypotheses further and found it necessary to invoke a highly surface-active Aitken mode, assumed to be EP, externally mixed with a sulphur-containing population in order to explain the observed CCN over the Arctic pack ice area.

A simple sulphate-and-sea-salt model appears to be inadequate for marine Arctic summer aerosol. It is important to establish whether that is also the case for lower latitude oceans if calculations of the effects of marine aerosol on climate or climate change are to be firmly based. The aim of the present work was to find the extent to which marine high Arctic aerosol resembled that in a very different situation—the tropical Lizard Island located in the Great Barrier Reef.

2. The sampling site and methods

2.1. Time and location

Particles were collected throughout the days 1–10 September, 1998 and 13–22, July 2005 at a point 50m from the shoreline on the windward side of Lizard Island (latitude 14.6°S, longitude 145.5°E) at about 40km from the Australian mainland. The location is shown in Fig. 1. A coral-filled lagoon with a fringing reef was immediately upwind. Further upwind there were other reefs, culminating in the main Barrier Reef at a distance of about 15 km. In both periods, the southeast trade-winds blew

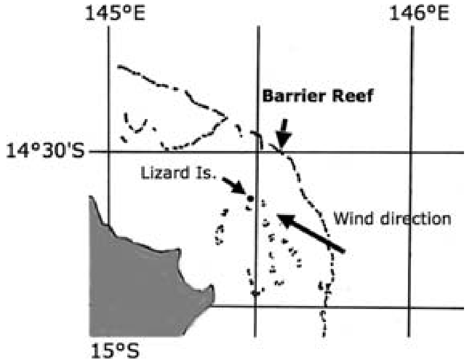

Fig. 1. The location of Lizard Island.

continuously, usually at 5–7 ms^{-1}, the weather was mostly fine and sunny, air temperatures ranging from 24 to 28 °C and relative humidity 70–90%. As a result of the long fetch of these winds over the ocean, continental influence should have been very low.

2.2. *Aerosol collection*

Aerosol samples were collected directly onto the polyvinylbutyral ('butvar') surfaces of 3 mm transmission electron microscopy (TEM) grids. Three different impactors were used, with nozzle diameters of 1 mm, 100 nm and 70 nm the latter two using electron microscope apertures as nozzles and a vacuum pump for sampling. Estimated 50% collection efficiency cut-points were about 200, 70 and 50 nm. In 1998 only the impactor with a 1 mm nozzle was used.

An electrostatic precipitator was used in addition to the impactors on both expeditions. Particle charges were imparted at the air inlet by a ^{63}Ni β-emitting radioactive source and the particles precipitated by a 12 kVcm^{-1} electric field between air inlet and collecting surface. Flow rate was kept very low (0.17 ml s^{-1}) in order to collect particles up to about 1 μm diameter. The collection efficiency of the electrostatic precipitator used was intercompared with the TSI 3089 Nanometer Aerosol Sampler. Both collected few particles smaller than 25 nm. More details on the various TEM sampling methods can be found in Bigg and Leck (2001a). Particles >400 nm diameter were also collected using Nuclepore 0.4 μm filters and examined by scanning electron microscopy (SEM). Number concentration of particles larger than 10 nm diameter was monitored continuously with a TSI 3010 particle counter.

2.3. *Identification of the particles by morphology and chemical properties*

To allow a three-dimensional structure to be deduced, and the diameter of a sphere of equivalent volume (DES) to be calculated, artificial shadows were imposed by vacuum evaporation of platinum onto the plastic 'butvar' collecting surface of the TEM grid, such that shadow length was twice the height of the particle. The platinum coating also preserved the original outline of a particle that evaporated in an electron beam, or otherwise changed during treatment. In September 1998, all particles were shadowed with platinum. However, one drawback with metal shadowing of TEM grids is that it makes particles less electron-transparent and difficult, or impossible, to see inclusions within them. Therefore, 90% of all grids were left unshadowed in the July 25 expedition. The penalty is the uncertainty concerning calculating particle volume. This had to be estimated by comparison with the three-dimensional shapes of shadowed particles having a similar appearance. In 1998, 135 pictures of particles or groups of particles were obtained using the Philips CM-12 TEM at Sydney University's Electron Microscopy Unit and in 2005, 400 pictures. The elemental composition of unshadowed particles collected on Nuclepore filters were examined by SEM and analysed using its X-ray backscatter facility (Bigg et al., 2004 give more details).

After a preliminary examination of unshadowed TEM grids, a further procedure was to float grids on distilled water to reveal inclusions in soluble particles, or on weak solutions of compounds that would react with certain ions in the particles. The plastic substrate on which the particles were collected allowed ion exchange between water and particle. The soluble material diffused into the water and insoluble reaction products were left on the surface.

The three solutions used were barium chloride, silver sulphate and flavianic acid. All allowed inclusions to be seen that were previously hidden by overlying soluble material. The first tested whether the soluble material was sulphate, by leaving a ring of insoluble barium sulphate around where the particle had been. The second allowed the detection of poorly soluble silver salts such as halides, or insoluble organic complexes through the formation of very electro-dense crystals or particles. The third was used to detect amino acids, possibly useful since Kuznetsova and Lee (2002) found surface microlayers in the ocean to be greatly enriched with amino acids. It used an old method for detecting amino acids due to Doherty et al. (1940) which showed that most amino acids formed very insoluble compounds with flavianic acid (8-hydroxy-5,7-dinitro-2-naphthalene sulfonic acid). Some grids were exposed instead to the vapour of an organic solvent such as decane or cyclohexane. This procedure resulted in components soluble in those vapours to spread across the surface around the particles.

3. Predominant morphology and properties

Sea salt and ammonium sulphate are the well-known particles of the marine aerosol. Experience in the Arctic showed that exopolymers and AMA derived from the ocean not only influenced their properties but in the case of sulphates were often directly responsible for their formation. Those components of the Lizard Island aerosol will therefore be described before describing properties of the better known particles.

3.1. *Exopolymer gels and AMA*

EP-gels and the more electron-dense particles within them were much more obvious in the Lizard Island (LI) collections than in those from the Arctic, forming 22% of the identified particles in the 1998 shadowed specimens, and 30% in the unshadowed but not dialysed or floated 2005 specimens. In the latter they were by far the most common insoluble particles. Particles <80 nm diameter were ignored in the above statistics and larger unidentified particles (often having a mixed nature) formed 36 and 33% of the 1998 and 2005 collections respectively. Dialysed and floated specimens were not counted since soluble material had been removed. Figure 2a–d show particles containing angular

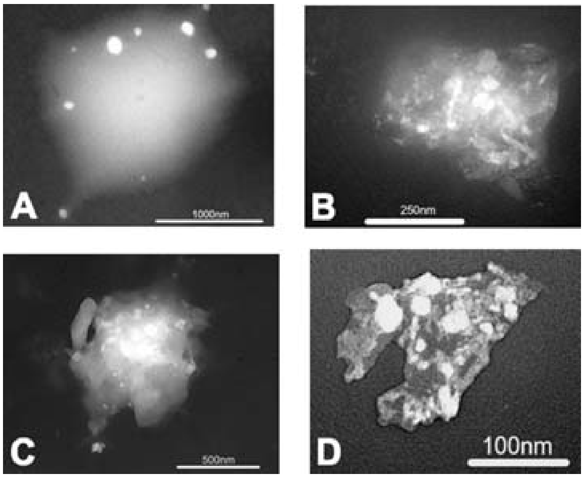

Fig. 2. Particles thought to be exopolymer gels in varying stages of decay. Note the electron-dense (white) angular inclusions within them.

electron-dense (white) inclusions in a matrix that becomes progressively flatter, firmer and less transparent moving from Fig. 2a–d. For the reasons given in the Introduction, very diffuse transparent gels such as that of Fig. 2a are assumed to have been in the air only a short time, while those that were opaque or reduced to a dark flat thin film with the inclusions on the surface (c and d) have had a longer atmospheric residence time. The changes are consistent with the collapse of the gels under the influence of ultraviolet light and acidification (Chin et al., 1998; Orellana and Verdugo, 2003).

Figure 3a–d show a similar sequence of AMA. The particle of Fig. 3a retains a gel coating, contracting to a thickening of the joints in Fig.3b and c, continuing to a particle (Fig. 3d) with lightly joined components. Exposure to decane or cyclohexane vapours left particles such as those of Figs. 2a or 3a unaffected, but dissolved parts of those that were more compact, implying that the shorter-chain compounds resulting from the collapse of the gel were soluble in those solvents.

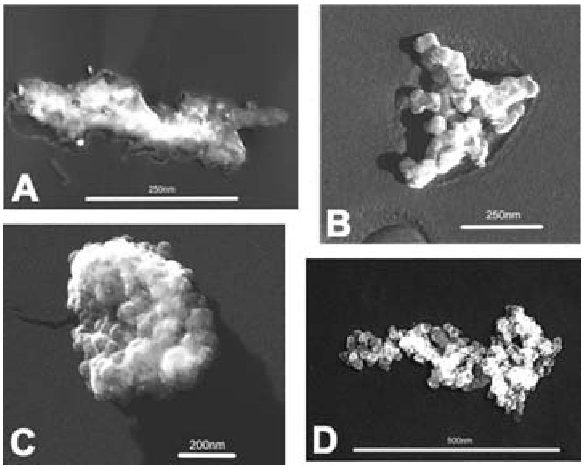

Fig. 3. Aggregates of microcolloid particles (AMA). (A) Surrounded by exopolymer material, (B–D) changes thought to be due to increasing exposure time to the atmosphere. (B and C) Shadowed. (A and D) Unshadowed.

3.2. *Components of AMA*

Most of the particles collected in sizes <50 nm diameter (corresponding to a small Aitken mode size range) were polyhedral (four to six sides, both regular and irregular), water-insoluble and stable in the electron beam (heat resistant), and were entirely similar to particles in that size range identified by Leck and Bigg (1999, 2005a) as components of marine microcolloid aggregates. Examples are shown in Fig. 4a–d, scale bars in each being 50 nm. Fig. 4a and b show unshadowed polyhedral virus-like particles. In Fig. 4b two of the particles appear to have tails so that they might actually be viruses. The largest particle appears to have a pentagonal shape with smoothed corners, suggesting that it might be like one of its smaller neighbours but was covered with some material. The lack of a surrounding halo of droplets implies that the covering material was not sulphuric acid. Figure 4c is a shadowed hexagonal particle without visible associated material. Figure 4d shows a particle with six smoothed corners beside a much smaller pentagonal particle. The smoothing again is likely to be due to a coating, but also not of sulphuric acid. Heintzenberg et al. (2004) has classified particles <25 nm diameter as ‘ultrafine’ and some of those in Fig. 4b and one in Fig. 4d come into that category. The absence of morphologically detectable sulphuric acid on particles <50 nm diameter was entirely consistent with the Arctic findings by Bigg and Leck (2001b) and Leck and Bigg (1999).

Leck and Bigg (1999) speculated that oxidation of L-methionine may have been responsible for new particle formation and described laboratory experiments in which L-methionine dissolved in seawater was nebulized, then exposed to ultraviolet light. New particles formed and were captured on TEM grids. Figure 4e is an example and the largest particle, perhaps coincidentally, has a shape resembling that of the two uppermost particles of Fig. 4b. An alternative explanation for the presence of at least some of the pentagonal particles may therefore exist.

3.3. *Bacteria and other marine organisms and their fragments*

Airborne bacteria ranged in length from 3.7 to 7.5 μm (median 4.6 μm), considerably larger than those reported in the Arctic by Bigg and Leck (2001a,b) and Leck and Bigg (2005a), where the range was 0.5–3 μm (median 1.2 μm). In the Arctic rod-shaped particles resembling bacteria with a median length of only 200 nm were also found. Similar objects were present in the LI samples, but their median length was 300 nm.

Figure 5a–d show a selection of solid airborne particulates that are clearly marine organisms or parts of them. None had any

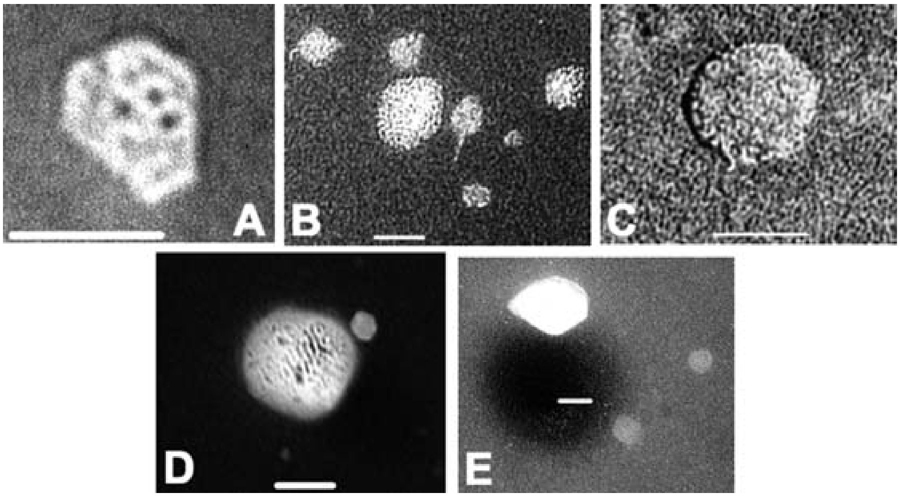

Fig. 4. Small virus-like particles. Scale bars are 50 nm long. C was shadowed, remainder unshadowed.

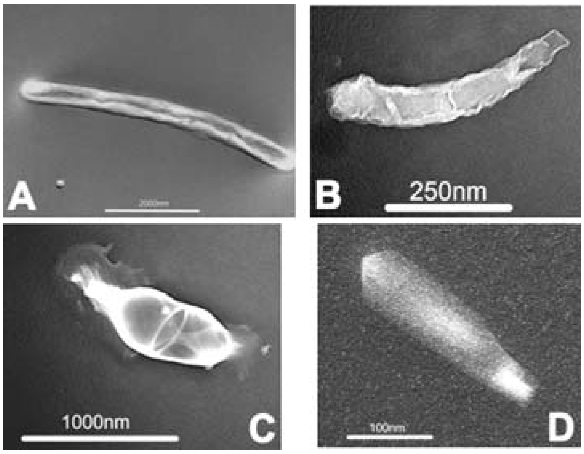

Fig. 5. Marine organisms or fragments of them.

attached salt in spite of their marine origin. Bacteria in marine aerosol having no associated salt have also been noted by Pósfai et al. (2003). Other objects having no associated salt included smooth electron-dense particles >400 nm caught on Nuclepore filters. Examined by SEM and X-ray analysis showed them to be mainly calcium carbonate. In an environment where there was so much coral, these are likely to have been of marine origin. Silicon-rich diatom fragments were also present and had no salt on them. The proportion of accumulation mode particles thought to be marine organisms and their fragments varied greatly from day to day in the Arctic and at LI. In the former samples proportions between 15 and 33% occurred at times (Leck and Bigg, 2005a). Overall the proportion at LI was 9% and in the Arctic 8%.

3.4. *The well-known components of the aerosol: ammonium sulphate*

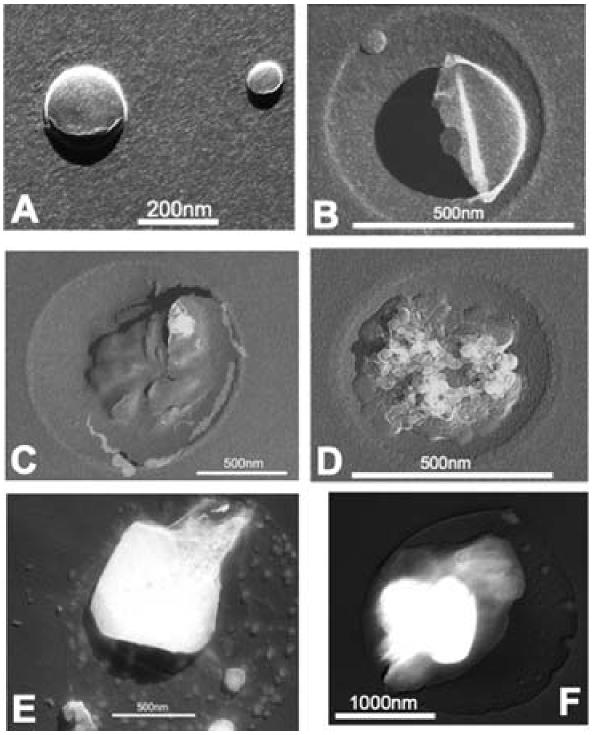

Fig. 6. The well-known marine aerosol particles: (A and B) mainly sulphates but with organic components (test in Fig. 7B). (C and D) Dialysed sulphate particles revealing internal inclusions. (E and F) Sea salt with associated EP.

Shadowed artificial ammonium sulphate particles show a circular outline and a nearly hemispherical shape. They are partly volatile in the electron beam, the shadowing metal curling up to form a ragged edge. The LI particles with a circular outline (Fig. 6a and b are examples) had a lower profile than hemispherical (shadow lengths are twice the height), evidently containing some additive that made them less rigid than pure ammonium sulphate. They were also less volatile. Particles like that of Fig. 6b had partially evaporated before examination and left deep impressions in the plastic substrate as though they had had a volatile component that dissolved it. Floated on water most particles like those of Fig. 6a and b revealed the presence of insoluble inclusions, shown in Fig. 6c and d. Forty-six such particles were photographed and one or more inclusions were visible in 30 of them. Because many of the remainder had not been dialysed, the true proportion containing inclusions would have been higher. In comparison Leck and Bigg (2005a,b) reported that 50–90% of similar particles collected in the Arctic contained inclusions that appeared to be AMA components.

Particles >80 nm diameter and morphologically similar to ammonium sulphate formed 29% of the identified particles of the 1998 collection and 37% in 2005. Because of the high variability and the relatively short observational periods, overall proportions may be misleading.

3.5. *Sea salt particles*

Pruppacher and Klett (1998) state that salt particles smaller than 1 μm diameter usually show cubic outlines. All LI particles with a cubic outline were larger than 200 nm diameter, while most were >400 nm but <1 μm. Collected on Nuclepore filters and examined by SEM, cubic crystals formed a much larger proportion of the total than on TEM grid collections. As about 1000 times the volume of air sampled on TEM grids was sampled by the Nuclepore filters and particles <400 nm diameter passed through the pores, the difference is not surprising. Salt particles are very electron-dense and stable in the electron beam compared with ammonium sulphate or most organic particles and these are further aids to identification. Consistent with the Arctic findings none of the particles smaller than 200 nm diameter, with the exception of the polyhedral AMA components appeared to be electron dense.

Amorphous transparent material thought to be EP accompanied all sea salt particles in variable amounts but usually as a minor constituent. Figure 6e shows a transparent veil surrounding a roughly cubic crystal with attached needle shaped crystals from other sea water components. In the presence of a larger proportion of organic material, the development of cubic crystals is suppressed, as in the example of Fig. 6f.

Identifiable salt particles were fewer than might have been expected because of the continuous surf on the outer edge of the Barrier Reef about 15 km upwind, being 14% of identified particles (in diameters >200 nm) counted over both expeditions.

3.6. *New particle production*

Very strong daytime generation of particles larger than 10 nm in diameter was registered by the TSI 3010 particle counter at LI on each day of the September 1998 observations, with concentrations up to 40 000 cm^{-3}, and to a smaller extent in July 2005 (maximum 4000 cm^{-3}) except on the last two days when there was an overcast of high cloud and stronger winds. Nocturnal concentrations were about 600 cm^{-3} in 1998 and 400 cm^{-3} in 2005. Both expeditions were chosen to coincide with periods of the largest tides (about 2 m in amplitude), but unlike experiences of particle formation at some coastal sites (Mäkelä et al., 2002; McFiggans et al., 2004), the particle generation was not tidally related. With the possible exception of a small number of particles like those of Fig. 4a–d, none of these created particles was detected amongst the specimens examined. This implies that the upper limit of their size was below the collection limit of about 20 nm, or that they evaporated before examination.

4. The effects of floating specimens on reagent solutions

4.1. *Flavianic acid solution*

Flotation on flavianic acid solution, with which amino acids form very insoluble precipitates, broke apart gels like those of Fig. 2a–c. Figure 7c is an example, probably resembling Fig. 2a rather than the more aged specimens which produced more diffuse precipitates and revealed included AMA components. AMA such as that of Fig. 3a developed a dense mass of precipitate with fragile needle-shaped crystals at the edges. Decho (1990) noted that amino acids as well as proteins and peptides are among the compounds readily bound to EP.

4.2. *Silver sulphate solution*

Trapped seawater in exopolymers would be expected to form silver chloride crystals when floated on silver sulphate solution. However, particles like those of Figs. 2a or 3a developed angular corners that suggested hexagonal or pentagonal crystal habits

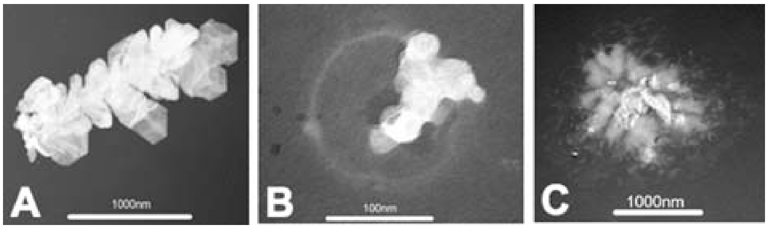

Fig. 7. Reaction of particles to floating on a weak solution. Soluble material is removed by this process. (A) An AMA floated on silver sulphate solution. (B) A sulphate-containing particle with an inclusion of AMA components after floating on a barium chloride solution. The white ring denotes sulphate present in the particle. (C) A gel floated on flavianic acid solution. Amino acids form precipitates.

rather than the cubic habit that would be expected from the formation of silver chloride. Particles with a cubic habit can appear hexagonal if viewed from the correct angle but cannot appear pentagonal. Figure 7a shows the development on a particle resembling that of Fig. 3a and suggests that chlorine, if present at all, was part of a more complex ion. Silver readily reacts with proteins and this reaction is another possible source of crystalline development. Aged AMA like that of Fig. 3d broke apart when floated on silver sulphate solution and showed little or no crystal development. An insoluble but not visibly crystalline mass of silver chloride formed around supermicrometre salt particles but were surrounded by many small predominantly hexagonal or pentagonal electron-dense particles. Salt particles that were wet when collected will be surrounded by any solid components present in the EP accompanying the salt particle when the water evaporates. Silver ions will react with organic particles but the shape of the reacted particle will be retained. Reaction with polyhedral components of AMA could produce the observed result.

One of the functions of the EP-gel is to regulate osmosis (Decho, 1990). Also according to Decho (1990), the exopolymers react with chlorine, so salt content of the trapped water may be low relative to seawater. Bigg et al. (2004) and Leck and Bigg, (2005a) showed EP-gels collected from the surface microlayer of open water in the Arctic and in the air above to have relatively weak X-ray sodium signals and a large excess of chlorine compared with sea salt ratios.

4.3. *Barium chloride solution*

Floated on a barium chloride solution, particles >200 nm containing sulphate developed a ring of electron dense (white) barium sulphate around their periphery. This test is useful in confirming that particles with an ammonium sulphate morphology contain sulphate and reveals insoluble components but does not rule out the presence of other soluble compounds. The hypothesis that small groups of aggregate components act as centres for the condensation of sulphate is illustrated by Fig. 7b. The thin circular ring surrounding the group shows that sulphate deposition had commenced.

5. Sizing of gels, AMA and their components

Sizes were calculated as the diameters of spheres of an equivalent volume, DES. However, sizes could only be determined with reasonable accuracy on the relatively few shadowed specimens with regular shapes. For aggregates, the components were assumed to be approximately spherical with diameters equal to the inscribed circles and their volumes to be the sum of volumes of their components. For gels a shape factor was estimated from gradations in transparency. Figure 8a is therefore only a rough approximation to the true distributions. It shows for both classes a very broad distribution centred on about 300 nm DES. The secondary peak at about 120 nm DES in AMA was also present in Arctic specimens.

Six hundred easily distinguished individual components of AMA or single inclusions within larger particles were sized. The size distribution is compared in Fig. 8b with that found for comparable particles in the Arctic (Leck and Bigg, 2005b). The similarity is remarkable.

6. Discussion

Comparison of the LI tropical aerosol properties with those of the summer central Arctic Ocean showed stronger similarities than might be expected for such very different climatological environments. The similarities can be summarized as:

(1) The presence of amorphous transparent EP-gels and of AMA.
(2) The size distribution of the AMA components, mainly 25–50 nm in diameter.
(3) The presence of aggregate components within the majority of particles thought to be mainly sulphates.
(4) The apparent absence of sea salt on particles <200 nm diameter.
(5) The presence of airborne micro-organisms of marine origin and their fragments that do not appear to have any associated sea salt.
(6) The large variability in the proportion of marine organisms between different collection periods and the similarity of the overall averages as a percentage of the accumulation mode.

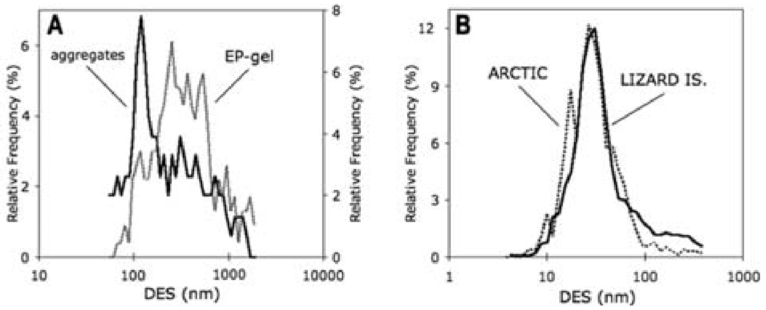

Fig. 8. (A) Size distribution of gels and AMA. (B) Size distribution of individual microcolloids and components of aggregates compared with those in the Arctic.

(7) The generation of ultrafine particles.

There were also differences.

(1) Droplet haloes characteristic of sulphuric acid content were found around particles in the Arctic, but not around LI aerosols. Sulphate (revealed by the barium chloride test) was present in particles at the latter site but evidently in a neutral form, $[(NH_4)_2SO_4]$.
(2) EP-gels and microcolloid aggregates appeared to form a greater proportion of the accumulation mode aerosol at LI than in the Arctic, but the difference was at least partly due to differing methods of treatment.
(3) Ultrafine particle generation was more frequent and more vigorous at LI than in the Arctic.

The observed similarities imply that EP, EP-gels and marine microcolloids within the ocean surface microlayer are not very different in the two regions and strongly influence particle production when bubbles burst. The process of EP-gel degradation postulated for the Arctic airborne aerosol by Leck and Bigg (2005a,b) appears to apply also at LI, the sequence of Figs. 2 and 3 showing a transition from very diffuse transparent types to compact opaque types. Perhaps the most important conclusion from what has been presented in this study is that at least three quarters of the particles resembling ammonium sulphate, like their Arctic counterparts, were found to have within them electron-dense inclusions that appeared to be thee components of AMA (Fig. 6c and d). The conclusion reached by Leck and Bigg (2005b) that the inclusions had acted as centres for condensation of supersaturated gases (e.g. DMS oxidation products) is consistent with observations at this low latitude site. It might therefore apply much more widely than just in the Arctic and represent a major factor in the development of CCN number population. That in turn will have an influence on the properties of marine clouds and on climate. Possible aerosol–cloud–climate relationships (feedback mechanisms) will differ from those so far proposed (Charlson et al., 1987).

Given these apparent and overall similarities between LI and the central Arctic Ocean many aspects of this work in relation to the Arctic findings require a much more detailed understanding. For example, why there should be any similarity at all in the aerosol of two such very different climatological regions as LI and the central Arctic Ocean. Bubble production from wave action must be vastly greater at LI and yet overall average particle number concentrations (excluding ultrafines) differed only by a factor of about four. It implies that there is a non-wind related source of bubbles in both regions. The presence of such a source had already been deduced by Leck et al. (2002).

The absence of detectable sea salt on particles <200 nm diameter and on all airborne bacteria and other marine organisms or their fragments is consistent with a number of studies elsewhere including those over the Arctic pack ice (Gershey, 1983; Gras and Ayers, 1983; Leck et al., 2002; Pósfai et al., 2003; Leck and Bigg, 2005a) but also in apparent conflict with a large number of other observations (Murhy et al., 1998; Andreae et al., 1999; O'Dowd et al., 1999; Quinn and Coffman, 1999). These include laboratory experiments in which seawater was bubbled, chemical analysis of high volume impactor samples, automated scanning electron microscopy, laser mass spectroscopy, thermal stability of small particles and hygroscopic growth factor measurements. A thorough discussion of these observations as well as those that support our finding is necessarily lengthy and involves a consideration of the nature of bubble walls. It will therefore form the subject of another paper.

The increased cloud droplet concentrations found by Meskhidze and Nunes (2006) over phytoplankton blooms in the Southern Ocean needs to be considered in relation to the present work. The authors' explanation was that oxidation products of isoprene released by the bloom provided the extra CCN. Growth to CCN size by such a process is relatively slow and the effects on clouds would be most likely at a considerable distance downwind from the blooms. A more direct influence is indicated. Phytoplankton blooms are accompanied by a great increase in bacterial and viral activity and therefore in production of EP, EP-gels and AMA. Intense episodes of bubble formation are likely to occur due to release of supersaturated oxygen from the water and enhanced DMS release will occur. We suggest that the EP-gels and AMA may form an immediate source of CCN and that deposition of oxidation products of DMS (or of isoprene) on fragments of AMA will add to the concentration.

Topics requiring further research include the sea salt question in the preceding paragraph, identification and properties of soluble organic compounds in aerosols and whether they originate directly from seawater or are products of decomposition of larger molecules. More specific information on the nature of AMA components is needed, in particular the proportion that is actually viruses. The processes involved in ultrafine particle formation in both regions and the absence of tidal influence at LI unlike some coastal sites represent further unknowns.

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