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Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer

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There has been considerable debate about the relative importance of sea-salt and sulphate from non-sea-salt sources in determining aerosol radiative effects in the marine boundary layer. In the marine boundary layer, the most numerous aerosols are volatile sulphate particles smaller than about 0.08 μm (ref. 1) and most of the aerosol mass is in a few sea-salt particles larger than 1 μm. Yet intermediate-size aerosols between about 0.08 and 1 μm diameter are the most relevant to the radiative forcing of climate because they efficiently scatter solar radiation and also serve as cloud nuclei². Indeed, Charlson *et al.*³ hypothesized that oceanic production of sulphate aerosols from the oxidation of dimethyl sulphide could be a powerful feedback in the climate system. It is generally assumed that marine aerosols smaller than about 1 μm are non-sea-salt sulphate, but a recent review cites indirect evidence that many aerosols in the sub-micrometre range contain at least some sea-salt^{4,5}. Here we present direct observational evidence from a remote Southern Ocean region that almost all aerosols larger than 0.13 μm in the marine boundary layer contained sea-salt. These sea-salt aerosols had important radiative

effects: they were responsible for the majority of aerosol-scattered light, and comprised a significant fraction of the inferred cloud nuclei.

The first Aerosol Characterization Experiment (ACE-1) included complementary techniques to assess the chemical and radiative properties of aerosols in the marine boundary layer (MBL). The composition of aerosols was measured by electron microscopy and mass spectrometry of single particles, aerosol volatility and bulk analysis of size-segregated aerosol samples. At Cape Grim, Tasmania (41°S, 145°E), the elemental composition of individual particles collected on filters and grids was determined using automated scanning and manual transmission electron microscopy (SEM),

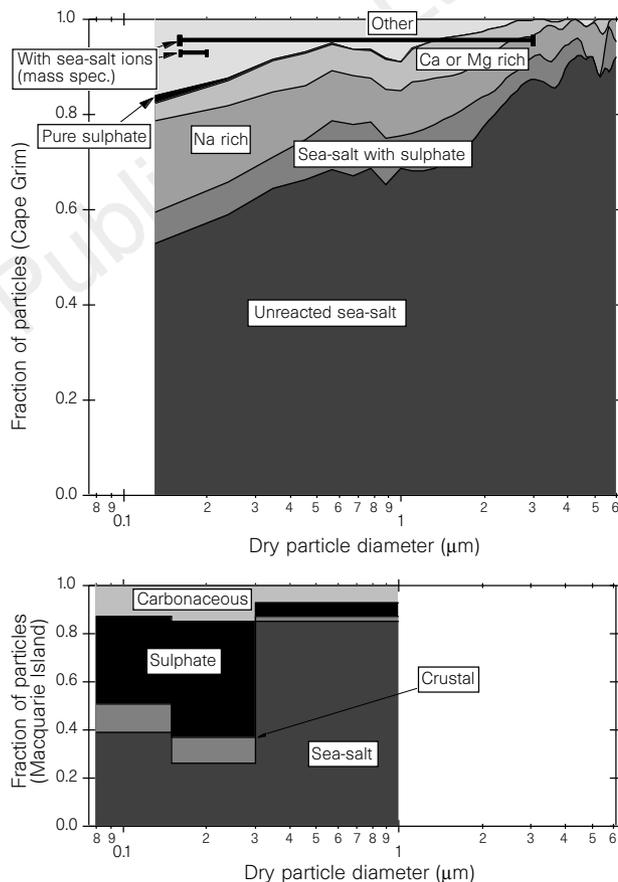


Figure 1 The chemical composition of particles at Cape Grim and Macquarie Island as a function of their diameter. Top, composition at Cape Grim from automated SEM analysis (filled areas, $n = 19,640$). Also shown are the fraction of particles analysed by mass spectrometry that contained detectable sea-salt ions ($n = 5,240$). The two bars are for samples taken with or without a mobility analyser to select only a limited size range for analysis. Bottom, composition at Macquarie Island from manual TEM analysis ($n = 4$ samples, 300 particles). SEM data at Cape Grim were classified using cluster analysis, then the clusters were grouped into the categories shown here 'Unreacted sea-salt' includes particles with elemental compositions very close to natural sea-salt. The 'other' category includes particles that contained only light elements, salt particles with compositions far from sea-salt, and unusual particles such as soot or metals. For samples from Macquarie Island, sea-salt-containing particles were defined as those containing appropriate quantities of Na, Mg, Ca, K and variable quantities of S, with or without measurable quantities of Cl. In the mass spectra, particles containing sea-salt were identified by the presence of Cl in the negative ions and Na or K in the positive ions. The mass spectrometer measured a higher fraction of sea-salt-containing particles because it is very sensitive to Cl and Na. However, as typified in Fig. 2, most of the mass spectra showed a substantial fraction of sea-salt.

TEM) with energy dispersive X-ray analysis^{6,7}. Electron microscope samples were taken only during clean air conditions from the 55 m level of a tower located on a 90 m cliff next to the ocean. Single particles sampled at Cape Grim were also analysed *in situ* with a laser ionization mass spectrometer^{8,9}. The elemental composition of individual particles collected at Macquarie Island (54° S, 158° E) was independently determined using TEM with energy dispersive X-ray analysis¹⁰⁻¹² and aerosol volatility. Onboard the NOAA ship *Discoverer*, a 7-stage multi-jet Berner-type impactor was used to sample aerosol from an inlet 18 m above the ocean surface for gravimetric and ion chromatographic analysis¹³.

The measurements made at Cape Grim, Macquarie Island, and onboard the *Discoverer* all showed sea-salt in the accumulation mode. Both the SEM and mass spectrometer data show that many particles at Cape Grim, even those smaller than 0.2 μm, contained elements characteristic of sea-salt (Figs 1 and 2). During unpolluted conditions, over 90% of aerosol particles larger than 0.13 μm diameter contained sea-salt and fewer than 1% of these were pure sulphate particles. The percentage of particles containing sea-salt dropped rapidly for smaller particles, with some suggestion (Fig. 1) that the change from sea-salt to sulphate was at a slightly larger size at Macquarie Island than at Cape Grim. For particles between 0.05 and 0.15 μm diameter, independent manual TEM analyses found sea-salt in 5 to 25% of the particles at Cape Grim and 5 to 47% of particles at Macquarie Island. Most 0.05 μm diameter aerosols were volatile at temperatures between 95 and 150 °C, indicating that they did not contain sea-salt. Microdiffraction patterns of particles smaller than 0.1 μm suggested an ammonium sulphate crystalline structure.

These data, which indicate a concentration of sea-salt-containing particles from about 30 to over 100 per cm³, differ from some previous estimates of fewer than 1 sea-salt particle per cm³ in the MBL^{3,14}. However, they agree with a recent parameterization of sea-salt particles⁴. The average wind speed at Cape Grim during clean periods of ACE-1 was 11 m s⁻¹. High wind speeds assist in the production of new sea-salt particles^{4,15}. However, it is difficult to explain the dominant role for sea-salt in ACE-1 based on wind speed alone. Some previous measurements in the Northern Hemisphere may have been influenced by anthropogenic sulphate, resulting in a larger role for sulphate particles than in the ACE-1 study area^{16,17}. For example, SEM analysis of particles at Spitsbergen and Bermuda by the same techniques used at Cape Grim found large concentrations of sulphate particles larger than 0.1 μm^{7,18}. Measurements elsewhere in the MBL have shown mixed results on the relative

importance of sulphate and sea-salt to submicrometre particles¹⁹⁻²². The ACE-1 study area had low sulphate concentrations: measurements on the *Discoverer* showed 150 ng m⁻³ compared to 1,300 ng m⁻³ for the Northern Hemisphere mid-latitudes and 400 ng m⁻³ for the equatorial Pacific²³.

The fraction of aerosol scattering and backscattering due to sea-salt or non-sea-salt (n.s.s.) sulphate aerosol was calculated using the aerosol chemical composition from impactor measurements, the particle size distribution and Mie scattering theory¹³. Size-segregated aerosol samples collected onboard the *Discoverer* were analysed gravimetrically and with ion chromatography (Fig. 3a). The ionic mass consisted of sea-salt, n.s.s. sulphate plus associated ammonium, and methanesulphonate (MSA, an oxidation product of dimethylsulphoxide, DMS). The size distribution for the calculations was derived from a differential mobility analyser for particles 0.02 to 0.57 μm in diameter and an aerodynamic sizer for particles from 0.85 to 5 μm. Measured sizes were converted to geometric sizes using densities derived from the impactor data¹³. Particles were assumed to be spherical and the sea-salt and n.s.s. sulphate were assumed to be in different particles. However, the assumption of an external or internal mixture does not significantly affect scattering calculations of salt and sulphates²⁴.

Most of the light scattering by the aerosol was due to sea-salt (Fig. 3b). Even considering just the submicrometre portion of the aerosol, over 75% of either the total scattering or backscattering was due to sea-salt. Sea-salt appears to have been the dominant chemical

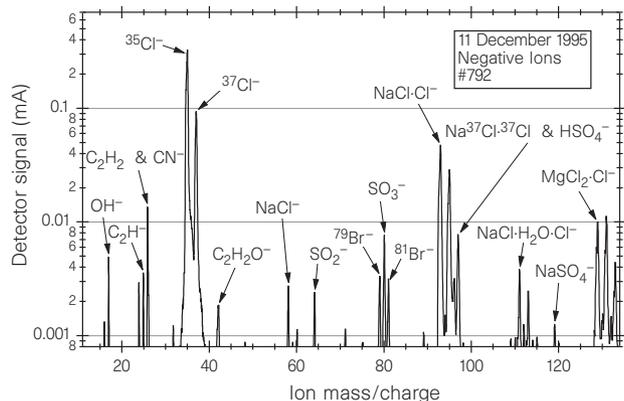


Figure 2 A typical negative ion mass spectrum of a single particle at Cape Grim. This particular spectrum is chosen to be as close as possible to the average of 0.17 μm dry diameter particles, as determined by a differential mobility analyser. The dominant peaks are from sea-salt, but sulphate and organic peaks are also present.

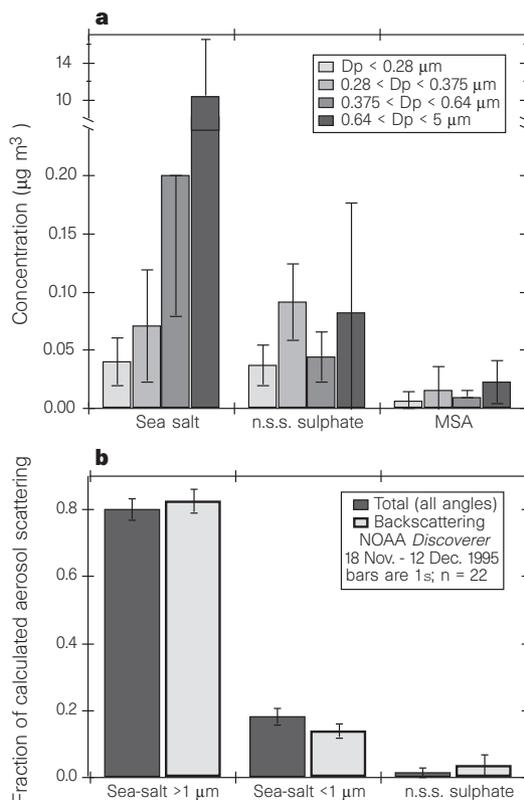


Figure 3 Composition and backscattering of aerosols. **a**, The chemical composition of aerosols for several size ranges measured from the NOAA *Discoverer* in the Southern Ocean. **b**, The calculated light scattering and backscattering at 550 nm due to sub- and supermicrometre sea-salt and n.s.s. sulphate. Because of its small mass fraction, the scattering due to MSA was negligible. Sea-salt dominated both the total scattering (all angles) and backscattering (hemispheric) by the aerosol. Total aerosol calculated backscatter was between 0.0005 and 0.004 km⁻¹.

constituent in determining the direct radiative effects of the aerosol in this remote Southern Ocean region.

The radiative forcing of aerosols through their influence on cloud nucleation processes has been estimated to be as large as that of the direct effect but has a much larger associated uncertainty which is partly due to the complex relationship between aerosol concentration and cloud droplet concentration²⁵. Changes in the number concentration of cloud condensation nuclei (CCN) can have an especially great influence on cloud albedo in the cleanest environments. In the MBL, the approximate size of particles serving as the smallest cloud nuclei can be determined from a minimum in the aerosol size distribution²⁶. Particles that act as cloud nuclei acquire additional mass nuclei, because of both liquid-phase chemistry and the large surface area for uptake of condensable species. When the clouds evaporate, the nuclei are larger than they were before the cloud processing. Smaller particles that do not act as cloud nuclei do not experience this growth. Repeated cycling through clouds creates a minimum in the size distribution at diameters of about 0.08 μm (Fig. 4a). We infer the number of cloud nuclei as $N_{0.08}$, the number of particles larger than 0.08 μm . This definition has the advantage that it reflects the supersaturations actually achieved in the MBL.

From the discussion above of sea-salt content in submicrometre aerosols, it might be expected that a large fraction of $N_{0.08}$ in the Southern Ocean region contained sea-salt. Measurements from Macquarie Island confirm this. The concentrations of non-volatile particles at 300 °C (Figure 4b) usually accounted for more than 50% of $N_{0.08}$. The time series of non-volatile particles and $N_{0.08}$ were also

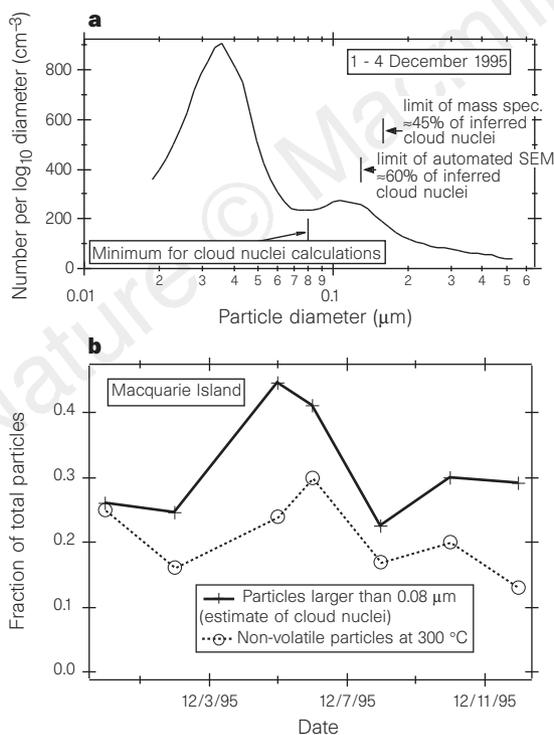


Figure 4 Size distribution and number of particles. **a**, An average size distribution from Macquarie Island while measuring pristine marine air. The distribution shows the characteristic dip near 0.08 μm caused by growth of certain particles in clouds²⁶. Most larger particles are cloud nuclei and most smaller particles are not. The units on the vertical axis are chosen for visual comparison: the number of particles in a given size range is proportional to the area under the curve in that range. The integral of this distribution is 470 cm^{-3} , which is a typical concentration of particles in a remote marine environment. **b**, The number of non-volatile particles and number of inferred cloud nuclei as fractions of the total number of particles measured at 25 °C. (Date is given as month/day/year.)

correlated. In addition to measuring the number of non-volatile particles at various temperatures, subsets of non-volatile particles were collected with a low-pressure impactor ($D_{50} = 0.06 \mu\text{m}$) for TEM analysis. These samples confirmed that most of the non-volatile particles at 300 °C were sea-salt and were large enough to act as cloud nuclei.

The correlation between seasonal cycles of CCN and MSA at Cape Grim has been used to support the theory that sulphate influences marine CCN concentrations^{27,28}. However, the strongest correlations were for CCN measured at a 1.2% supersaturation, which activates particles much smaller than those that actually serve as cloud nuclei in the MBL. Such smaller particles are mostly sulphate. The correlations were weaker at 0.23% supersaturation, which is more representative of the MBL¹. In addition, most of our data were taken before the DMS production in the ACE-1 region reached its annual peak in December of 1995.

Our results indicate an important role for submicrometre sea-salt particles in determining the radiative properties of aerosols in the remote MBL. The SEM, TEM, mass spectrometer and bulk analyses are all consistent with the presence of sea-salt in the vast majority of particles larger than 0.13 μm dry diameter. Although most of these particles contained sea-salt, the radiative properties are also influenced by other species. Non-seasalt sulphate may contribute enough mass to enlarge some of the smallest sea-salt particles to more effective cloud nuclei. The Cape Grim data show that many aerosols were internal mixtures (in the same particles) of sea-salt and sulphates. In such mixtures it is difficult to separate the contributions of sulphate and salt, especially because salt aerosols provide important reaction sites for converting SO_2 to sulphate^{17,29}. The Cape Grim mass spectrometer data indicate that organics also contribute a small fraction of the content of the submicrometre salt particles³⁰.

If sulphate particles acted as cloud nuclei, then some of them should have acquired enough additional mass through cloud processing to be large enough to be observed by the SEM and mass spectrometer. The rarity of pure sulphate particles larger than 0.13 μm at Cape Grim shows that particles formed through the condensation of sulphur-containing precursor gases did not often grow that large, at least not without coagulating with some sea-salt. This places a strong constraint on models of the dynamics of aerosols in the marine boundary layer, and may even indicate that few pure sulphate particles were acting as cloud nuclei in that region. □

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Transition from dome-forming to plinian eruptive styles controlled by H₂O and Cl degassing

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The transition from a plinian (pumice) to an effusive (dome-forming) eruptive style is frequently observed in volcanic systems and is generally attributed to the progressive loss of volatiles from magma stored in a superficial reservoir. This explosive–effusive transition has been explained by the evolution from a closed to an open system of degassing^{1–4}. But in this context, an eruption at Mt Pelée (Martinique, French West Indies) dated at 650 years ago, which exhibited a rarely observed^{5,6} succession from dome-forming to plinian activity in a short interval of time⁷, is at odds with such an explanation. In this eruption, near-surface explosions of the dome produced two peléean turbulent pyroclastic flows, whose

deposits are similar to those of the effusive 1902 eruption, and then plinian activity produced pumice fallouts and flows. The reconstruction of the degassing paths of both eruptive regimes using the densities and the H₂O and Cl contents of the clasts shows that the interaction of rising magma with hydrothermal fluids at shallow depth may play a critical role in determining eruptive style.

The differences in eruptive styles during the Mt Pelée eruption at 650 years before present (650 yr BP; the P1 eruption) are not related to differences in pre-eruptive conditions, as shown by the homogeneity of the mineralogical and the trace- and major-element compositions of all erupted magmas^{8,9}. However, the existence of ²³⁸U–²³⁰Th disequilibrium and some mobile-element anomalies (for example, arsenic) show that the dome-forming magma chemically interacted with fluids from the near-surface hydrothermal system⁸. Magma erupted during the plinian activity is in radioactive equilibrium and chemically homogeneous, showing that it has remained as a closed system from the magma source. To assess the degassing history of both eruptive regimes, geochemical and textural measurements have been made on clasts selected from the

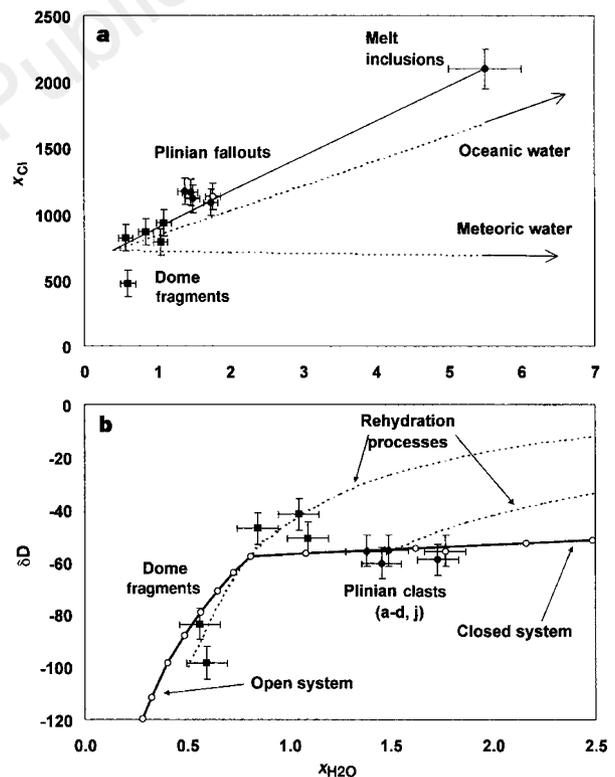


Figure 1 Correlations between x_{H_2O} , x_{Cl} and δD . Trends are shown for volcanic samples and also for rehydration by meteoric or oceanic water (dashed lines). **a**, H_2O and Cl contents of all clasts and pre-eruptive melts are well correlated, indicating a close degassing behaviour for both species. **b**, δD and H_2O contents may be well explained by simple closed- (plinian clasts) and open- (dome fragments) system degassing. (x_{Cl} is in p.p.m., x_{H_2O} is in %.) Closed-system degassing model is calculated for an initial δD value of -40 and $\alpha_{vapour-melt} = 1.02$. Open-system degassing model is calculated using a Rayleigh distillation law with an initial δD value of -58 and $\alpha_{vapour-melt} = 1.06$. Rehydration models (dashed lines) have been calculated using mixing with pure water with $\delta D = +10\%$. We note that late contamination cannot be ruled out for dome products, but the initial chemical homogeneity of P1 eruption magmas requires an open-system degassing to produce the less- H_2O -rich dome fragments. δD values are from B. R. Rahaingoson and P. A. Agrinier (personal communication). Here $\delta D = \{[(R/H)_R/(D/H)_S] - 1\} \times 10^3$, where R and S stand for rock and standard, respectively; $\alpha_{vapour-melt} = (D/H)_{vapour}/(D/H)_{melt}$.