Calcium enrichment in sea spray aerosol particles

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Abstract  Sea spray aerosol particles are an integral part of the Earth’s radiation budget. To date, the inorganic composition of nascent sea spray aerosol particles has widely been assumed to be equivalent to the inorganic composition of seawater. Here we challenge this assumption using a laboratory sea spray chamber containing both natural and artificial seawater, as well as with ambient aerosol samples collected over the central Arctic Ocean during summer. We observe significant enrichment of calcium in submicrometer (<1 μm in diameter) sea spray aerosol particles when particles are generated from both seawater sources in the laboratory as well as in the ambient aerosols samples. We also observe a tendency for increasing calcium enrichment with decreasing particle size. Our results suggest that calcium enrichment in sea spray aerosol particles may be environmentally significant with implications for our understanding of sea spray aerosol, its impact on Earth’s climate, as well as the chemistry of the marine atmosphere.

1. Introduction

Sea spray aerosol particles are comprised of a complex mixture of inorganic salt and organic substances and are one of the largest sources of natural aerosol particles on Earth. Due to their size and chemical composition, sea spray aerosol particles are considered effective cloud condensation nuclei and in the absence of anthropogenic aerosols exert a strong influence on cloud microphysical properties [Andreae and Rosenfeld, 2008]. These particles also affect the Earth’s radiation budget via the scattering of incoming solar radiation [e.g., Haywood et al., 1999].

Sea spray aerosol particles are predominantly produced at the sea surface through the action of the wind [Woodcock, 1953]. As a result of wind stress, breaking waves entrain air, which resurfaces as bubbles that subsequently burst, ejecting seawater droplets into the atmosphere. There are two distinct mechanisms of droplet formation by bursting bubbles: disintegration of the bubble film produces a large number of seawater droplets with radii smaller than ~ 1 μm and a mode centered around 0.1 μm, often referred to as film droplets [Knelman et al., 1954; Spiel, 1998], while the ejection of a jet formed by the collapse of the sides of the bubble cavity results in a handful of seawater droplets with radii between ~ 1 and 50 μm that are generally referred to as jet droplets [Lewis and Schwartz, 2004]. The number and size of the seawater droplets produced depends on the size of the bubbles [Blanchard, 1983], the surface tension and the concentration and speciation of surfactants present [Blanchard, 1990], the age of the bubble, and the seawater temperature via its influence on the viscosity and density of the seawater [Salter et al., 2014].

It is well known that particulate substances [Blanchard, 1964; O’Dowd et al., 2004; Orellana et al., 2011; Leck and Bigg, 2008], surface active substances [Tseng et al., 1992; Bigg and Leck, 2008], the transition metals [Weisel et al., 1984; Guasco et al., 2014], and marine microorganisms [Blanchard and Syzdek, 1970; Leck and Bigg, 2005] are enriched in sea spray aerosol particles relative to the seawater from which they originate. A number of recent studies have also observed directly or inferred significant enrichment of calcium (Ca2+) in sea spray aerosols relative to bulk seawater. However, both the nature of the Ca2+ enrichment and its dependence on the sea spray aerosol particle size were not resolved in these studies. Sievering et al. [2004] suggested that Ca2+ excess over that from bulk seawater at Baring Head, New Zealand, was derived from nascent sea spray aerosol. They attributed variability in the inferred enrichment of Ca2+ to changes in seawater primary
productivity. Leck and Svensson [2015] suggested that the significant enrichment of Ca$^{2+}$ in a number of ambient aerosol samples collected over the central Arctic Ocean during summer using a low pressure impactor originated from bubbles bursting in open leads. When observed, this enrichment was dependent upon particle size with increasing enrichment observed as particle size decreased. The authors attributed this enrichment to Ca$^{2+}$ complexed to organic matter in the form of polymer gels (see Verdugo [2012] for a review on polymer gels). A difficulty in interpreting both these studies is that nonmarine sources of Ca$^{2+}$ cannot be completely excluded as both studies sampled ambient aerosol populations. Keene et al. [2007] observed significant Ca$^{2+}$ enrichment in sea spray aerosol particles generated by bubbling North Atlantic seawater at a model air-sea interface. Of 26 individual experiments 24 exhibited enrichment of Ca$^{2+}$ with a median enrichment factor (relative to Mg$^{2+}$ rather than Na$^{+}$) of 1.2. In another laboratory study, Cochran et al. [2016] observed enrichment of Ca$^{2+}$ in nascent sea spray aerosol generated from artificial seawater spiked with linear carboxylates. They observed Ca$^{2+}$ enrichment factors of up to 5 that increased with decreasing particle size. Since these were laboratory studies, only nascent sea spray aerosol resulting from bursting bubbles should have been present. This suggests that a mechanism for Ca$^{2+}$ enrichment in aerosols generated by bursting bubbles in the marine environment may exist.

Despite these recent studies the prevalent view in the sea spray aerosol community is that the inorganic elements such as magnesium (Mg$^{2+}$), Ca$^{2+}$, and potassium (K$^{+}$) are not enriched during the bubble bursting process and that the ratio of these substances to sodium (Na$^{+}$) is the same in sea spray aerosol particles (irrelevant of size) as it is in bulk seawater [Lewis and Schwartz, 2004]. This view stems from a period of considerable research and controversy that culminated some 40 years ago. During this period a number of authors presented work indicating that many or all of these inorganic elements were significantly enriched in sea spray aerosol particles compared to seawater [Sugawara et al., 1949; Komabayasi, 1962]. However, a comprehensive review discussing these studies attributed observations of significant fractionation during sea spray aerosol particle production to poor experimental techniques and failure to exclude non-sea-spray aerosol particles, e.g., mineral dust, from measurements [Duce and Hoffman, 1976].

Knowledge of the chemical composition of sea spray aerosol particles is critical to understanding their effect on climate and the chemistry of the marine boundary layer aerosol. For example, it determines both the alkalinity of the particles as well as their hygroscopicity, which in turn determines their behavior as cloud condensation nuclei. Thus, determining the nature, extent, and size dependence of any Ca$^{2+}$ enrichment in sea spray aerosols has wide-ranging relevance.

The aim of this study was to investigate the potential enrichment of Ca$^{2+}$ in sea spray aerosol particles through the use of size-resolved aerosol chemical composition measurements. To do so we have utilized both laboratory-generated nascent sea spray aerosol particles and ambient aerosol samples collected over the central Arctic Ocean during summer.

2. Methods

2.1. Laboratory Sea Spray Chamber

We have used a laboratory sea spray chamber equipped with a plunging jet to generate sea spray aerosol particles. The chamber is described in detail in Salter et al. [2014, 2015] but further details pertinent to this study can be found in the supporting information. Prior to all experiments all internal Teflon-coated surfaces were rinsed thoroughly with reagent grade ethanol followed by low-organic-carbon standard deionized water (MilliQ, $> 18.2 \text{ M} \Omega \text{cm}$), hereafter referred to as deionized water (DIW). The use of a plunging jet rather than the submerged sintered glass filters (frits) used in previous work [Hoffman and Duce, 1977] is an important development given that differences in the sea spray aerosol particle production mechanism are projected onto the composition of the aerosol particles produced. In this regard a pulsed plunging-waterfall apparatus has been shown to reproduce the size-resolved chemical composition of sea spray aerosol particles generated by breaking waves more accurately than submerged sintered glass filters [Collins et al., 2014]. Although our continuous plunging jet has a different geometry and periodicity compared to the aforementioned plunging waterfall it is likely to be more representative of aerosol production by breaking waves than submerged frits.

The chamber experiments were conducted with two seawater sources. Three replicate experiments were conducted using artificial seawater (Sigma Aldrich, S9883; mass fraction: 55% chloride (Cl$^{-}$), 31% Na$^{+}$, 8% sulfate (SO$_4^{2-}$), 4% Mg$^{2+}$, 1% K$^{+}$, 1% Ca$^{2+}$, < 1% other; rehydrated to an absolute salinity of 35 g kg$^{-1}$ using DIW). A second set of three replicate experiments were conducted with natural seawater that was obtained...
from a Norwegian fjord (69.6433°N, 18.9507°E) in late September 2015, hereafter referred to as North Atlantic seawater. Here, 100 L of surface seawater was collected from a pier at the shore by submerging high density polyethylene carboys through the surface of the seawater (capturing surface water). The sampled seawater was stored in the same carboys and shipped to Stockholm University for the experiment. Upon return to Stockholm University the seawater was stored in the dark below 5°C for ~2 months. Prior to the experiment no further treatment of the seawater took place. Each of the three replicate experiments for the two seawater sources studies was conducted over exactly 1 h. Thus, six 1 h experiments were conducted. The seawater samples in the chamber were not changed between each replicate run, so differences in the surfactants present at the water surface in subsequent replicate experiments due to bubble scavenging of surfactants cannot be ruled out [Long et al., 2014].

2.2. Ambient Aerosol Collection
The ambient aerosol data presented in this study were collected during the ASCOS campaign (Arctic Summer Cloud Ocean Study; 3 August 2008–8 September 2008) on board the Swedish icebreaker Oden. For more details on the campaign and sample collection see Tjernström et al. [2014] and Leck et al. [2001]. The ambient aerosol samples were obtained using a PM10-inlet mast located at about 25 m above sea level. To avoid direct contamination from the ship an automatic pollution controller was utilized [Leck et al., 2001]. A total of five samples of marine aerosol was analyzed for this work.

2.3. Sea Spray Chamber Aerosol Sampling
In order to determine the bulk chemical composition of the sea spray particles generated using the sea spray chamber we used a 13-stage (30 L min⁻¹) low pressure impactor (LPI, Dekati). Immediately upstream of the impactor the relative humidity was measured using a Vaisala model HMT333 probe. During all measurements both the sample flow to the LPI and the LPI itself was heated by placing a heating jacket around the sample line and the LPI. This meant that the relative humidity at the inlet of the LPI was always below 50%. The LPI had 50% cutoff diameters of 0.029, 0.060, 0.104, 0.165, 0.253, 0.391, 0.634, 0.990, 1.60, 2.45, 3.96, 6.57, and 10.16 μm aerodynamic diameter and no backup filter was used to sample particles smaller than 0.029 μm aerodynamic diameter. Prewashed polycarbonate collection foils (Whatman Nuclepore Track-Etch Membrane; 800203) were used as the collection substrate. During the wash procedure the polycarbonate collection foils were first rinsed with DIW in a glove box and then placed in prewashed centrifuge tubes in an ultrasonic bath for 60 min. This procedure significantly reduced the blank loading on the filters (see supporting information). A dynamic handling blank was also conducted after the experiment to account for any contamination of the LPI filter substrates during handling of the substrates and transport to and from the sea spray chamber. Each LPI substrate was extracted in 5 mL of DIW in a glove box. The samples were then placed in an ultrasonic bath for 60 min prior to analysis.

The bulk chemical composition of the ambient aerosol collected during the ASCOS cruise was determined with the same LPI as that used during the sea spray chamber experiments. See supporting information as well as Leck and Svensson [2015] for details of the collection and analysis of the ambient LPI samples.

2.4. Inorganic Ion Analysis
Determination of the major ionic constituents was conducted by chemically suppressed ion chromatography (IC; Dionex ICS-2000), see supporting information and Leck and Svensson [2015] for further details. The artificial and North Atlantic seawater samples used to generate the sea spray aerosol were analyzed for the major ionic constituents using IC in the same manner. The seawater samples were diluted 1 to 1000 with DIW into the same analytical range as the aerosol extracts.

3. Results
Figure 1a presents the mean size-resolved inorganic mass fractions of aerosol particles generated in the sea spray chamber from North Atlantic seawater and artificial seawater. The mass fraction was calculated using the average constituent concentrations of the three replicates for each seawater sample. The contribution of NH₄⁺ and NO₃⁻ was excluded from this calculation due their likely source in the gas phase and their extremely low concentration in both seawater sources (mass fraction < 0.002 for both ions). From Figure 1a it is clear that those particles with aerodynamic diameters < 1 μm contain increasing amounts of Ca²⁺ relative to the other major seawater constituents as particle size decreases. This behavior is observed in both the North Atlantic seawater and the artificial seawater in similar proportions. Particles with aerodynamic diameters >1 μm have a mass fraction that is identical to the mass fraction of the seawater. The observed size dependence of the
Ca$^{2+}$ concentration is significantly different to all the other measured ions (see Figure S5 in the supporting information). As a check for contamination the measured concentrations of Ca$^{2+}$ in the samples can be compared to the mean values of the dynamic handling blank (see Figure S2 as well as Tables S1 and S2 in the supporting information). The measured concentrations of the Ca$^{2+}$ ion in the aerosol samples were 2.5–8.4 and 4.0–8.8 times higher than the dynamic handling blank for the artificial seawater and the North Atlantic seawater, respectively, over the submicrometer size range in which we observed the Ca$^{2+}$ enrichment. This is a strong indication that contamination of the sample substrates during handling and transport cannot account for the Ca$^{2+}$ enrichment we observe.

To facilitate comparison between seawater sources and particle composition it is common practice to present the observations as enrichment factors. Classically, the enrichment factor, EF, is defined as the ratio of the concentration of the substance X to the concentration of one of the major constituents of seawater in the particle (e.g., Na$^+$ or Mg$^{2+}$) to the same ratio for bulk seawater:

$$EF(X) = \frac{([X]/[Na^+])_{\text{particle}}}{([X]/[Na^+])_{\text{seawater}}}.$$  \hspace{1cm} (1)

This enrichment factor assumes that at least one substance in the aerosol is expected to behave conservatively in that its mass fraction is the same in both the seawater and the resulting aerosol.

Figures 1b and 1c present EF(X) relative to Na$^+$ of each ion as a function of particle size for both the North Atlantic seawater and the artificial seawater. Presenting the data in this way clearly reveals the enrichment.
Figure 2. Ca^{2+}-mass fraction of the total inorganic mass measured in five ambient aerosol samples collected during the Arctic summer as a function of particle size. The central red line denotes the median value, the edges of the boxes denote the 25th and 75th percentiles, and the error bars denote the extent to the most extreme values that are not considered outliers (red crosses; outliers are defined as values ±2.7× standard deviation). Blue crosses denote mean values.

The nature of the Ca^{2+} enrichment we observe has implications for its atmospheric importance (see section 4). The two most likely explanations for the Ca^{2+} enrichment are complexation of the Ca^{2+} to organics and the presence of inorganic Ca^{2+} (e.g., CaCO_3). Since we observe the same magnitude of Ca^{2+} enrichment in both the natural and artificial seawater experiments, complexation of the Ca^{2+} to organics seems less likely or it suggests that only relatively low amounts of organic compounds are required. However, to rule out a potential contamination of the Sigma sea salt by organics two methods were used to determine the contribution of surface active organic substances. Both X-ray photoelectron spectroscopy and vibrational sum frequency spectroscopy (VSFS) did not observe any surface active organic matter for fresh Sigma sea salt dissolved in DIW (see Figures S3 and S4 in supporting information). However, it should be noted that the VSFS analysis of the North Atlantic seawater, conducted after the experiments, also showed no signs of organic compounds at the water surface. The reason for this is unknown and the apparent lack of surface-active organic compounds in the North Atlantic seawater contrasts other measurements in the literature [Laß et al., 2013]. However, it is noteworthy to mention that Laß et al. [2013] did not observe surface-active organic compounds for water samples collected during winter months.

In order to investigate further the organic matter content of our seawater samples we conducted total organic carbon (TOC) analysis (which includes both particulate and dissolved organic carbon). The TOC measured for the artificial seawater and North Atlantic seawater (at approximately 30 cm depth) was 51 ± 7 μmol L^{-1} C and 198 ± 101 μmol L^{-1} C, respectively. Gašparović et al. [2007] reported TOC concentrations of ~140 μmol L^{-1} C for the same fjord in June. According to a personal communication with the authors TOC in this fjord reaches a maximum in August before decreasing toward a minimum in winter. For reference, the DIW contained ~9 ± 8 μmol L^{-1} TOC.

Similar to the results from our laboratory experiments, enrichment of Ca^{2+} has also been observed in ambient marine aerosol as shown in Figure 2. Here the Ca^{2+} mass fraction of the ambient aerosol samples is presented as a function of size using box and whisker plots to show the variability amongst samples. The contributions
of NH₄⁺ and NO₃⁻ were omitted since in the ambient atmosphere they originate from sources not present in the laboratory experiments (e.g., secondary sources). For the same reason, we have removed non-sea-salt SO₄²⁻ from the ambient data. To do so we calculated the fraction of SO₄²⁻ likely to result from nascent sea spray aerosol assuming a mass ratio of SO₄²⁻ to Na⁺ of 0.06 [Millero, 1974]. As can be seen in Figure 2, the mass fraction of Ca²⁺ increases with decreasing particle size (<1 μm). This is similar to the sea spray chamber observations (see Figure 1a).

The observed increase in Ca²⁺ for particles >1 μm may result from resuspension of crustal material present at the surface of the ice. Such crustal material has been shown to originate from rivers entering the Arctic Ocean from Siberia [Maenhaut et al., 1996]. The enrichment of Ca²⁺ in both the supermicrometer and submicrometer particles may also have originated from long-range transport but this seems unlikely given that the polar front is so far north during summer, isolating the region of the measurements from most long-range dust sources. Further, back trajectories suggested no major influence of free-tropospheric or long-range transported aerosols during the periods of ambient sampling [Leck et al., 2013; Leck and Svensson, 2015]. It is also unlikely that resuspension of crustal material present at the surface of the ice can explain the enrichment of Ca²⁺ at smaller sizes given that as particle sizes decrease, it becomes more difficult to remove them from surfaces [Hinds, 1999]. Combining this with the knowledge that the wind speeds in the region during the measurements were also low (< 6 m s⁻¹) [Tjernström et al., 2012] suggests that the most likely source of the Ca²⁺ in the smallest particles is bubble bursting in the open leads.

4. Discussion and Implications

We have found a significant enrichment of Ca²⁺ in submicrometer sea spray aerosol particles generated using a sea spray chamber filled with both artificial seawater (relatively low in organic substances) and North Atlantic seawater (containing relatively high amounts of natural organic substances). The pattern of Ca²⁺ enrichment is almost identical between the two seawater sources despite their different organic content (see Figure S6 in the supporting information for a direct comparison); the North Atlantic seawater had 4 times more TOC than the artificial seawater. Interestingly, the size-dependent variability in the reported submicrometer Ca²⁺ enrichment seems to be driven almost entirely by size-dependent variability in inorganic sea salt and not by size-dependent variability in Ca²⁺. Ca²⁺ enrichment in submicrometer particles was also observed in ambient samples taken during the Arctic summer. That we observed this enrichment in both the laboratory and the field suggests that a similar mechanism may be responsible.

Perhaps, Ca²⁺ is enriched at the seawater surface resulting in Ca²⁺ ions becoming enriched in the submicrometer sea spray aerosol particles via the film drops. In support of this, Ca²⁺ has been found enriched in sea surface microlayers on occasion [Barker and Zeitlin, 1972; Pattenden et al., 1981; Bigg et al., 2004]. Similar to Hunter [1997], we observed no enrichment of Ca²⁺ in microlayer samples collected using a glass plate from both seawater samples following our experiments (with the plunging jet turned off). However, sampling the sea surface microlayer is notoriously difficult and it is quite possible that our samples were diluted by bulk water.

The mechanism behind any enrichment of Ca²⁺ at the seawater surface can only be speculated on. One possible mechanism is the complexing of Ca²⁺ to organic matter [Bigg et al., 2004; Gao et al., 2012]. However, that we observe enrichment of Ca²⁺ in submicrometer particles produced in the sea spray chamber using both North Atlantic seawater (containing natural organic substances) and artificial seawater (relatively low in organic substances) suggests either that only minor amounts of organic matter are required or that the enrichment we observe is not the result of Ca²⁺ complexing to organic matter. Another explanation might be that Ca²⁺ ions are enriched close to the water surface in the form of ionic clusters (most probably with carbonate ions). It is interesting to note that the enrichment of Ca²⁺ was slightly larger in the artificial seawater which had relatively low amounts of organic carbon compared to the North Atlantic seawater. Again, this suggests that only relatively low amounts of organics are required or that they are not important for the enrichment of Ca²⁺.

Given that we observe enrichment of Ca²⁺ in submicrometer sea spray aerosol relative to bulk seawater it is pertinent to discuss the potential implications (see also Figure 3):

1. If the enrichment of Ca²⁺ in sea spray aerosol particles is not in the form of complexes with organic matter, it may complex with carbonate (CO₃²⁻) or bicarbonate (HCO₃⁻). This may change the alkalinity of sea spray aerosol with profound consequences for the chemistry of the marine boundary layer, in particular, the
Figure 3. Schematic of sea spray aerosol production. Ca$^{2+}$ is enriched at the air-sea interface and subsequently in the film drops. In contrast the jet drops have the same inorganic composition as bulk seawater. This has implications for the chemistry of the marine boundary layer and aerosol related climate effects.

chemistry of sulfur (S). This is because the aqueous oxidation of S (IV) by ozone (O$_3$) is highly pH dependent and only efficient in aerosol particles with pH $> 6$ [Faloona, 2009; Sievering et al., 2004]. Given that the pH of sea spray aerosol particles decreases quickly after formation, any increase in alkalinity over that expected from the bulk seawater composition increases the potential importance of the aqueous O$_3$ oxidation pathway of sulfur (S(IV) pathway) and thus the SO$_2$− aerosol formation in the marine boundary layer.

We have estimated the effect of the Ca$^{2+}$ enrichment we observe on the alkalinity of the particles using a similar approach to Sievering et al. [2004] (for details see supporting information). We observe a total excess alkalinity of 13.0 nEq m$^{-3}$ and 97.5 nEq m$^{-3}$ for particles generated from the North Atlantic seawater and the artificial seawater, respectively, which can be compared to the value estimated for ambient marine aerosol by Sievering et al. [2004] of 12.3 nEq m$^{-3}$ (see Figure S7a in the supporting information). Interestingly, we observe that $\sim 20\%$ and $\sim 4\%$ of the excess alkalinity in the particles generated from the North Atlantic seawater and the artificial seawater, respectively, results from the submicrometer particles. As discussed by Sievering et al. [2004] if the Ca$^{2+}$ enrichment does contribute to excess alkalinity, as estimated here, it would be a potential source of significant amounts of non-sea-salt sulfate and would likely be important for the pH-dependent aqueous chemistry of marine aerosols.

2. Attempts to model the hygroscopicity of inorganic sea spray aerosol routinely assume that its chemical composition is similar to that of bulk seawater or even simply equivalent to NaCl. While this may be the case for large particles [Tang et al., 1997], if size-dependent chemical fractionation of the inorganic ions occurs then the bulk seawater composition may not be representative for all sea spray aerosol particles. This may have implications for cloud droplet activation.

In order to test this hypothesis, we have used the E-AIM accent model [Wexler and Clegg, 2002] to calculate the bulk hygroscopic growth factor using the observed chemical composition (see supporting information for details). E-AIM predicts a 2–4% decrease in hygroscopic growth compared to NaCl with a clear dependence on particle size (see Figure S7b in the supporting information). The smaller the particle size the lower the predicted hygroscopic growth. This suggests that the Ca$^{2+}$ enrichment we observe in submicrometer particles has an effect on the predicted hygroscopic growth. Given that we were unable to model the hygroscopicity of the two smallest size stages using E-AIM, because the model predicted precipitation of CaCO$_3$ and MgCO$_3$, the hygroscopicity of these particles may have been even lower should solids not have precipitated.
3. The organic carbon concentration of sea spray aerosol particles collected using filters is often estimated using a thermal/optical analyzer [Quinn et al., 2014; Facchini et al., 2008]. Since this approach also detects carbonate carbon, if a correction is not made and carbonate ions are enriched (i.e., in the form of calcium carbonate; CaCO$_3$), then estimates of organic carbon may be erroneous. However, under most conditions, the alkalinity of fresh marine aerosol is rapidly titrated within seconds to minutes following production [e.g., Chameides and Stelson, 1992]. Consequently, significant bias of this nature is unlikely.

Although our study is not the first to observe enrichment of Ca$^{2+}$ in sea spray aerosol particles relative to seawater [Keene et al., 2007], it is the first that has observed this behavior in aerosol generated from both natural seawater which contains organic substances and artificial seawater that contains relatively low amounts of organic substances at improved particle size resolution. That we observe a significant Ca$^{2+}$ enrichment in both laboratory experiments, which had a broad range of organic matter, and in the ambient atmosphere suggests that Ca$^{2+}$ enrichment may occur in all natural submicrometer sea spray aerosols.

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