Enrichment of submicron sea-salt-containing particles in small cloud droplets based on single-particle mass spectrometry

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Abstract. The effects of the chemical composition and size of sea-salt-containing particles on their cloud condensation nuclei (CCN) activity are incompletely understood. We used a ground-based counterflow virtual impactor (GCVI) coupled with a single-particle aerosol mass spectrometer (SPAMS) to characterize chemical composition of submicron (dry diameter of 0.2–1.0 µm) and supermicron (1.0–2.0 µm) sea-salt-containing cloud residues (dried cloud droplets) at Mount Nanling, southern China. Seven cut sizes (7.5–14 µm) of cloud droplets were set in the GCVI system. The highest number fraction of sea-salt-containing particles was observed at the cut size of 7.5 µm (26 %, by number), followed by 14 µm (17 %) and the other cut sizes (3 %–5 %). The submicron sea-salt-containing cloud residues contributed approximately 20 % (by number) at the cut size of 7.5 µm, which was significantly higher than the percentages at the cut sizes of 8–14 µm (below 2 %). This difference was likely involved in the change in the chemical composition. At the cut size of 7.5 µm, nitrate was internally mixed with >90 %, >80 %, 39 %–84 %, 71 %–86 %, 52 %–90 %, and 32 %–77 % of the submicron sea-salt-containing cloud residues. The proportion of sea-salt-containing particles in the supermicron cloud residues generally increased as a function of cut size, and their CCN activity was less influenced by chemical composition. This study provided a significant contribution towards a comprehensive understanding of sea-salt CCN activity.

1 Introduction

Atmospheric aerosol particles can directly influence the global radiative forces by scattering and absorbing solar radiation, and can indirectly influence them by serving as cloud condensation nuclei (CCN) (Boucher et al., 2013). The oceans represent one of the largest sources of natural aerosols, with an estimated global production rate of 2000–10 000 Tg per year (Gantt and Meskhidze, 2013). Modeling simulations showed that the indirect radiative forces of sea-salt particles were about twice those of the direct forces (Ma et al., 2008). The addition of the sea-salt particles over the remote ocean was estimated to enhance its CCN concentration.
by up to 500 % (Pierce and Adams, 2006). The ability of sea-
salt particles acting as CCN is dependent on their size and
chemical composition at a specific supersaturation (Andreae
and Rosenfeld, 2008). Therefore, it is important to evaluate
the impact of chemical composition and particle size on the
CCN behavior of sea-salt particles.

Numerous studies have revealed that fresh sea-salt par-
ticles consist of inorganic salts and biologically produced
organic species rather than just sodium chloride (NaCl)
(Prather et al., 2013; Quinn et al., 2015; Bertram et al.,
2018). The size-resolved chemical composition of fresh sea-
spray aerosols is dependent on complex factors including bi-
ological sources (e.g., phytoplankton and bacteria), physico-
chemical (e.g., sea-surface active organic species) properties,
and wind speeds (Quinn et al., 2015). Previous studies have
shown that an increasing fraction of fresh sea-salt particles
is an internal mixture of inorganic salts (mainly including
NaCl) and organic species as a result of the decreasing parti-
cle size (Prather et al., 2013; Bertram et al., 2018). However,
the fraction of organics (i.e., aliphatic organic material) in
small sea-spray aerosols exhibited some levels of variability
in the similar simulation of ocean seawater conditions (Wang
et al., 2015). Heterogeneous/multiphase reactions or atmo-
spheric aging processes during transport can further lead to
the size-dependent change in the chemical composition of
sea-salt particles (Dall’Osto et al., 2004; Chi et al., 2015;
Bondy et al., 2017). Bondy et al. (2017) found that sulfate
was enriched in the submicron sea-salt particles, while ni-
trate dominated in the supermicron sea-salt particles (Bondy
et al., 2017). However, Kirpes et al. (2018) observed that sul-
fate was also more prevalent than nitrate in supermicron sea-
salt particles (Kirpes et al., 2018). Additionally, sea-salt par-
ticles could also react with various organic acids (e.g., ox-
alate, malonate, and succinate) during transport (Mochida
et al., 2003; Laskin et al., 2012). Uncertainty in the formation
of secondary species (e.g., sulfate, nitrate, or organic species)
would complicate the size-dependent change in the chemical
composition of sea-salt particles and thus the CCN activity.

Twohy et al. (1989) observed that small ammonium sul-
fate particles grew to small droplets and large sea-salt parti-
cles grew to large droplets. Previous observations also con-
sidered that the supermicron or giant sea-salt-containing par-
ticles readily became large cloud droplets, and their CCN be-
behavior was less affected by chemical composition (Noone
et al., 1988; Monger et al., 1989; Andreae and Rosenfeld, 2008;
Tao et al., 2012). So far, studies on the submicron sea-salt-
containing particles in cloud droplets have been scarce in the
literature. Additionally, the existence of secondary species
(e.g., sulfate, nitrate, or organic species) on the submicron
sea-salt-containing particles might significantly impact their
cloud activation (O’Dowd et al., 1999; Gibson et al., 2006;
Nguyen et al., 2017).

In this study, a ground-based counterflow virtual im-
pactor (GCVI) combined with an online single-particle
aerosol mass spectrometer (SPAMS) was used to character-
ize the chemical composition of sea-salt-containing cloud
residues at Mount Nanling, southern China. This was per-
formed in the downwind direction from the South China Sea
during the study period of May–June 2017. The main goal
of this work was to identify the discrepancies in the relative
contributions of sea-salt-containing particles as a function of
the cloud droplet cut size (> 7.5, > 8.0, > 8.5, > 9.0, > 10.0,
> 11.0, and > 14.0 µm were set in the GCVI system). To elu-
cidate the cloud activity of submicron (dry diameter of 0.2–
1.0 µm) sea-salt-containing particles, the chemical composi-
tion of submicron sea-salt-containing particles within various
cloud droplet cut sizes was also addressed.

2 Experimental section

2.1 Observation site

The sampling site, which is a National Air Background Mon-
itoring Station, is situated at Mount Nanling, southern China
(112°53′56″ E, 24°41′56″ N at 1690 m above sea level). This
station is surrounded by a national park forest (273 km²)
minimally affected by local anthropogenic activities. The
sampling site is located 50–100 km northeast or north of the
Pearl River delta (PRD) urban agglomeration and 350 km
north of the South China Sea (Fig. S1 in the Supplement).
The sampling site is affected by the East Asian summer mon-
soon system (Ding and Chan, 2005). Generally, air masses
would spend some time traveling across the South China Sea
and then travel over the PRD region before reaching the sam-
ping site during the summer period. The SO₂, NOₓ, NH₃,
and volatile organic compound emissions in the PRD region
are approximately 711, 891, 195, and 1180 kiloton per year,
respectively (Zheng et al., 2009, 2012). Hence, the sea-salt-
containing particles that originate from the South China Sea
could interact with anthropogenic gaseous pollutants during
their movement across the PRD region.

2.2 Instrumentation

The measurements took place from 18 May to 11 June 2017.
The real-time air quality and meteorological parameters were
continuously monitored. A GCVI inlet system (GCVI Model
1205, Brechtel Manufacturing Inc.) was used to sample the
cloud droplets with various cut sizes. The cloud droplet cut
sizes and duration time set in the GCVI system are pre-
cented in Table S1 in the Supplement. The minimum sam-
ping time for each cut size was 12 h. The cut size was ad-
justed by modifying the air velocity in the wind tunnel of
the GCVI inlet system (Shingler et al., 2012). It should be
noted here that the transmission efficiency increased as the
cut size increased (Shingler et al., 2012). The sampled cloud
droplets passed through an evaporation chamber to remove
the water and the dry residue particles remained. The en-
richment factor of the particles that were collected by the
GCVI inlet was estimated to range from 6.6 in 7.5 µm to 2.0
in 14.0 µm based on theoretical calculations (Shingler et al., 2012). Pekour and Cziczo (2011) observed that the breakthrough of large particles tended to increase at the lower size cut. In this study, the number concentration of ambient particles in the GCVI downstream inlet was below 1 cm² at the lowest cut sizes during cloud-free periods, and hence the large particle breakthrough at the lowest cut size seemed to be quite low. The cloud residues were subsequently characterized using an online SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China). In order to reliably identify the presence of clouds, an upper-limit visibility of 3 km and a lower-limit relative humidity (RH) of 95% were set in the GCVI software (Lin et al., 2017). During precipitation periods, the GCVI automatically shut down to protect against interference from raindrops.

The SPAMS conducts the real-time characterization of the chemical composition of aerosol particles using vacuum aerodynamic diameters (dₐ) between 0.2 and 2.0 µm. The detailed operations of the SPAMS have been described elsewhere (Li et al., 2011). Briefly, aerosol particles are introduced into the SPAMS through a nozzle inlet. The particle velocity is derived from the measurement of two continuous diode Nd: YAG laser beams (532 nm) and is then converted to the particle size (dₐ). The particles are subsequently desorbed and ionized by a pulsed laser (266 nm). The positive and negative mass spectra generated are recorded with the corresponding particle size. The laser pulse energy was regulated at 0.5–0.6 mJ during the whole sampling period. Polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) of 0.2–2.0 µm in diameter were used to calibrate the sizes of the detected particles. It should be noted that the particles detected by the SPAMS are mostly in the size range of dₐ, 0.2–2.0 µm (Li et al., 2011).

### 2.3 Screening of sea-salt-containing particles

According to prior laboratory and field studies, sea-salt-containing particles generally exhibit a set of sodium-related peaks at m/z 23 [Na⁺], 46 [Na₂⁺], 62 [Na₃O⁺], 63 [Na₂OH]⁺, 81 [Na₂₃²Cl]⁺, and 83 [Na₂₃²Cl]⁺ (Dall’Osto et al., 2004; Herich et al., 2009; Prather et al., 2013). Thus, the sea-salt-containing particles in this study were identified by the simultaneous existence of peaks at m/z 23, 46, 62, 63, 81, and 83. Because biologically produced organic species (e.g., m/z = 26 [CN]⁻, = 42 [CNO]⁻, or 59 [NC₃H₆]⁺) were internally mixed with sodium-related peaks (Prather et al., 2013; Sultana et al., 2017), these primary organic species were not intended to define sea-salt-containing particles. Additionally, these organic species might also be produced from secondary aerosol processes (Dall’Osto et al., 2009; Zhang et al., 2012). Therefore, biologically produced organic species that externally mixed with sea-salt particles were not considered in the current study. One may expect that chlorine ion peaks at m/z = 35 [³⁵Cl]⁻ or = 37 [³⁷Cl]⁻ in the negative mass spectrum should be considered. Sea-salt-containing particles in the atmosphere might not contain chloride due to the complete displacement of chloride by sulfate, nitrate, or organic acids during transport (Laskin et al., 2012; Ueda et al., 2014; Arndt et al., 2017). Bondy et al. (2017) also suggested that the identification of sea-salt-containing particles without using chloride might give more detailed results on the atmospheric aging processes during transport (Bondy et al., 2017). Thus, a total of 30,275 sea-salt-containing cloud residues including 8,317 submicron and 21,958 supermicron particles were obtained in this study.

### 3 Results and discussion

#### 3.1 General characteristics

Figure 1 displays the hourly averaged data of the meteorological and air quality parameters during the whole sampling period. The wind direction prevailed southwesterly or southerly during the cloud events and most corresponding air masses originated from the South China Sea (Fig. S2), which had abundant moist airflows that were probably responsible for the formation of the cloud events. The maximum concentrations of PM₂.₅, SO₂, and NOₓ were 76 µg m⁻³, 2.8, and 12 ppb, respectively, during the cloud-free periods. When the cloud events occurred, the levels of PM₂.₅, SO₂, and NOₓ clearly decreased, which was indicative of cloud scavenging. The ambient temperature was above 10 °C during the whole study period, which allows the formation of liquid cloud droplets.

The average mass spectrum of the sea-salt-containing cloud residues during the sampling period is shown in Fig. 2. The highest peak at m/z 23 and some small ion peaks at m/z 24 [Mg]⁺, 39 [K]⁺, 40 [Ca]⁺, and 56 [CaO]⁺ or [Fe]⁺ were observed in the positive mass spectra. This result was in agreement with the previous findings from laboratory and field studies (Guazzotti et al., 2001; Dall’Osto et al., 2004; Gaston et al., 2011; Prather et al., 2013). The significant ion peaks at m/z = 46 [NO₂]⁻ or = 62 [NO₃]⁻ and = 97 [HSO₄]⁻ in the negative mass spectrum represented nitrate and sulfate markers, thus suggesting aged sea-salt-containing cloud residues. The presence of organic nitrogen peaks at m/z = 26 [CN]⁻ or = 42 [CNO]⁻ in the negative mass spectrum may be from biologically produced sources or the subsequent accumulation of secondary organic aerosols (Herich et al., 2009; Prather et al., 2013). The small peak areas of other organic species including hydrocarbon organic species (i.e., m/z 15 [CH₃]⁺, m/z 27 [C₂H₃]⁺, 43 [C₂H₃O]⁺), amines (m/z 59 [C₃H₇N]⁺ or 86 [C₅H₁₂N]⁺), or organic acids (m/z = 89 oxalate, = 103 malonate, or = 117 succinate) can also be detected in the sea-salt-containing cloud residues (Fig. S3).
3.2 Number fraction and chemical composition of sea-salt-containing cloud residues

The number fraction (NF) of sea-salt-containing particles in the total cloud residues was dependent on the cut sizes. The highest NF was observed at the cut size of 7.5 µm (26 %, by number), followed by 14 µm (17 %) and the other cut sizes (3 %–5 %) (Fig. 3a). These values were higher than the NF (2 %, by number) of sea-salt-containing particles in the detected ambient aerosol particles during cloud-free periods. Sea-salt-containing particles contributed approximately 1 % (by number) of cloud residues at the cut size of 5.0 µm over Mount Schmücke in central Germany, despite air masses that frequently originated over the Atlantic Ocean (Roth et al., 2016). The proportion reached 5 %–10 % (by number) at the cut size of 11 µm at the North Slope of Alaska (Zelenyuk et al., 2010). Additionally, the cloud water measurement showed that sea-salt-containing particles might accumulate in large cloud droplets (Monger et al., 1989). In contrast to these findings, the maximum NF of sea-salt-containing cloud residues was found at the minimum GCVI cut size in this study. Twohy and Anderson (2008) observed an increased NF of sea-salt-like cloud residues from coastal areas at the cut size of 20 µm to clean remote oceans at the cut size of 8 µm (Twohy and Anderson, 2008). However, it cannot interpret the enhancement of sea-salt-containing cloud residues at the cut size of 7.5 µm in this study because of the comparable air quality and meteorological environments at all the cut sizes.

There was a significant difference in the chemical composition of the sea-salt-containing cloud residues between the cut sizes of 7.5 µm and 8–14 µm, as shown in Fig. 4. Nitrate was internally mixed with above 90 % of the sea-salt-containing cloud residues at all the cut sizes. However, notably decreased sulfate (32 % versus 87 %–93 %, by number), ammonium (below 1 % versus 21 %–32 %), organic nitrogen (70 % versus 87 %–96 %), amines (6 % versus 30 %–64 %), hydrocarbon organics (2 % versus 22 %–70 %), and organic acids (7 % versus 42 %–76 %) were found internally mixed with the sea-salt-containing cloud residues at the cut size of 7.5 µm compared to 8–14 µm. Roth et al. (2016) found that both sulfate and nitrate were internally mixed with the sea-salt-containing cloud residues (Roth et al., 2016). Another study by Zelenyuk et al. (2010) observed that the sea-salt-containing cloud residues were composed of four particle types, including fresh NaCl, NaCl internally mixed with nitrate, sulfate, and organics. In this study, abundant nitrate was found to internally mix with the sea-salt-containing
cloud residues at all the cut sizes, while sulfate, ammonium, and organic species showed more diversity between the cut sizes of 7.5 and 8−14 µm. These differences in the chemical mixtures of sea-salt-containing cloud residues dependent on the location suggest that sea-salt-containing particles would experience various aging process in the atmosphere and subsequently participate in the formation of cloud droplets. More importantly, together with the enrichment of sea-salt-containing cloud residues at the minimum cut size of 7.5 µm observed here, this might indicate that the distribution of sea-salt-containing cloud residues that were dependent on cloud droplet size is likely influenced by changes in the chemical mixtures of sea-salt-containing nuclei. It should be noted here that, relative to small cloud droplets, larger cloud droplets might undergo longer-duration cloud (Nakajima et al., 2010), thus increasing the in-cloud formation of secondary species such as sulfate, ammonium, or oxalate. The extreme high fraction of nitrate in the sea-salt-containing cloud residues at all the cut sizes was more likely due to the aging processes during atmospheric transport, rather than the in-cloud formation.

It is well-known that the chloride depletion in sea-salt-containing particles is mainly due to the formation of secondary species, such as sulfate, nitrate, or organic acids (Laskin et al., 2012; Bondy et al., 2017). The chloride depletion might lower the hygroscopic and CCN properties of sea-salt-containing particles (i.e., NaCl) (O’Dowd et al., 1999; Gupta et al., 2015). In this study, chloride was internally mixed with above 80% (by number) of the sea-salt-containing cloud residues at the cut sizes of 8−14 µm, which was clearly higher than 51% at the cut size of 7.5 µm. That is, chloride depletion was weakened in the sea-salt-containing cloud residues at the cut sizes of 8−14 µm, despite abundant sulfate and organic acids, as mentioned above. Based on a laboratory study, Ault et al. (2014) found that organic nitrogen can inhibit the heterogeneous reaction of sea-salt-containing particles with HNO₃ (Ault et al., 2014). They used a peak area ratio of chloride to (chloride + nitrate) to estimate the extent of the chloride depletion (Ault et al., 2014). Because the heterogeneous reaction with H₂SO₄, HNO₃, or organic acids and sea-salt-containing particles is also present in the atmosphere (Laskin et al., 2012; Chi et al., 2015), a modified peak area ratio (chloride/(chloride + nitrate + sulfate + organic acids)) was applied in the present study. This ratio was found to increase as a function of the increase in the peak area of organic nitrogen, as shown in Fig. 5, thereby reflecting the effect of organic nitrogen on the depletion of chloride in sea-salt-containing particles in the atmosphere. At the cut sizes of 8−14 µm, abundant organic nitrogen in the sea-salt-containing cloud residues likely lowered the chloride depletion. The ratio was not found to be related to the hydrocarbon organic species. The sensitivity of chloride displacement to the presence of organic species was complex (Ault et al., 2014; Bertram et al., 2018), and further studies must be conducted to identify whether diverse organic species affect the heterogeneous reactivity of individual sea-salt-containing particles.

3.3 Submicron sea-salt-containing cloud residues

The modeling calculation showed that submicron sea-salt-containing particles may have a dominant contribution to aerosol−cloud interactions when evaluating the indirect impacts of sea-salt aerosols, despite the uncertainty in the sizes and concentrations of sea-salt aerosols (Gong, 2003). Few field studies have focused on the submicron sea-salt-containing particles within cloud droplets. In this work, approximately 25% (by number) of the sea-salt-containing cloud residues was found to be at the submicron size. It should be noted that the size distribution of the sea-salt-containing cloud residues that were detected by the SPAMS cannot represent the real atmosphere because the highest detection efficiency for the SPAMS was in the size range of 500−800 nm (Li et al., 2011). The relative contribution of sea-salt-containing particles to the cloud residues in the given size range is presented to eliminate the detection efficiency of single-particle mass spectrometry (Roth et al., 2016), as shown in Fig. 3b. At the cut size of 7.5 µm, 20% (by number) of the submicron cloud residues was composed of sea-salt-containing particles. This value was prominently higher than that at the cut sizes of 8−14 µm (below 2%, by number) or that during cloud-free periods (1%) (Fig. S4). The difference at least reflects that the submicron sea-salt-containing particles could be enriched in the small cloud droplets.

The diverse chemical composition of the submicron sea-salt-containing cloud residues was found between the cut sizes of 7.5 and 8−14 µm. At the cut size of 7.5 µm, nitrate was internally mixed with 90% (by number) of the sub-
micron sea-salt-containing cloud residues, which was much higher than the fractions of sulfate (20%) and ammonium (below 1%) (Fig. 4). It implies that the secondary inorganic species in the submicron sea-salt-containing cloud residues at the cut size of 7.5 µm was dominated by nitrate, mostly from the partitioning and heterogeneous/aqueous chemistry of HNO₃ and other precursors (e.g., N₂O₅) in the atmosphere (Chang et al., 2011; Schneider et al., 2017). However, prominently higher fractions of sulfate (86%–94%, by number) and ammonium (38%–83%) were found to internally mix with the submicron sea-salt-containing cloud residues at the cut sizes of 8–14 µm, thus reflecting more chemically aged or longer cloud processes. This was also supported by the increase in the relative peak areas of these secondary species in the submicron sea-salt-containing cloud residues at the cut sizes of 8–14 µm compared to 7.5 µm (Fig. S5). The enrich-
ment of sulfate in the submicron sea-salt-containing parti-
cles has also been reported extensively in the literature (Jour-
dain et al., 2008; Kelly et al., 2010; Bondy et al., 2017),
which is largely a result of the preferential formation of sul-
fate in submicron particle sizes with great surface area-to-
volume ratios (Song and Carmichael, 1999). Initially, fresh
sea-salt-containing particles generally appear to be alkaline
due to carbonate, and they subsequently experience the reac-
tive uptake of SO$_2$, H$_2$SO$_4$, or HNO$_3$ during transport (Siev-
ering et al., 1999; Alexander et al., 2005). The lack of am-
nium suggests that the accumulated secondary acids during
transport insufficiently acidize the submicron sea-salt-
containing cloud residues at the cut size of 7.5 µm, which,
in turn, causes the uptake of gaseous NH$_3$ to fail. In con-
trast, the accumulated ammonium in the submicron sea-salt-
containing cloud residues at the cut sizes of 8–14 µm (Fig. 4)
indicate that the alkaline sea-salt-containing cloud residues
have been eventually consumed by secondary acids and thus
uptake gaseous NH$_3$ to neutralize these acidic species (Song
and Carmichael, 1999). Furthermore, a higher number frac-
tion of amines was found to internally mix with the submi-
cron sea-salt-containing cloud residues at the cut sizes of 8–
14 µm compared to 7.5 µm (71 %–87 % versus 6 %, by num-
ber). Despite the biologically produced amines being inter-
ally mixed with fresh sea-salt-containing particles (Sultana
et al., 2017), a similar feature of ammonium and amines in
the submicron sea-salt-containing cloud residues observed
here implies that the presence of amines mainly comes from
the partitioning of the gas into the aqueous phase, particu-
larly during cloud processing (Roth et al., 2016; Lin et al.,
2017).

A laboratory study showed that biologically produced
organic nitrogen that internally mixed with fresh sea-salt-
containing particles was found to increase in the submicron
size range (Prather et al., 2013). This likely led to the en-
richment of organic nitrogen (58 %, by number) relative to
hydrocarbon organic species (2 %) or organic acids (4 %)
in the submicron sea-salt-containing cloud residues at the
cut size of 7.5 µm (Fig. 4). Meanwhile, at the cut sizes of 8–
14 µm, higher fractions of organic nitrogen (80 %–94 %, by
number), hydrocarbon organic species (52 %–90 %), and
organic acids (32 %–77 %) were observed (Fig. 4), indica-
tive of the more chemically aged processes, as mentioned
above. Note that magnesium and calcium internally mixed
with above 85 % (by number) and above 88 % of the sub-
micron sea-salt-containing cloud residues at the cut sizes of
8–14 µm might increase the presence of organic nitrogen due
to the probable complexation with organic species and these
cations (Bertram et al., 2018). Hydrocarbon organic parti-
cle types coupled with the peak area Mg >> Na can be pro-
duced from biological sources in seawater, but they are ex-
ternally mixed with fresh submicron sea-salt-containing par-
ticles (Sultana et al., 2017). Thus, the abundant hydrocarbon
organics observed here might originate from accumulation
during transport. The uptake of gaseous organic acids or the
organic acids that formed through heterogeneous reactions
were responsible for the increased organic acids presented
herein (Mochida et al., 2003; Sullivan and Prather, 2007). We
cannot preclude that the decreased organic species of the sub-
micron sea-salt-containing particles at the cut size of 7.5 µm
might also be due to having shorter-duration cloud relative
to other cut sizes. Further study needs to compare the contri-
bution of aging degree during transport and duration time of
cloud process to the secondary species.

Petters and Kreidenweis (2007) described the CCN ac-
tivity of multicomponent aerosol particles using a single pa-
rameter ($\kappa$) as follows:

$$\kappa = \varepsilon_{\text{org}} \cdot \kappa_{\text{org}} + \varepsilon_{\text{inorg}} \cdot \kappa_{\text{inorg}},$$

where $\varepsilon_{\text{org}}$ and $\varepsilon_{\text{inorg}}$ represent the bulk volume fractions of organic
and inorganic species, respectively, and $\kappa_{\text{org}}$ (generally be-
low 0.5 for organic species) and $\kappa_{\text{inorg}}$ (1.28 for NaCl, 0.88
for NaNO$_3$, 0.80 for Na$_2$SO$_4$, 0.67 for NH$_4$NO$_3$, and 0.61
for (NH$_4$)$_2$SO$_4$) refer to the CCN-derived hygroscopicity pa-
rameters of the organic and inorganic species, respectively.

Relative to the cut sizes of 8–14 µm, the reduction of organic
species in the submicron sea-salt-containing cloud residues
at the cut size of 7.5 µm is likely to increase $\kappa$ and hence
CCN property. Additionally, the submicron sea-salt parti-
cles contained higher proportions of organic nitrogen (73 %–
94 % versus 58 %, by number), hydrocarbon organic species
(51 %–81 % versus 2 %), and organic acids (35 %–72 % ver-
sus 4 %) in the ambient aerosol particles than in the cloud
residues at the cut size of 7.5 µm. This further indicates that
the enhancement of organic species in the submicron parti-
cles likely reduced CCN activity of sea-salt particles.

### 3.4 Supermicron sea-salt-containing cloud residues

The supermicron (dry diameter of 1.0–2.0 µm) sea-salt-
containing particles contributed more to cloud residues with
the increasing cut sizes (Fig. 3b). For instance, up to 70 % of
the supermicron cloud residues were found to consist of sea-
salt-containing particles at the maximum cut size of 14 µm.
The enrichment of the large supermicron or giant sea-salt-
containing particles in large cloud droplets has also been
reported in previous studies (Noone et al., 1988; Twohy et
al., 1989; Tao et al., 2012). Nitrate was internally mixed
with above 90 % (by number) of the supermicron sea-salt-
containing cloud residues at all the cut sizes (Fig. 4). The propor-
tions of sulfate, ammonium, and organic species in supermicron
sea-salt-containing cloud residues at the cut size of 7.5 µm were lower than those at the cut sizes of 8–
14 µm (Fig. 4), which was similar to the submicron parti-
cles. However, the increased organic species in the super-
micron sea-salt-containing cloud residues at the cut sizes of
8–14 µm were not expected to reduce their CCN behavior.
It was likely that their CCN activity was less affected by
the change in the chemical composition. For coarse or gi-
nant nuclei (dry particle size $>1$ µm), their CCN abilities were
dependent on their size rather than their chemical composi-
tion (Andreae and Rosenfeld, 2008; Tao et al., 2012). Hud-
son and Rogers (1986) also found that large nuclei increased in large cloud droplets due to lower critical supersaturation of larger nuclei compared to smaller nuclei (Hudson and Rogers, 1986).

4 Atmospheric implications and conclusion

This work focused on the size-resolved chemical composition of sea-salt-containing cloud residues as a function of the cloud droplet cut size. Nitrate internally mixed with above 95 % (by number) of the sea-salt-containing cloud residues at all the cut sizes emphasized that the sea-salt-containing nuclei had undergone chemical evolution during transport. For simplicity, modeling simulations assumed that the externally mixed NaCl and secondary species (e.g., sulfate) mode or pure NaCl instead of sea-salt aerosols was used to predict the size-dependent cloud droplet chemistry or the residence time of sea-salt aerosols in the atmosphere (Twohy et al., 1989; Gong et al., 2002; Ma et al., 2008). The change in chemical composition of the submicron sea-salt-containing particles might have an impact on their CCN activity. Our result showed that the reduction of organic species in the submicron sea-salt-containing cloud residues at the cut size of 7.5 µm is likely to increase CCN activity, leading to the enrichment of the submicron sea-salt-containing particles. The resulting effect might prolong the residence time of submicron sea-salt-containing aerosols in the atmosphere. This differed from the supermicron sea-salt-containing particles, which readily become large cloud droplets, consistent with the previous measurements (Noone et al., 1988; Yuan et al., 2008). More work is needed to evaluate the contribution of atmospheric aged processes to the change in the chemical composition that is associated with the CCN activity of sea-salt-containing particles, particularly in the submicron size range.

Data availability. All the data can be obtained by contacting the corresponding author Xinhui Bi (bixh@gig.ac.cn).

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Author contributions. XB, GZ, and QL planned and designed the experimental setup. YY, YF, LP, FI, XL, FL, and JO performed the atmospheric measurement and collected the data. QL and XB analyzed the data and wrote the manuscript. LL, DC, ML, MT, XW, PAP, and GS contributed comments.

Competing interests. The authors declare that they have no conflict of interest.

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