Atmosphere-Ocean Interaction through Atmospheric Aerosol Particles Observed in a Single Nanoparticle Aspect

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Introduction

Biogeochemical cycles consist of processes such as the flow and circulation of chemical substances in the Earth's systems, the transformation of circulating chemical substances, and the accumulation/removal of chemical substances in the Earth's reservoir systems. The flux and budget of chemical substances and their variations in the Earth's systems during biogeochemical cycling, are often a central issue and thus the impact of perturbed biogeochemical cycling, for example, by increased human activity, is usually gauged by the extent/size of flux and budget changes. However, this measure does not always apply. For example, it has been demonstrated that the availability of *micro*-nutrient(s) in seawater, such as iron, actually controls phytoplankton growth in a high-nutrient low-chlorophyll (HNLC) region such as the western North Pacific Ocean. It is also well-known that atmospheric nanoparticles with a diameter less than 100 nm, which makes only a minor contribution to the total mass of atmospheric aerosols, play a central role in forming atmospheric clouds and perturbing the Earth's radiation budget. These are good

examples, showing that even a small mass or budget in biogeochemical cycling can affect the Earth's environmental system and therefore one of the major research areas in the current W-PASS project. In this study, we applied single particle mass spectrometry to investigate the impact of atmospheric aerosols on the atmosphere-ocean interaction, for the first time. As single particle mass spectrometer analyzes both the size and chemical composition of each individual particle in *real-time* and provides size-resolved chemical composition and a unique mixing of chemical components, and their temporal variation. Using the unique set of information at a single particle level, a new aspect of atmosphere-ocean interaction through atmospheric aerosols has been studied with a special emphasis on its relationship to marine biological activity.

Single Particle Mass Spectrometer (ATOFMS)

An Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS, TSI Model 3800-100) was used as a single particle mass spectrometer in this study. Size measurement and chemical analysis was carried out

sequentially for individual particles in the ATOFMS. The aerodynamic particle size (D_a) was determined by measuring the particle velocity, which is a function of D_a, and then a laser desorption/ionization (LDI) mass spectrometer is used to perform a chemical analysis. LDI is capable of detecting a wide range of chemical components, such as trace metals (e.g., Fe, Al, Si, Co, Cr, Ba, V, Pb), alkali metals (e.g., Li, Na, K, Ca), other inorganic elements (e.g., Cl, F, Br), and their oxides and inorganic salts (e.g., sea salt, sulfate, nitrate, carbonate) including elemental and organic carbons. Since ATOFMS analyzes particles one by one, aerosols observed can be classified based on a unique chemical composition/mixing, whereby chemical aerosol types are reported on a number concentration basis rather than a mass concentration, as ordinary aerosol chemical analysis does. The ability to simultaneously detect broad compounds, including refractory ones, at a single particle level makes ATOFMS quite unique, compared with other *on-line* and *real-time* aerosol chemical analyzers which can detect only a limited range of compounds. Size-resolved single particle chemical information (D_a from ~100 nm to 2 μm) was achieved by ATOFMS in field observations.

Field Observations in Biogeochemically Different Regions

Single particle chemical composition of atmospheric aerosols was characterized by ATOFMS, along with other aerosols measurements, through several shipboard and ground-based field campaigns in regions with different biogeochemical characteristics. Three shipboard campaigns were conducted in subarctic and subtropical western North Pacific region (KH-08-2 cruise, August to September 2008, see Fig. 2), North and South Pacific Ocean from 30°N to 50°S and 135°E to 120°W (MR08-06 and MR09-01 cruises, January to April,

and July, 2009, see Fig. 4) and a ground-based campaign was conducted at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) on Okinawa Island. The subarctic western North Pacific region is characterized as a HNLC ocean, while the cruise in the North and South Pacific region (from 30°N to 50°S) encompassed both oligotrophic subtropical, relative eutrophic equatorial and subantarctic regions. Cape Hedo is located downstream of the Asian continent and is frequently impacted by long-range transported Asian outflow, which brings abundant anthropogenic and/or natural aerosols.

Results and Discussion

Fe-containing anthropogenic aerosols in the Asian outflow

It has been considered that the atmospheric deposition of Kosa (natural dust) aerosol onto the ocean surface is an important supply source of Fe to the HNLC region in the western North Pacific Ocean (e.g., Jickells *et al.* 2005; Mahowald *et al.* 2005). Single particle chemical characterization was carried out by the ATOFMS at CHAAMS on Okinawa Island during the spring Asian outflow season. Of the 2210000 atmospheric aerosols analyzed and recorded during the field observation, Fe-containing aerosols were selected from the data set for further detailed analysis based on the presence of an ion peak pattern similar to the isotopic composition of Fe (*m/z* 54, 56, 57). The fraction of the Fe-containing particles among the total aerosols varied in time and size (0.02–0.14, on average ~0.06). Particle classification using ART-2a clustering, based on similarity/dissimilarity in positive and negative ion peak patterns (equivalent to chemical composition), showed that Fe-containing aerosols could be classified into five major types (Fig. 1(a)). The five types were characterized as not only having a different composition, but also a unique mixing
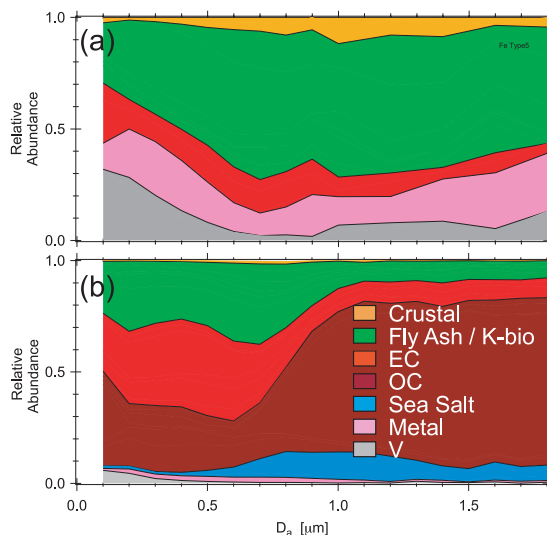
Fig. 1. Size-resolved single particle chemical composition observed by ATOFMS at Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) during March to April, 2008. Relative contribution of (a) Fe-containing aerosol types in atmospheric aerosols, and (b) atmospheric aerosols in each size bins (bin width: 0.1 μm).

of specific element(s) and compound(s) which are indicative of their formation processes/sources. Both the relative abundance and size distribution of the five Fe-containing aerosol types were different from those of atmospheric aerosols (Figs. 1(a) and (b)), indicating that Fe-containing aerosols were emitted from specific sources. The relative contribution of dust aerosol, which has been thought as a primary transporter of atmospheric particulate Fe, was found to be very small, while anthropogenic aerosols dominated. The largest contributor was the Fly-ash/K-biomass burning type particle (~60%) which frequently contained Li, which is indicative of its origin from coal-burning. The large contribution of aerosols of a coal-burning origin corresponded to higher coal usage in China (Ohara *et al*. 2007). Coal usage is about four times larger than that of oil in China and coal usage even dominates (~50%) total fuel consumption in East Asia (Ohara *et al*. 2007). Although the concentration of Fe-containing aero-

sols varied significantly with the change in air mass types (e.g., marine or continental type), the relative contribution of the five Fe-containing aerosol types remained rather unchanged; in particular, when V-type was excluded, it almost remained constant regardless of air mass types. It is quite interesting that the relative contribution of the four Fe-containing aerosol types remained almost constant, although the concentrations of the four types changed significantly. Since Fe is not volatile in the atmospheric condition and Fe-containing aerosols should thus be emitted as primary aerosols (directly emitted from their sources), the unique mixing of specific elements and compounds in the five classified aerosol types is indicative of their formation processes and sources. Therefore, the observed constant relative contribution of the four Fe-containing aerosol types suggests that their relative ratios reflects the emission source strength of the four aerosol types in East Asia, and that they are preserved on a regional scale. The tem-
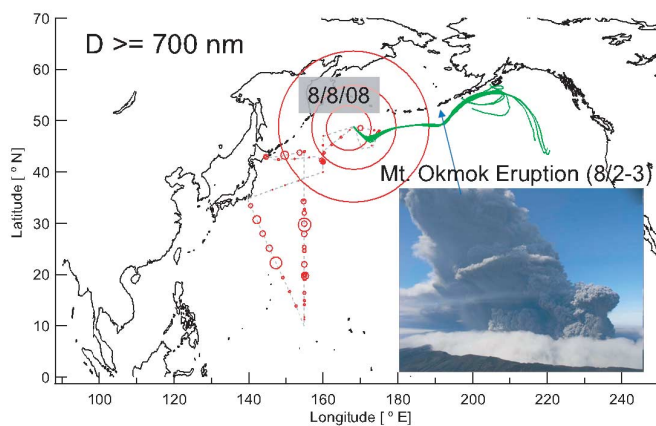
Fig. 2. Geographical numbers of Fe-containing atmospheric aerosols (D_a > 700 nm) observed by the ATOFMS in 12 hours during KH-08-2 research cruise by R/V Hakuho (August–September, 2008). Diameter of the circles represents number of the detected aerosols. On August 8, an unexpected anomalous increase of the Fe-containing crustal aerosols was observed. Backward air trajectory (tracked back to past 7 days) suggested the increased Fe-containing aerosols were volcanic ash particles emitted from Mt. Okumoku during its explosive eruption on August 2 to 3, 2008.

poral variation of the V-type was quite different from the other four aerosol types, and no clear correlation was found with any meteorological/aerosol parameters and trace gases, suggesting that the V-type aerosol was emitted from source(s) different from those of the other four types. It has been reported that V-type/elemental carbon is emitted from ship exhaust with low grade diesel fuel (Ault *et al.* 2009). We consider that the exhaust from ships around the island is the source of the V-type aerosol observed in this study. A recent report shows that anthropogenic Fe from fossil fuel combustion has a much higher water solubility than that of Fe in natural dust aerosols, by one to two orders of magnitude (Schroth *et al.* 2009). Due to the much higher water solubility of anthropogenic Fe from a fossil fuel origin, the deposition of the anthropogenic Fe may have a similar impact on marine primary production as does Fe in natural dust aerosol (Luo *et al.* 2008). The current study showed that Asian outflow containing

abundant anthropogenic Fe, in particular of a coal combustion origin, is transported to North Pacific Ocean, and this is expected to have a large impact on marine primary production in the HNLC ocean in the western North Pacific. Further quantitative observation, and estimates are required to gauge the impact.

Enhanced deposition and chemical processing of Fe-containing volcanic aerosols by sea fog

Atmospheric aerosols were observed during a research cruise (KH-08-2 cruise, August–September 2008) in the HNLC region in the western North Pacific and Fe-containing aerosols, the deposition of which supplies Fe to the ocean, were examined in the same way as the aerosols observed in Cape Hedo. During the cruise, an anomalously high concentration of Fe-containing aerosol for D_a > 700 nm was observed on August 8 (around 168°E, 48°N, see Fig. 2). Fe-containing aerosols observed during the high concentration

period consisted of Fe, crustal elements (Al, Si, P, Li), sulfate, and sea salt composition (Na, Cl, K, Mg) which suggested mixing with sea salt aerosols. Backward air trajectory analysis showed that the origin of the air mass was off the Pacific coast of Alaska, although no large natural dust source such as a desert exists in this region. It is quite unlikely that an ordinary dust source, like a desert, was the origin of the observed high concentration of the Fe-containing aerosol and other unusual source(s) may contribute. We found that the Mt. Okmok volcano in the Aleutian Islands was active and an increased ash plume ejection was observed during August 2 and 3, 2008 (Neal *et al.* 2011). The Mt. Okmoku volcano is located along the air mass backward trajectory when the high concentration was observed (see Fig. 2) and the increased activity almost coincided with when the air parcels passed nearby Mt. Okumok volcano and the ash plume ejection. Since the Fe-containing aerosols during the event also contained crustal elements, we concluded that the origin of the observed high concentration of Fe-containing aerosols, on August 8, was volcanic ash emitted from Mt. Okumoku volcano. It is worth noting that all Fe-containing aerosols of volcanic ash origin were mixed with sea salt aerosol. Ordinary cloud processing, and particle coagulation in the atmosphere, is not enough to lead to all ash particles being mixed with sea salt aerosols within several days. We consider that sea fog, which is regularly developed on a regional scale in the western north Pacific during summer (Wang 1985), accelerated the observed unique mixing. Coarse size-distribution measurement on board clearly showed that atmospheric aerosols with D > 500 nm, decreased significantly as a result of their activation to sea fog (D = 20~50 μm). Since large sea fog droplets have a much higher coagulation probability than that for particles with D < several μm, activated atmospheric aerosols will rapidly coagulate with each other and aerosols will be rapidly mixed. The activation of atmospheric aerosols to sea fog is expected to affect several atmospheric and biogeochemical processes. Large sea fog droplets have a much shorter atmospheric lifetime than atmospheric aerosols (D < several μm) and the deposition of atmospheric aerosols activated to sea fog will be significantly accelerated. Moreover, acidic sea fog water (pH = 3~5) should enhance the water-solubility of insoluble trace metal composition in the sea-fog droplets, which will increase the deposition flux of bioavailable trace metals such as Fe. It was found, by revisiting the area five days after the high concentration of Fe-containing aerosols was observed, that phytoplankton concentration actually increased significantly in the area (for more detail, refer to the report by the A03-1 group), suggesting that enhanced atmospheric deposition of volcanic ash, and increased solubility by sea fog processing, may trigger the phytoplankton bloom in the HNLC region over the western North Pacific. In the western North Pacific, dense sea fog chronically covers a large region during summer (Wang 1985). As in the case of volcanic aerosols, other types of atmospheric aerosols should also experience such sea fog processing. Therefore, current observation suggests that sea fog may also play an important role in biogeochemical cycling; in particular, to atmospheric deposition and subsequent micronutrient supply to the HNLC region in the western North Pacific.

New particle formation and long-range transport by gas-to-particle conversion of volcanic SO$_2$ emitted from Mt. Kilauea volcano

During the KH-08-2 cruise, an unexpectedly high sulfate mass concentration (4–5 μg/m^3), which is comparable to that in the Asian outflow observed at Okinawa Island, was observed in the subtropical
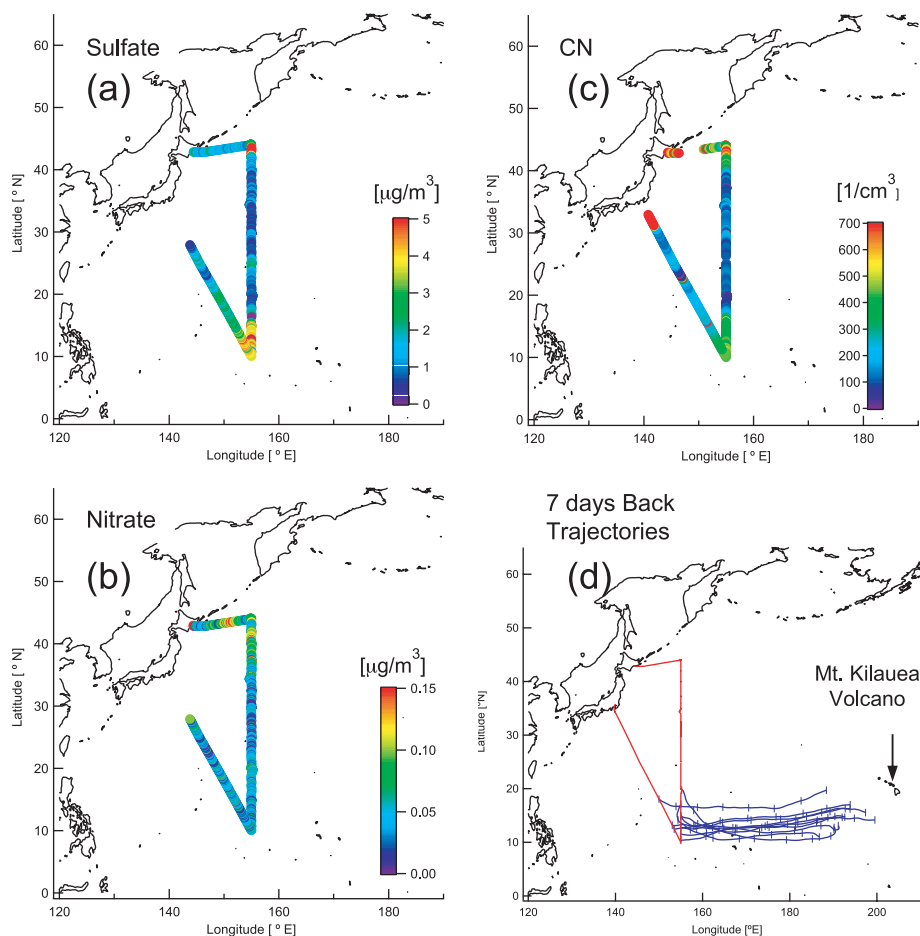
Fig. 3. Atmospheric aerosol properties observed on-board R/V Hakuho during the KH-08-2 cruise (Leg 1, August–September, 2008). (a) Particulate total sulfate (SO_4^{2-}) mass concentration, (b) particulate nitrate (NO_3^-) mass concentration, (c) number concentration of atmospheric aerosols with D > 5 nm, and (d) backward trajectories of air masses encountered during the high sulfate concentration period (past 7 days).

Pacific Ocean (10–15°N, 155°E, see Fig. 3), although the encountered air mass originated from the middle of the Pacific Ocean, where no large anthropogenic activity exists. Not only the sulfate mass concentration, but also the condensation nuclei (CN, aerosols with D > 5 nm) and cloud condensation nuclei (CCN) number concentrations also notably increased by a factor of 2–3, while no increase of nitrate was observed, which suggested that

the observed enhancement was not due to anthropogenic activity, but by natural activity. In the early stage of data analysis, we considered that the observed high sulfate concentrations might have originated from biogenic sulfur compounds, such as dimethyl sulfide (DMS), and were related to high marine production in the equatorial region, although the sulfate mass concentration was too high to be of marine biogenic origin. But Prof.

Fukushima's group (A01 group) found that it was not of biogenic origin but, actually, of volcanic origin. Satellite images of aerosol optical depth (AOD) obtained by a moderate resolution imaging spectroradiometer (MODIS) sensor clearly showed that aerosol plume emerged from Hawaii Island and was long-range transported to the western subtropical Pacific Ocean (~5500 km) and reached the region where the high sulfate mass concentration was observed. It was reported that the volcanic activity of Mt. Kilauea during 2008 was mainly the emission of volcanic gas (e.g., SO_2) rather than the explosive ejection of volcanic ash (U.S. Geological Survey Hawaiian Volcano Observatory website) which indicated that aerosol plumes observed by the MODIS satellite sensor were mainly not volcanic ash but sulfate aerosols converted from emitted volcanic SO_2 gas by gas-to-particle (SO_2 gas to particulate sulfate) conversion in the atmosphere. From the retrieved MODIS satellite data, it was found that the cloud effective radius, over the passage of the long-range transported aerosol plume, decreased, due to the increased aerosol number concentration, as expected from the observed increase in CCN concentration by a factor 2 to 3 in the subtropical western North Pacific (see Fig. 3). The observed modulation of the cloud property was well simulated by a global chemical transport aerosol model which considered the additional atmospheric input of volcanic SO_2 from Mt. Kilauea volcano (Eguchi *et al*. 2011). The model also found that the modified cloud property affected the solar radiation budget at the surface of the ocean (Eguchi *et al*. 2011).

Single particle chemical composition and its geographical variation and relationship to marine primary productivity in the North and South Pacific Ocean

Anthropogenic activity differs significantly between the southern and northern hemispheres, since most industrialized countries are in the northern hemisphere. On the contrary, because there are fewer industrial countries in the southern hemisphere, the contribution of natural aerosols to the atmospheric aerosols, which is often eclipsed in the northern hemisphere due to the higher concentration of anthropogenic aerosols, is expected to be large in the southern hemisphere. The composition of atmospheric aerosols in the northern and southern hemispheres should show a clear and interesting contrast. The research cruises (MR08-06 and MR09-1) provided a unique opportunity to observe a broad region in the North and South Pacific Ocean with a different marine primary productivity (Fig. 4). Figure 4 shows the geographical distributions of number-based concentrations of atmospheric aerosols containing organic nitrogen (Org-N) and an oxidized organic composition (Oxy-OC), along with surface chlorophyll-a concentration (Chl-a) retrieved by satellite observation. Aerosol concentrations with these specific compositions had a clear relationship with the surface chlorophyll concentration in the South Pacific Ocean, while such a relationship was masked, as expected, in the North Pacific Ocean. In the South Pacific, high Org-N was observed in high Chl-a regions (e.g., equatorial and high-latitude regions), while high Oxy-OC was observed in low Chl-a regions (e.g., mid-latitude region). In addition to the Org-N and Oxy-OC composition, a unique sulfur-containing particle type was also observed. The sulfur type appeared only in the high Chl-a regions, and only during night time, which quite differs from other aerosol types. The observed correlation/anticorrelation between the surface Chl-a and the unique atmospheric aerosols (Org-N, Oxy-OC, and S-containing) suggests the existence of a new pathway in the link between marine biota and atmospheric aerosol composition, which differs from the ordinary link via
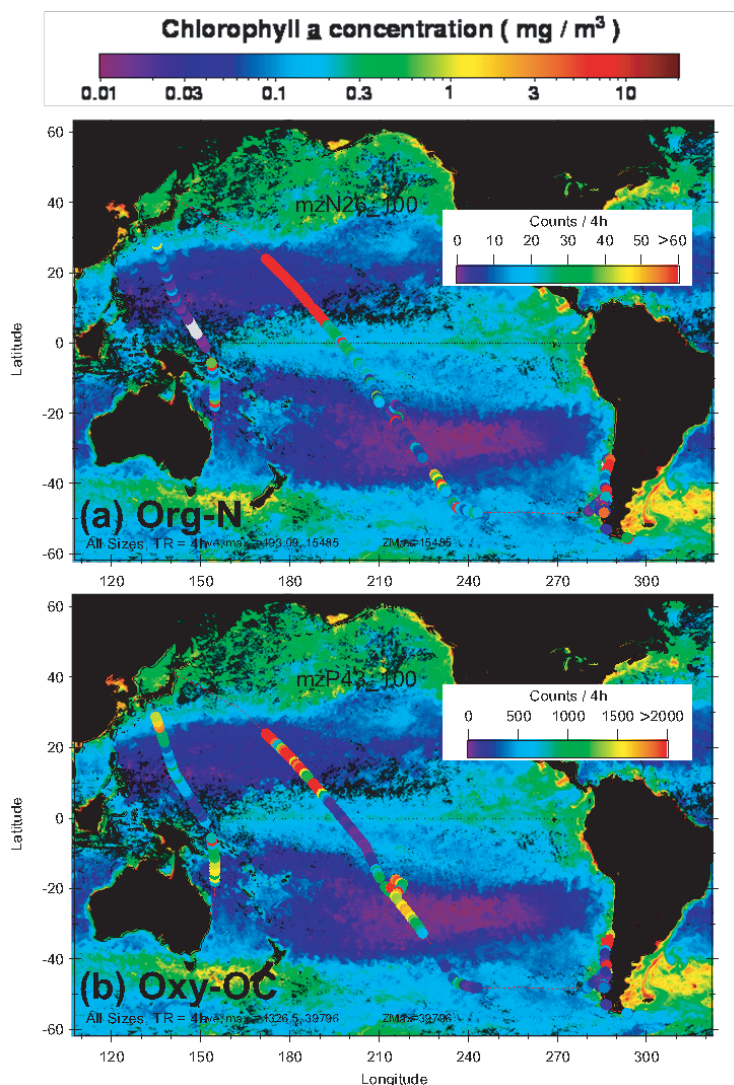
Fig. 4. Geographical distribution of the number of atmospheric aerosols containing (a) organic nitrogen and (b) oxidized organic composition observed by ATOFMS during R/V Mirai MR08-06 (Japan to Chile, January to March, 2009) and MR09-01 (Australia to Japan, June–July, 2009) cruises. The background image is the distribution of the average surface chlorophyll-a concentration (February 2009) observed by MODIS satellite sensor.

biogenic DMS emission and sea salt aerosol formation at the ocean surface. Direct observation demonstrating a link between marine biota and atmospheric aerosol composition has been quite limited and the current observation is one of the excellent examples supporting the existence of a natural environmental link between marine biota and atmospheric aerosols, other than sea salt aerosol and particulate sulfate of a biogenic DMS origin.

Summary

We applied single particle mass spectrometry to investigate the atmosphere-ocean interaction via atmospheric aerosols and its impact on biogeochemical cycles from a single particle perspective in the W-PASS project. Aerosol characterization by a single particle mass spectrometer (ATOFMS) provided a unique data set of aerosol chemical information, such as a size range from 100 nm to 2.0 μm and a broad range of chemical compositions of each individual aerosol, the mixing of compounds/elements, and their geographical distribution and temporal variation on a particle number-basis, which is different from ordinary bulk aerosol chemical information. In the current study, the origins of Fe-containing atmospheric aerosols in East Asia were identified based on unique chemical mixing at a single particle level. A clear correlation between surface chlorophyll-a concentration and number concentrations of aerosols containing oxidized organics and organic nitrogen was found in the southern hemisphere, which suggests the potential existence of a natural link between aerosol composition and marine biota rather than that via the well-known DMS gas emission, and its subsequent transformation to particulate sulfate. Single particle mass spectrometry has enabled us to explore biogeochemical cycles from a new angle.

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