

Unique ocean-derived particles serve as a proxy for changes in ocean chemistry

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[1] Oceans represent a significant natural source of gases and particles to the atmosphere. Relative to gas phase compounds, less is known regarding the influence of changes in biological activity in the ocean on the chemistry of sea spray aerosols produced in marine environments. To gain insight into the influence of ocean biology and chemistry on atmospheric aerosol chemistry, simultaneous real-time measurements were made of atmospheric aerosol size and chemical mixing-state, gas phase dimethyl sulfide (DMS), as well as seawater DMS and chlorophyll *a*. In three different marine environments with elevated chlorophyll *a* and DMS, unique Mg particles were detected containing Mg²⁺, Ca²⁺, K⁺, and organic carbon. These particles were segregated from sea salt particles highlighting that two subpopulations within the sea spray were being ejected from the ocean. Strong temporal correlations were observed between these unique ocean-derived particles and freshly emitted sea salt particles ($R^2 = 0.86$), particularly as wind speed increased to at least 10 m/s, and atmospheric DMS ($R^2 = 0.76$). Time series correlations between ocean measurements and atmospheric aerosol chemistry suggest that chlorophyll *a* and DMS serve as indicators of changes in the chemistry of the ocean, most likely an increase in organic material, which is directly reflected in the single particle mixing-state. This is the first time such *real-time* correlations are shown between ocean chemistry and atmospheric aerosol mixing-state. The reasons behind these observed changes in aerosol chemistry are critical for understanding the heterogeneous reactivity, water uptake, and cloud forming potential of sea spray aerosols.

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1. Introduction

[2] Aerosols influence global climate directly by scattering and absorbing incoming solar radiation and indirectly by acting as cloud condensation nuclei (CCN) [Lohmann and Feichter, 2005; Pöschl, 2005]. The size and chemical composition of aerosols influence whether particles can act as CCN and participate in cloud droplet formation [McFiggans *et al.*, 2006; Quinn *et al.*, 2008]. In the marine environment,

biological activity has been proposed to change the chemical composition of marine aerosols through secondary oxidation reactions involving the gaseous compound dimethyl sulfide (DMS) formed from the enzymatic cleavage of phytoplankton-derived dimethylsulfoniopropionate (DMSP) [Bates *et al.*, 1992; Andreae and Crutzen, 1997] and, more recently, by changing the chemical composition of primary sea spray aerosol [O'Dowd *et al.*, 2004]. Sea spray particles are directly emitted to the atmosphere primarily from air bubbles formed by breaking waves [O'Dowd and De Leeuw, 2007]. Bursting bubbles result in the formation of jet drops, which result from the breakup of the vertical jet of water that forms after the bubble cavity collapses, and the more numerous film drops, which result from the collapse of the thin film surrounding the bubble [Blanchard and Woodcock, 1957]. Bubble bursting can be enhanced by high wind velocities that increase whitecap production [Monahan *et al.*, 1983] and by the impact of raindrops on the ocean surface [Marks, 1990]. In addition to sea salt, organic material produced by marine biota can be ejected to the atmosphere from the bubble bursting mechanism. As bubbles rise in the water

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column, they can scavenge surface active material including organic matter and marine organisms, which become enriched in ejected sea spray particles compared to bulk seawater [Aller *et al.*, 2005; Blanchard, 1964; Blanchard and Syzdek, 1970; Cloke *et al.*, 1991; Duce and Hoffman, 1976; Zhou *et al.*, 1998]. Oceanic biological activity provides a source of both organisms as well as organic material to the ocean [Aluwihare and Repeta, 1999; Passow, 2002; Zhou *et al.*, 1998], and thus can directly impact the chemical composition of sea spray particles. A number of publications highlight the influence of biological activity on the chemical composition of marine aerosols through the enrichment of organic material, particularly in submicron particles [Bigg, 2007; Bigg and Leck, 2001, 2008; Blanchard, 1964; Cavalli *et al.*, 2004; Duce and Hoffman, 1976; Facchini *et al.*, 2008; Keene *et al.*, 2007; Leck and Bigg, 2005a, 2005b, 2008; Leck *et al.*, 2002; Mayol-Bracero *et al.*, 2001; Middlebrook *et al.*, 1998; Novakov *et al.*, 1997; O'Dowd *et al.*, 2004; Oppo *et al.*, 1999; Russell *et al.*, 2010; Yoon *et al.*, 2007]. Primary organic material resulting from bubble bursting is water insoluble in nature [Ceburnis *et al.*, 2008; Leck and Bigg, 2005a; Facchini *et al.*, 2008]. These primary organic particles are proposed to grow large enough to act as CCN through the condensation of DMS oxidation products potentially linking marine biota, sea spray aerosol, clouds, and climate [Leck and Bigg, 2005a, 2005b, 2007].

[3] Exopolymeric secretions (EPS) represent one large source of organic material in the ocean. EPS constitutes ~10% of the dissolved organic material (DOM) pool (7×10^{16} gC) [Chin *et al.*, 1998; Orellana *et al.*, 2007; Orellana and Verdugo, 2003; Verdugo *et al.*, 2008] that, unlike most DOM, is bioavailable making EPS one of the most significant contributors to the global carbon cycle [Verdugo *et al.*, 2008]. EPS or microgels are the result of gel assembly/dispersion equilibria from dissolved polymers (namely polysaccharides, proteins, and lipids) [Chin *et al.*, 1998; Verdugo *et al.*, 2004; Wells, 1998]. The polymer network of these microgels has been shown to be stabilized through ionic bonding with the use of divalent cations (Ca^{2+} , Mg^{2+}) [Chin *et al.*, 1998; Verdugo *et al.*, 2004; Wells, 1998]; the detection of EPS in the atmosphere has been highlighted in previous publications [Bigg and Leck, 2001, 2008; Leck and Bigg, 2005a, 2005b, 2008; Leck *et al.*, 2002]. Hence, in addition to being a source of organic carbon, atmospheric enrichment of inorganic ions associated with EPS could also occur in the marine environment. However, in contrast to the observed enrichment of organic material, enrichment of inorganic ions in sea spray aerosol compared to bulk seawater has been difficult to discern particularly in ambient measurements. The lack of conclusive evidence stems primarily from the inability of measurement methods to distinguish between inorganic ions directly ejected in marine particles versus input into the ocean from inorganic ions in atmospheric aerosols such as dust [Duce and Hoffman, 1976; Hoffman *et al.*, 1980]. Hence, without being able to directly determine the origin of the particles (i.e., ocean versus atmosphere), it is impossible to positively correlate changes in inorganic constituents in atmospheric aerosols with changes in ocean chemistry induced by biological activity.

[4] Understanding how ocean-derived organic compounds and inorganic ions are distributed within individual sea spray

particles (i.e., whether they are internally or externally mixed with other chemical compounds) is a requirement for properly assessing the heterogeneous reactivity, water uptake, and cloud nucleating abilities of marine-derived particles. Bulk, filter-based techniques collect chemical information over a relatively broad size range and provide an average picture of the ambient aerosol that may not be representative of any individual particles within the aerosol population. O'Dowd *et al.* [2004] hypothesized that the manner in which submicron organic material was mixed with sea spray aerosol would greatly impact the cloud droplet number concentration that could potentially be formed over the ocean during periods of high biological activity. Single-particle techniques elucidate the chemical mixing-state of individual particles. However, these measurements have been extremely scarce in marine environments. Electron microscopy has been used in marine environments to detect both single particles composed of organic material and bacteria in the absence of sea salt as well as sea salt particles associated with surface active EPS [Bigg and Leck, 2001, 2008; Leck and Bigg, 2005a, 2005b, 2008; Leck *et al.*, 2002; Pósfai *et al.*, 2003]; real-time single particle mass spectrometry observed the presence of organic material internally mixed with sea salt particles [Middlebrook *et al.*, 1998]. No previous studies have simultaneously probed *real-time* changes in single particle chemistry and changes in ocean chemistry with high time resolution.

[5] Aerosol time-of-flight mass spectrometry (ATOFMS) measurements of marine aerosols were conducted during three field campaigns in the eastern Pacific Ocean, Indian Ocean, and the western Pacific Ocean. ATOFMS can be used to differentiate between particle sources (e.g., marine versus continental) and particle age (reacted versus fresh sea salt) [Guazzotti *et al.*, 2001] as well as determine the chemical mixing-state (e.g., organics internally or externally mixed with sea salt) of individual particles in real-time [Noble and Prather, 1996]. Observations of marine aerosols in all of these campaigns reveal unique chemical fingerprints of ocean-derived particles during time periods influenced by increased levels of phytoplankton biomass (chlorophyll *a*) and/or DMS concentrations. The ocean-derived individual particles described herein are characterized by an enrichment of Mg^{2+} and/or Ca^{2+} , and organic carbon with K^+ . We hypothesize that the detection of these particles in the marine atmosphere serves as a proxy for changes in ocean chemistry. The atmospheric implications of these findings are discussed.

2. Experimental Setup

2.1. Single-Particle Measurements Using Aerosol Time-of-Flight Mass Spectrometry

[6] ATOFMS measurements were made aboard the NOAA RV Ronald H. Brown during the Indian Ocean Experiment (INDOEX) in March 1999 [Lelieveld *et al.*, 2001] and the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) from March–April 2001 [Huebert *et al.*, 2003]. Ground-based measurements were made during the Cloud Indirect Effects Experiment (CIFEX) at the coastal site Trinidad Head, CA in April 2004. The sampling inlet for all three studies was heated to control relative humidity (RH) at

55% [Bates *et al.*, 2004]. The details of each of these campaigns can be found in Table S1 and the cruise tracks of ACE-Asia and INDOEX can be found in Figure S1 of the auxiliary material.¹ ATOFMS makes real-time measurements of the aerodynamic size and chemical composition of individual particles between 0.2 and 3 μm diameter. A full description of the instrument has been given previously [Gard *et al.*, 1997; Prather *et al.*, 1994]. Briefly, aerosols are continuously pulled by vacuum into the instrument through a nozzle inlet and interface region, which collimates the particles into a narrow beam. Each particle passes through two continuous wave lasers (532 nm) separated by a known distance, producing scattered light signals, which are detected by two photomultiplier tube detectors. The time taken for each particle to traverse between the laser beams provides a measure of the aerodynamic diameter of each particle. The transit time and light signals are also used to trigger a third pulsed laser passing through the ion source region of a time-of-flight mass spectrometer. When each sized particle arrives in the ion source region, a pulsed UV laser fires to induce laser desorption/ionization, producing positive and negative ion mass spectra for each particle. The mass spectra show the chemical associations within each particle and can be coupled with the size information to derive size-resolved composition distributions of particles. Size-resolved chemical composition was monitored continuously and subsequently averaged into 1-h time bins; data is presented in this paper as day of year (DOY).

[7] The single particle mass spectra generated by this technique were imported into Matlab (The MathWorks, Inc.) using a software toolkit, YAADA [Allen, 2002]. An adaptive neural network (ART-2a), was used to classify particles based on the mass spectral peaks and intensities into distinct “clusters” indicative of particle sources and chemistry [Noble and Prather, 1996; Song *et al.*, 1999]. Each ion peak assignment presented in this paper corresponds to the most likely ion produced at a given mass-to-charge (m/z) (see Table S2). Particle types described in this paper are defined by characteristic ion peaks and/or possible sources and do not reflect all of the compounds present within a particular particle class.

2.2. Laboratory Bubble Bursting Experiments

[8] Natural seawater was collected on June 15, 2005 at the Scripps Institution of Oceanography pier and immediately used to generate sea spray aerosol particles in the laboratory. The collected seawater sample was divided into two aliquots and particle generation was performed either by atomizing or bubbling the seawater solution. The details of the apparatus used to generate sea spray aerosol through bubble bursting is provided by Moore *et al.* [2011]. Briefly, the apparatus consisted of a glass jar (ID ~ 70 mm, height ~ 120 mm), L-shaped glass tube with a fritted glass head (size of frit: ID = 5 mm, L = 10 mm, maximum pore size = 25–50 μm), and gas dispersion tube for particle carrier flow. Approximately 150 mL of seawater was added to the glass jar and the fritted glass bubbler head was placed approximately 15 mm below the surface of the seawater. A tube used to disperse the

carrier gas was placed about 25 mm above the surface of the seawater sample. Flow to the fritted glass bubbler head and carrier gas dispersion tube was regulated by mass flow controllers at 0.04 lpm and 1.0 lpm, respectively. For the atomizing generation method, ~ 150 mL of seawater was used; the tip of the atomizer spraying head, where sample seawater was aspirated, was placed about 10–15 mm below the surface of the seawater. To maintain the aspiration of seawater and subsequent atomizing, a flow rate of 1.1 lpm was used in this experiment. The particle concentration was reduced by subtracting 1.08 lpm of the atomizer output flow leaving only 0.02 lpm of the sample gas stream to reach the flow tube for further drying. This modification also produced a particle concentration similar to that generated by bubbling and was done to avoid coincidence errors in the ATOFMS where one particle causes the first light scattering signal and a different, faster particle, causes the second light scattering signal.

[9] The generated sea spray droplets were then introduced to a glass flow tube (ID = 48 mm, L = 1500 mm) where RH was kept low (RH ~ 1 –3% for atomizing and ~ 13 –15% for bubbling) by the co-infusion of dry nitrogen gas (RH $\sim 0\%$, 10 lpm for atomizing and 5 lpm for bubbling). The residence time of the gas stream in the flow tube was about 20–30 s, which was long enough to dry the liquid sea spray droplets. About 1 lpm of the airflow from the output of the flow tube was introduced to the ATOFMS. The excess sample flow was monitored by a RH/temperature sensor (HMP-237, Vaisala, Helsinki, Finland). Nitrogen gas was provided by a liquid nitrogen tank throughout the experiment and was filtered through a HEPA filter (HEPA capsule, Pall, NY, USA) to remove any particles. The temperature of the nitrogen gas was kept constant (25°C) by passing the gas through a temperature-regulated water bath. All experiments were conducted at room temperature.

2.3. Chlorophyll *a* and DMS Measurements

[10] Measurements of DMS (seawater and atmospheric) were made during the ACE-Asia and INDOEX field campaigns; chlorophyll *a* was only measured during INDOEX. Chlorophyll *a* is a proxy for phytoplankton biomass. As stated earlier, DMS is produced from the enzymatic cleavage of DMSP. It should be noted that the production of DMS is highly species specific [Keller *et al.*, 1989] and, as such, DMS concentrations are correlated with biological activity over large regional scales; however, DMS is typically poorly correlated with total phytoplankton biomass on smaller regional scales [Bates *et al.*, 1994; Leck *et al.*, 1990]. DMS concentrations also depend on complex biological and ecological processes [Bates *et al.*, 1994; Leck *et al.*, 1990] causing DMS to be a non-conservative tracer of biological activity.

[11] Ambient air and seawater were analyzed for DMS concentrations using an automated collection/purge and trap system [Bates *et al.*, 2000; Cooper and Saltzman, 1993]. Air samples were pulled through a Teflon filter and tubing to the analytical system where 0.1 lpm of the 4 lpm flow was pulled through a KI solution in the analytical system to eliminate oxidant interferences. The air sample volume ranged from 0.5 to 1.5 L depending on the DMS concentration. Seawater samples were collected from the ship’s seawater pumping system, which had an inlet located near

¹Auxiliary materials are available in the HTML. doi:10.1029/2010JD015289.

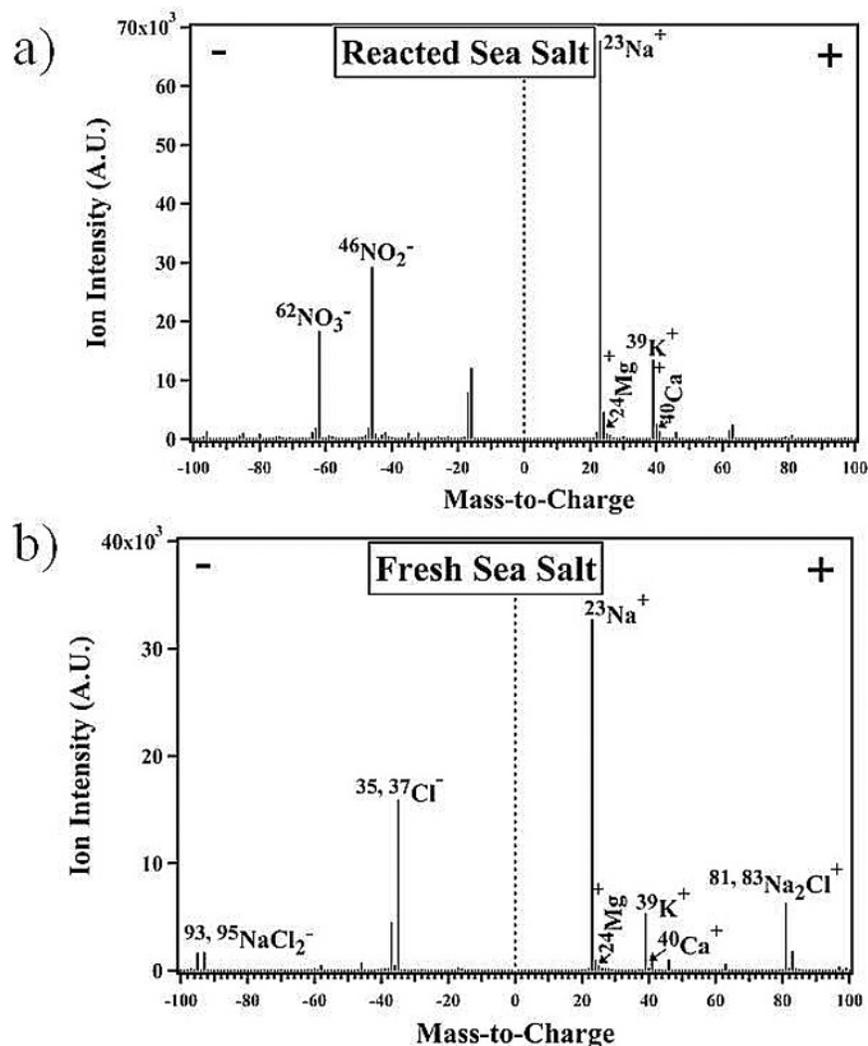


Figure 1. Mass spectra of individual particles representative of (a) reacted and (b) fresh sea salt.

the ship's bow at a depth of approximately 4 m. The samples were purged with hydrogen at 0.08 lpm for 5 min. Water vapor in either the air or purged seawater sample stream was removed by passing the flow through a -25°C Teflon tube filled with silanized glass wool. DMS was then trapped in a -25°C Teflon tube filled with Tenax. At the end of the sampling/purge period, the coolant was pushed away from the trap and the trap was electrically heated allowing DMS to desorb onto a DB-1 mega-bore fused silica column where the sulfur compounds were separated isothermally at 50°C and quantified with a sulfur chemiluminescence detector. System blanks were below detection limit. Water samples are reported in units of nanomoles/liter (nM). Air samples are reported in units of parts-per-trillion by volume (ppt). The mixing ratios were calculated at standard temperature (25°C) and pressure (1013 mbar) such that 1 nanomole/ m^3 equals 24.5 ppt.

[12] Continuous chlorophyll *a* measurements were made using a Turner 10-AU-005 fluorometer with a flow-cell. The distilled water blank (generally 4 mV) was subtracted from the remaining data (millivolt readings from 4 to 3000).

The detection limit (instrument resolution above zero) was 0.02 $\mu\text{g/L}$.

3. Results and Discussion

3.1. Chemical Composition of Particles in a Marine Environment

[13] ATOFMS can be used to distinguish between the relative proportions of fresh and reacted sea salt particles in marine environments based on their characteristic mass spectra [Gard *et al.*, 1998]. Representative mass spectra of reacted and fresh sea salt particles taken from the CIFEX field campaign are shown in Figure 1. In addition to an intense sodium peak ($^{23}\text{Na}^+$), fresh, unreacted sea salt particle spectra contain intense chloride ions ($^{81,83}\text{Na}_2\text{Cl}^+$, $^{35,37}\text{Cl}^-$, $^{93,95,97}\text{NaCl}_2^-$, etc.) in addition to smaller ion peaks from minor constituents such as $^{24}\text{Mg}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$, etc. Reacted sea salt contains secondary components including nitrate ($^{108}\text{Na}_2\text{NO}_3^+$, $^{46}\text{NO}_2^-$, $^{62}\text{NO}_3^-$) and sulfate ($^{165}\text{Na}_3\text{SO}_4^+$, $^{97}\text{HSO}_4^-$) formed by reactions of sea salt with acidic gases such as $\text{HNO}_{3(\text{g})}$ and $\text{H}_2\text{SO}_{4(\text{g})}$, which heterogeneously displace chloride [Gard *et al.*, 1998].

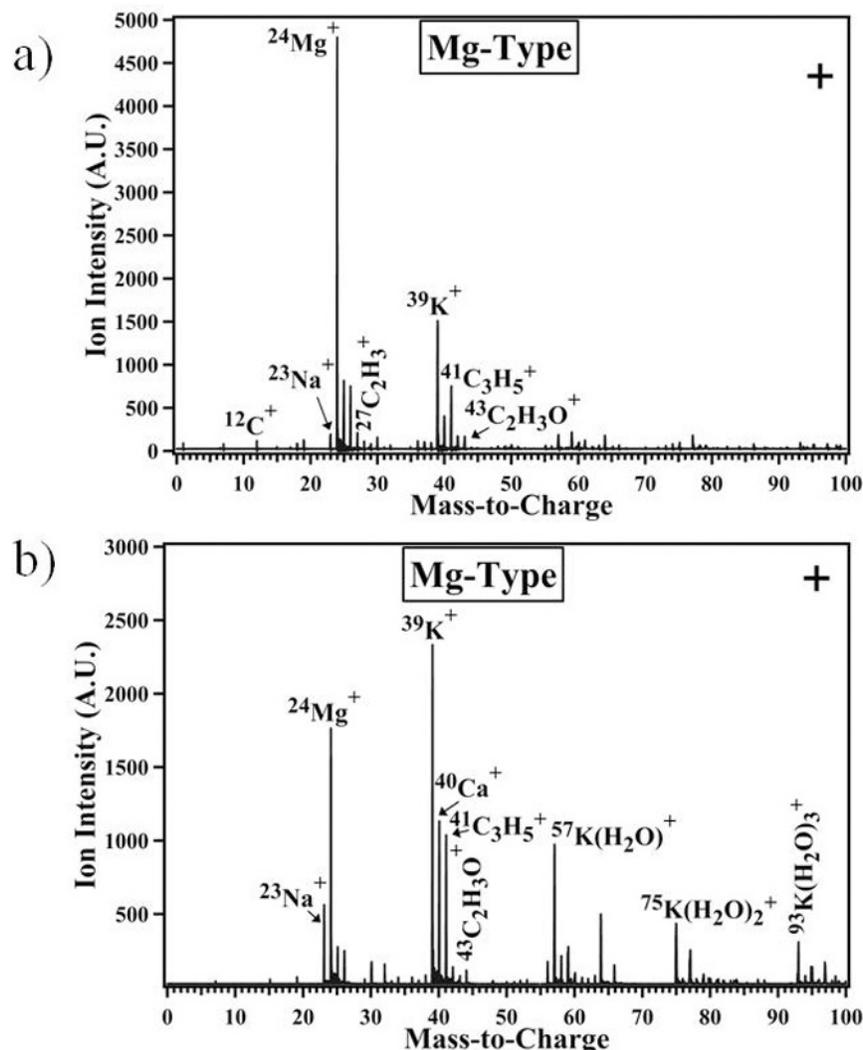


Figure 2. (a and b) Mass spectra of individual representative Mg-type particles containing $^{24}\text{Mg}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$, and organic carbon.

As such, distinctions between fresh and reacted particle types described herein are defined based on the relative intensities of chloride and nitrate peaks with fresh sea salt having more intense chloride peaks and reacted sea salt having more intense nitrate ion peaks. Reacted sea salt occurs in marine regions with low wind speed as a background marine particle type and is typically not temporally correlated with freshly emitted sea salt particles.

3.2. Chemical Composition of Particles in Regions With Elevated DMS and/or Chlorophyll *a*

[14] In addition to the fresh and reacted sea salt particles described above, particles measured in marine environments with elevated DMS and/or chlorophyll *a* revealed a unique and ubiquitous mass spectral signature containing Mg^{2+} , Ca^{2+} , K^+ , and organic carbon [Coffee, 2002]. It is important to note that these particles have not been detected in non-marine environments. Their mass spectra contain intense peaks due to $^{24}\text{Mg}^+$ and/or $^{40}\text{Ca}^+$ as well as $^{39}\text{K}^+$ and less intense organic ions (e.g., $^{27}\text{C}_2\text{H}_3^+$, $^{29}\text{C}_2\text{H}_5^+$, $^{41}\text{C}_3\text{H}_5^+$, $^{43}\text{C}_2\text{H}_3\text{O}^+$, $^{50}\text{C}_4\text{H}_2^+$) (see Figures 2a and 2b for example

mass spectra from INDOEX). Many of these particles lacked negative ion spectra even when a heated inlet was used to control RH at 55% [Bates *et al.*, 2004] during all three field campaigns. Using laser desorption/ionization as the ionization technique, a lack of negative ion spectra indicates the presence of particle-phase water [Neubauer *et al.*, 1997, 1998]. In contrast, sea salt particles typically produced both positive and negative ion spectra at the same RH, indicating that these unique particles have hygroscopic properties that differ from pure sea salt. Since Mg was often observed as the most intense ion in these ocean-derived particles, we refer to these particles herein as Mg-type particles. The mass spectral characteristics used to define the Mg-type particles (e.g., intense ion signal from $^{24}\text{Mg}^+$ and/or $^{40}\text{Ca}^+$ as well as $^{39}\text{K}^+$, lower intensity ion signals from organic carbon peaks, and a lack of negative ion spectra) were common across all three field campaigns.

[15] The Mg-type particles observed in marine environments are chemically distinct from sea salt and continental sources such as dust. In sea salt particles, the dominant peak is typically $^{23}\text{Na}^+$ rather than $^{24}\text{Mg}^+$ (see Figure 1b)

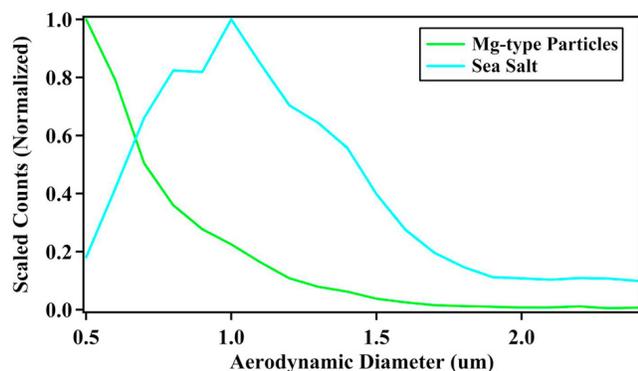


Figure 3. Number size distributions for Mg-type (green line) and sea salt (blue line) particles sampled at 55% RH during CIFEX. Particle counts have been scaled using an aerodynamic particle sizer (APS) to account for transmission biases in the ATOFMS. Particle counts have been normalized to total counts per size bin to show the relative fractions of scaled counts per size.

[Gross *et al.*, 2000; Guazzotti *et al.*, 2001] due to the higher concentration of Na^+ in seawater and also due to the lower ionization potential of Na versus Mg (5.14 eV versus 7.65 eV) [Lide, 2009] (see auxiliary material for detailed discussion) [Gross *et al.*, 2000]. However, the ratio of $^{23}\text{Na}^+$ to $^{24}\text{Mg}^+$ present in the Mg-type particles is reversed indicating that these particles represent a distinct aerosol population. Most Mg-containing dust particles also produce $^{27}\text{Al}^+$ and $^{56}\text{Fe}^+$ along with silicate peaks in the negative ion spectra [Silva *et al.*, 2000] (see Figure S2 for comparison). These peaks are absent from these marine Mg-type particles.

[16] Further evidence that Mg-type and sea salt particles represent distinct sea spray aerosol populations is shown during CIFEX where Mg-type particles were enhanced in smaller particle sizes compared to sea salt particles. ATOFMS has known transmission biases based on the inlet design that affect the raw number size distribution obtained with the instrument [Allen *et al.*, 2000; Dall'Osto *et al.*, 2006]; however, number concentrations obtained from ATOFMS can be corrected using a scaling factor derived from a sizing instrument such as an aerodynamic particle sizer (APS) to obtain accurate particle counts for discrete size bins [Qin *et al.*, 2006]. Since the lower limit of the APS is 0.5 μm , ATOFMS counts are only scaled down to this size even though the nozzle inlet ATOFMS can analyze particles down to 0.2 μm . Figure 3 shows scaled particle number counts normalized to the total particle counts per size range taken over several days during CIFEX for the two different particle types. As shown, sea salt particles peak in the supermicron size mode while Mg-type particles peak in the submicron size mode. We note that the observation of the Mg-type particles in smaller sizes compared to sea salt was observed for CIFEX; however, some variability in this result is expected for other studies. The enhancement in Mg-type particles in smaller sizes depends on conditions that affect the formation of this particle type such as wind speed; further research will be done to verify these results for differing oceanic and meteorological conditions.

[17] The particle types described in this paper contain intense inorganic peaks (e.g., Mg^{2+} , Ca^{2+} , K^+); however, in

the ATOFMS, the presence of inorganic ions in low relative abundance (<1–2%) along with water can suppress ion signal intensities particularly for some organic compounds, making the particles appear mostly inorganic [Gross *et al.*, 2000]. Thus, it is likely that the overall increase in absolute Mg^{2+} mass from these particles is quite small, and the particles contain a significant amount of organic material. Further support for this is given during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) [Heard *et al.*, 2006] when Mg-type particles detected using ATOFMS and high organic mass concentrations detected by aerosol mass spectrometry (AMS) were observed simultaneously in a pristine marine region at Mace Head [Dall'Osto *et al.*, 2005]. In these same marine regions where Mg-type particles are present, the number of total submicron particles that scatter light but are not chemically analyzed by ATOFMS increases. At this juncture, we can only hypothesize that these particles are composed of long chain hydrophobic organic species that do not absorb the 266 nm radiation. Overall, these observations suggest that the Mg-type particles detected online by the ATOFMS could serve as a proxy for an increase in carbonaceous material in the ocean in the dissolved and particulate phase that are transferred to the atmosphere through bubble bursting.

3.3. Evidence of an Oceanic Source for Mg-Type Particles

[18] If the Mg-type particles represent fresh, oceanic emissions rather than continental emissions, they should be temporally correlated with fresh sea salt particles. Measurements carried out during the CIFEX field campaign in Trinidad Head on the northern California coast exhibited relatively clean marine background sampling conditions over several days allowing for direct comparison between fresh sea salt and Mg-type particles. Before the campaign began, a rain event occurred on DOY 90 causing the percentage of reacted sea salt (indicated by the presence of nitrate ions) to decrease from 70 to 90% of the sea salt particles to 20%, whereas fresh sea salt increased to ~60% and a subsequent increase in the percentage of Mg-type particles also occurred. The increase in Mg and fresh sea salt particles mostly likely occurred because of an enhancement in the bubble bursting mechanism induced by high winds (reaching up to ~20 m/s) [Monahan *et al.*, 1983] and raindrops impacting the ocean surface [Marks, 1990]. To further probe whether a primary, oceanic source was responsible for the detection of Mg-type particles, the time series of Mg-type particles, fresh sea salt, reacted sea salt, and wind speed was compared for DOY 104–114 (Figure 4a). As shown in Figure 4, the time series of the Mg-type particles were strongly correlated ($R^2 = 0.86$) with that of freshly ejected sea salt particles (Figure 4b) particularly as the wind speed increased to at least 10 m/s; conversely, Mg-type particles were not correlated with reacted sea salt particles ($R^2 = 0.05$) (Figure 4c) or with dust particles ($R^2 = 0.04$) suggesting that Mg-type particles represent freshly emitted particles from the ocean via bubble bursting.

3.4. Temporal Correlations of Mg-Type Particles With DMS and Chlorophyll *a*

[19] During the INDOEX field campaign, measurements of atmospheric and seawater DMS and chlorophyll *a*

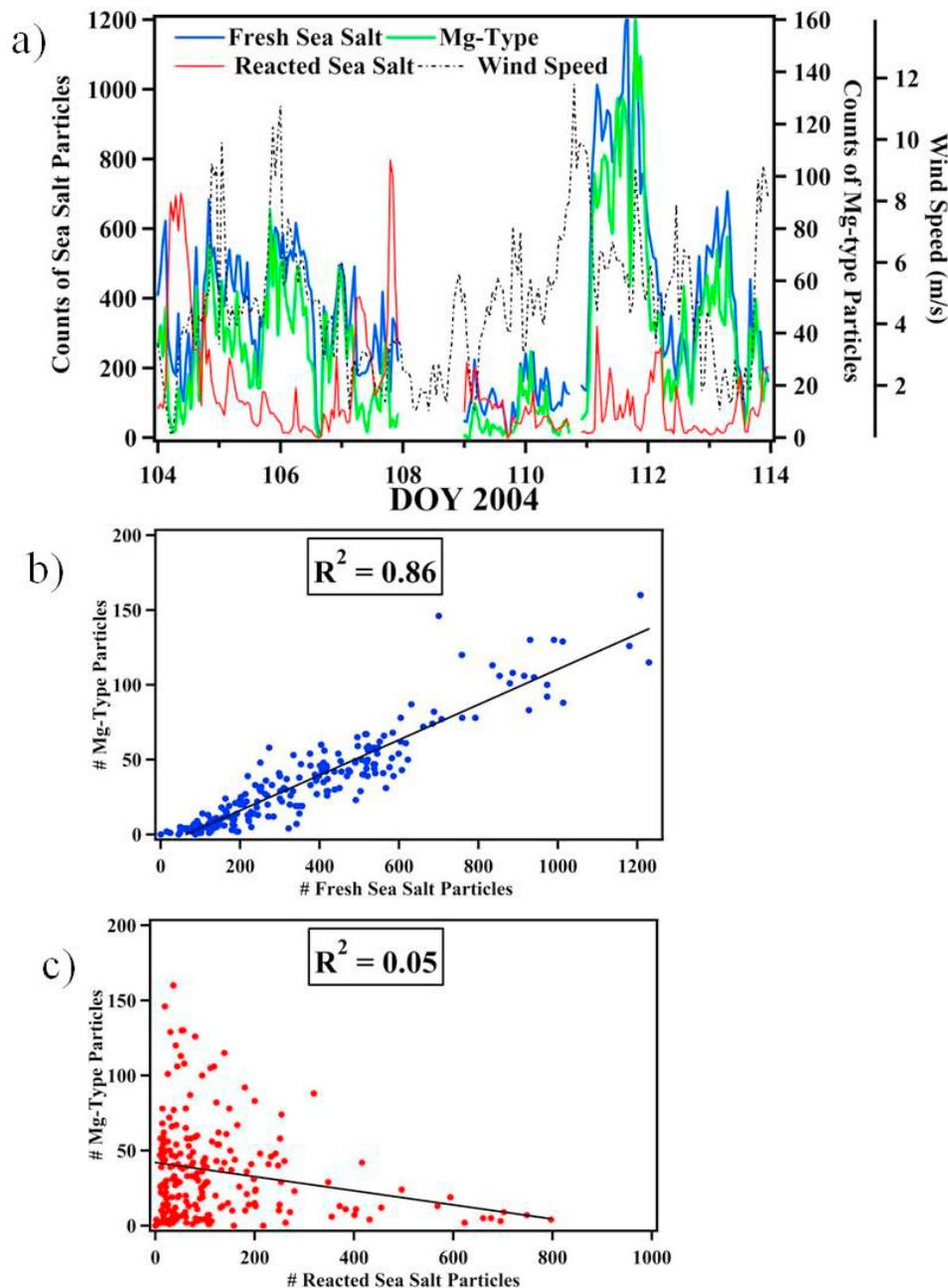


Figure 4. (a) Hourly time series of ATOFMS measurements showing the evolution of fresh, unreacted sea salt particles (blue line), Mg-type particles (green line), reacted sea salt particles (red line), and wind speed (black dotted line) during CIFEX. Scatterplots of particle counts show correlations between (b) Mg-type and freshly ejected sea salt particles and (c) Mg-type and reacted (background) sea salt particles.

concentrations were made concurrently with ATOFMS measurements. Figure 5 shows a time series of changes in Mg-type particles, dust particles, atmospheric DMS, and chlorophyll *a* as a function of cruise track during INDOEX. As the ship passed through the Intertropical Convergence Zone (ITCZ) and moved into the southern Indian Ocean, higher levels of chlorophyll *a* were observed in addition to high concentrations of DMS, both atmospheric and oceanic (see Figure 5) [Kumar *et al.*, 2002; Shenoy *et al.*, 2002]. Continental particle types were not transported across the ITCZ [Norman *et al.*, 2003], as shown in Figure 5, where the

percentage of dust particles reached zero at the southernmost point of the cruise. Overall, these observations suggest that particles encountered in the southern Indian Ocean were exclusively of marine origin. During the beginning of the cruise on DOY 74–76, fresh sea salt constituted up to ~60% of the particles; however, Mg-type particles were typically < 1% of the detected particles highlighting the observation that Mg-type particles are not always present in marine environments. Mg-type particles increased from 0% of the particles north of the ITCZ up to 14% of the particles south of the ITCZ during periods when wind speeds increased up to

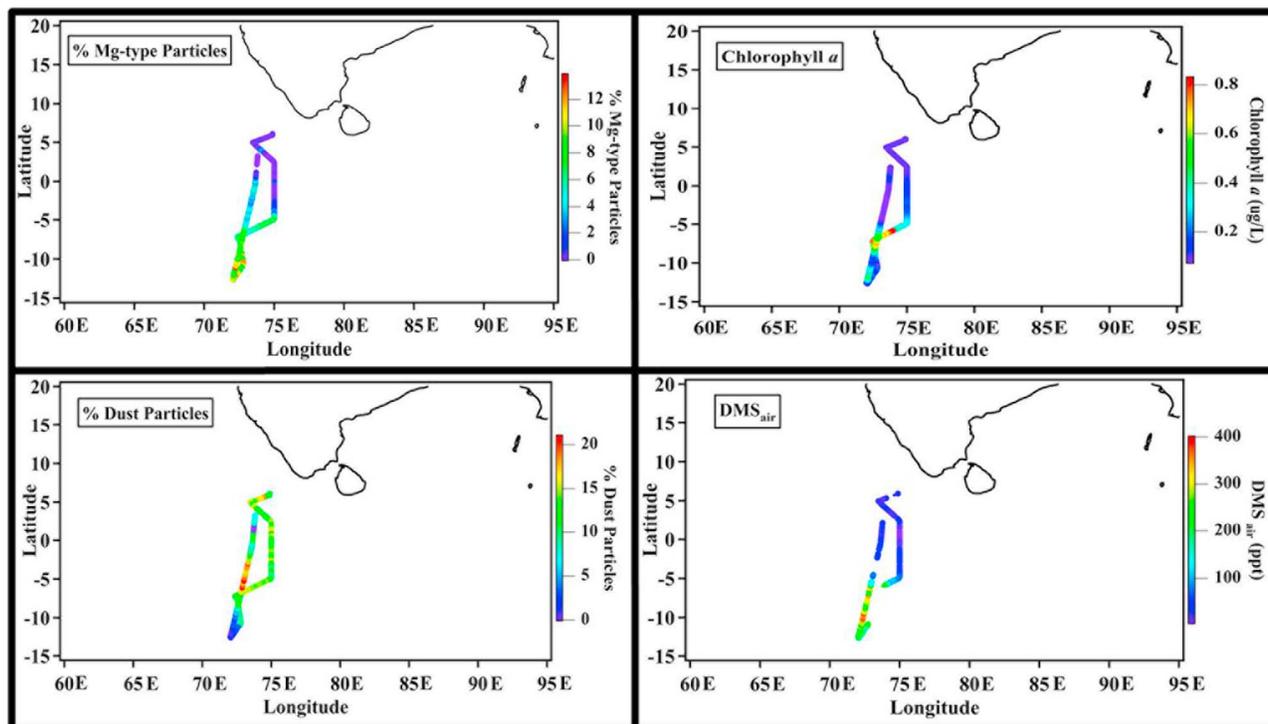


Figure 5. Percentages of (top left) Mg-type particles, (top right) chlorophyll *a* concentrations, (bottom left) dust particles, and (bottom right) atmospheric DMS concentrations as a function of cruise position during INDOEX.

12 m/s (see Figure S3 of the auxiliary material for further discussion) and as atmospheric DMS and chlorophyll *a* concentrations rose. Interestingly, unique S-ions were also detected in the southern Indian Ocean during periods of elevated Mg-type particles. This unique particle type will be the subject of a future publication by our group (C. J. Gaston et al., manuscript in preparation, 2011a). Figure 6 shows the correlations between Mg-type particles and dust observed by ATOFMS, DMS, and chlorophyll *a*. Mg-type particles were found to be anti-correlated with dust particles supporting their marine rather than continental origin. Mg-type particles were found to have a strong, positive correlation with atmospheric DMS ($R^2 = 0.76$), a positive correlation with seawater DMS ($R^2 = 0.48$), and a weak positive correlation with chlorophyll *a* ($R^2 = 0.25$). Similar correlations between atmospheric DMS and Mg-type particles ($R^2 = 0.54$) were also observed during ACE-Asia in 2001 on DOY 82–84 when clean marine conditions were encountered, as indicated by air mass back-trajectories and low radon concentrations [Bates et al., 2004]. Chlorophyll *a* was not measured during ACE-Asia. Overall, these correlations between Mg-type particles, atmospheric DMS, and chlorophyll *a* concentrations suggest that the Mg-type particles are detected due to changes in ocean chemistry associated with biological activity.

3.5. Laboratory Investigations of Ocean-Derived Particles via Bubble Bursting

[20] In order to better understand the differences in marine particle signatures observed in the ambient measurements, laboratory investigations were performed. Figure 7 shows the percentages of the different particle types formed by

bubbling and atomization generation methods, using the same seawater sample collected at the Scripps Institution of Oceanography pier. While sea salt is formed using both methods, the main difference is the enhancement in the percentage of Mg-type particles (light and dark green traces) when the seawater was bubbled (Figure 7a) rather than atomized (Figure 7b). This agrees with previous findings that the physicochemical properties of sea spray aerosol depend on the aerosol generation technique [Fuentes et al., 2010a]. The likely explanation for the increase in Mg-type particles when seawater is bubbled rather than atomized is that bubbles scavenge organic material along with any associated inorganic ions causing these compounds to be enriched in individual particles produced when the bubbles burst. Additional laboratory studies have been conducted to further characterize the single particle composition of sea spray aerosol using ATOFMS and are the focus of a future publication by our group (C. J. Gaston et al., manuscript in preparation, 2011b). While these laboratory studies demonstrate that Mg-type particles can be produced by bubble bursting using this particular set-up, this laboratory set-up may not be representative of the full complexity of sea spray aerosol generation under ambient oceanic conditions. Current efforts are underway in our group to test how different sea spray generation methods affect the chemistry of wave and bubble generated sea spray aerosols.

3.6. Impact of Chemical Segregation on Single-Particle Mixing-State

[21] The term chemical fractionation in marine aerosols typically describes the situation where certain chemical compounds exhibit higher concentrations relative to Na^+

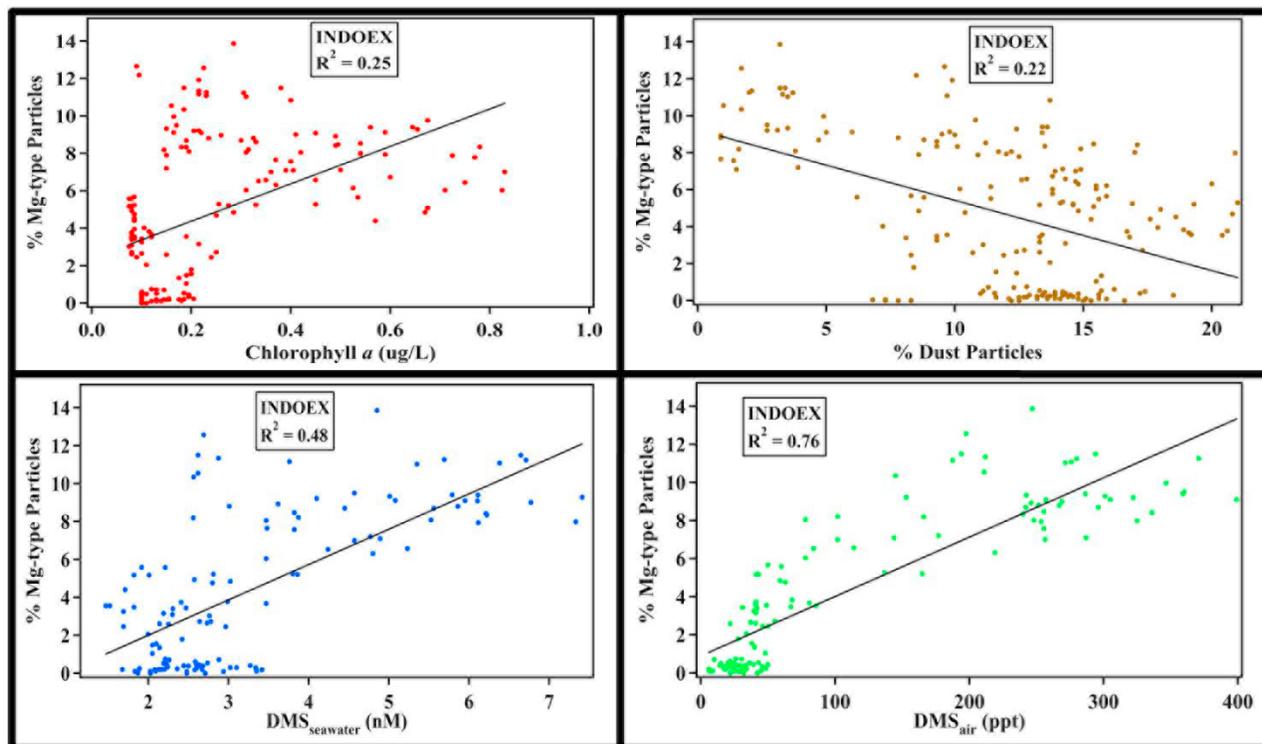


Figure 6. Correlation plots between (top left) Mg-type particles and chlorophyll *a* concentrations, (top right) Mg-type particles and dust particles, (bottom left) Mg-type particles and seawater DMS concentrations, and (bottom right) Mg-type particles and atmospheric DMS concentrations measured during INDOEX.

within atmospheric aerosols compared to the same ratio of ions in bulk ocean water [Duce and Hoffman, 1976; Hoffman and Duce, 1972]. While the transfer and enrichment of organic material is well documented [Blanchard, 1964; Duce and Hoffman, 1976], uncertainty remains regarding the enrichment of inorganic ions (i.e., Mg^{2+} , Ca^{2+}) owing to the difficulty in distinguishing between marine, continental, and anthropogenic sources (e.g., Mg associated with organics and biological material versus Mg in soil dust versus Mg in sea salt) [Duce and Hoffman, 1976; Hoffman and Duce, 1977; Hoffman et al., 1980]. One of the primary goals of this study is to use a single particle technique to probe whether chemical segregation of organic and inorganic ions occurs during the bubble bursting process.

[22] One question that arises is whether the unique Mg signature could be due to chemical fractionation occurring in the instrument. Fractional recrystallization has been postulated to occur when sea spray particles are dried out causing compounds with different solubilities to recrystallize and shatter creating particles with inorganic concentrations that differ from bulk seawater [Mouri et al., 1997; Mouri and Okada, 1993]. While composition dependent chemical fractionation within the instrument is possible, it is highly unlikely due to the following reasons. First, the sampling mast for these studies was conditioned to 55% RH and in the standard ATOFMS nozzle inlet used for these studies, the particles undergo minimal evaporation as they are only under vacuum for <1 ms before they are analyzed; hence, chemical fractionation due to efflorescence within the instrument is an unlikely explanation for the presence of these particle types.

Second, if segregation were occurring for sea salt particles in the single particle mass spectrometer, then Mg-type particles should be present during all time periods in marine environments when sea salt particles are detected; as discussed, this is not the case particularly during INDOEX when Mg-type particles increased only as chlorophyll *a* and DMS concentrations increased. This observation is consistent with other studies. Finally, laboratory investigations show that Mg-type particles were significantly enhanced when seawater was bubbled rather than atomized. If chemical fractionation were occurring within the instrument, then similar percentages of Mg-type particles should have been detected regardless of the aerosol generation technique used.

[23] Instead, we hypothesize that distinct sea spray particle populations at the single particle level form, as ocean-derived Mg-type and fresh sea salt in different particle populations, when changes in ocean chemistry occur. Single particle analysis provides direct insight into the presence of these individual populations, information that is not apparent from techniques that average the composition of sea spray particles into a single average chemical composition (see Figure S4 in the auxiliary material for comparison). Different sea spray aerosol populations have been shown by electron microscopy where organic-rich particles lacking sea salt were detected [Bigg and Leck, 2001; Leck and Bigg, 2005a, 2005b, 2008; Leck et al., 2002]. However, this study is the first to show real-time temporal correlations between changes in ocean chemistry (i.e., DMS and chlorophyll *a*) with changes in the mixing-state of sea spray aerosols. It is

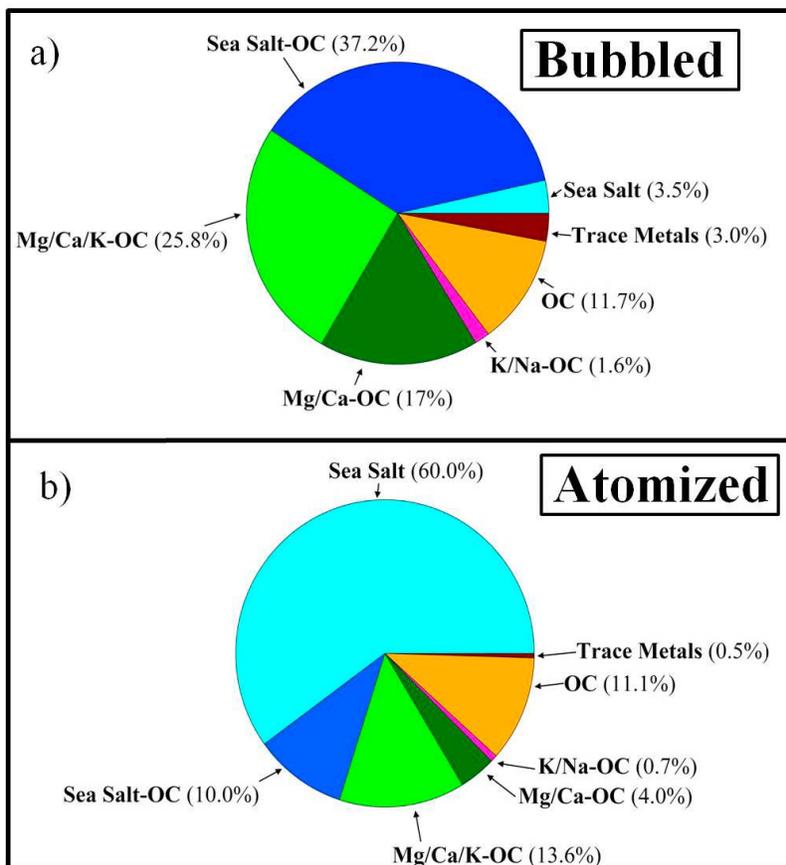


Figure 7. Differences in particle chemistry of (a) bubbled and (b) atomized natural seawater collected from the surface of the ocean at the Scripps Institution of Oceanography pier.

important to understand the factors leading to these chemical differences as they will impact the heterogeneous reactivity, water uptake, and cloud forming abilities of sea spray aerosols.

3.7. Potential Sources of Mg-Type Particles

[24] The Mg-type particles could result from EPS, cell debris or fragments, viruses, bacteria, or organics released by lysed cells. As stated previously, divalent cations such as Mg^{2+} and Ca^{2+} have been shown to facilitate the formation of microgels [Chin *et al.*, 1998; Verdugo *et al.*, 2004; Wells, 1998] and, thus, could be responsible for the detection of Mg-type particles by ATOFMS. If the origin of the Mg-type particles is due to the association of Mg^{2+} with organic material, then periods with enhanced organic material in the ocean, such as when ocean biota is present, could enhance the detection of this particle type. The bubble bursting process is known to lyse cells [Cherry and Hulle, 1992] potentially releasing organics and/or chlorophyll *a* into the water column that could be the source of enhanced organic material and Mg^{2+} in the particle phase. Furthermore, Mg^{2+} has been shown to deprotonate and associate with the polar head groups of surface active fatty acids creating a particle interface rich in Mg^{2+} and organics [Casillas-Iuarte *et al.*, 2010]. The Mg-type particles detected by ATOFMS could, thus, primarily reflect an organic-rich particle coating when water insoluble organic material is present in sea spray

aerosols. While the exact mechanism and source of the Mg-type particles are unknown, it is clear that chemical segregation appears to be occurring during the bubble bursting process in areas with increased organic material.

4. Conclusions and Atmospheric Implications

[25] Unique ocean-derived particle types enriched in organic carbon and Mg^{2+} and/or Ca^{2+} were detected by ATOFMS in marine environments. These particles were observed to increase during periods of elevated DMS and/or phytoplankton biomass, as measured by chlorophyll *a* concentrations, suggesting that the observation of these particles accompanies changes in ocean chemistry due to biological activity providing an unambiguous link between changes in ocean chemistry and sea spray aerosol chemistry. The Mg-type particles were externally mixed from sea salt particles providing evidence of chemical segregation occurring at the single-particle level, which is in agreement with other off-line electron microscopy measurements of single sea spray particles including those of Bigg and Leck [2008]. The characteristic spectra of these particle types can be reproduced experimentally by bubbling seawater solutions. The bubbling mechanism is known to scavenge organic material and microorganisms from the water column resulting in enriched levels of organic material in sea spray aerosol relative to bulk seawater. It is likely that the Mg-type

particles are associated with the scavenged organic material and/or microorganisms. Potential sources for these particles include microgels stabilized by divalent cations (e.g., Ca^{2+} and Mg^{2+}), structural changes in sea spray aerosol due to the presence of surface active fatty acids bound to Mg^{2+} , cell debris or fragments, viruses, bacteria, or organics released by lysed cells. Future research will be conducted to directly link these Mg-type particles to particular organic compounds including EPS, primary production, and particular phytoplankton species. Measurements of marine aerosols have demonstrated a peak in number concentration at sizes of ~ 0.1 μm and below [Fuentes et al., 2010a, 2010b; Mårtensson et al., 2003; Sellegri et al., 2006; Tyree et al., 2007]. Particle measurements presented in this paper have a lower limit of 0.2 μm ; however, the Mg-type particles described herein most likely extend to smaller sizes. We also hypothesize that the Mg-type particles described herein serve as a proxy for the production of particulate organic carbon in single particles associated with biological activity, which has also been shown to contribute to particles < 0.2 μm [Bigg and Leck, 2001, 2008; Leck and Bigg, 2005a, 2005b, 2008; Leck et al., 2002]. Current efforts are underway in our group to determine the lower size limit of this unique particle type. If the enhanced Mg in these particles is due to organic and Mg^{2+} enrichment at the particle interface, this has implications for reactivity, hygroscopicity, optical properties, and ice and cloud nucleating abilities, which will be quite different from traditional sea salt particles. These findings provide further support for how changes in ocean chemistry induced by biological processes can impact particle chemistry and, possibly, cloud formation.

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