Response to reviewer #2 comment on EGUSPHERE-2023-322 of Enrichment of calcium in sea spray aerosol through bulk measurements and individual particle analysis during the R/V Xuelong cruise over the Ross Sea, Antarctica

We would like to thank the reviewers for their valuable time, feedback, and comments. The suggested modifications have certainly improved the manuscript.

In this document, the review comments are shown in black. The author's response is shown in blue. The revision is shown in red. Line numbers in the responses correspond to the revised manuscript with tracked change. All modifications can be found in the revised manuscript with tracked changes.

This manuscripts present data on Ca enrichment in sea spray aerosol. This is an interesting topic in atmospheric research because of the CCN activation of sea spray aerosol particles. The mechanism of Ca enrichment is not yet fully understood. The data set itself (from a ship cruise at Antarctica) is rare and valuable.

However, there are some weaknesses in the presentation and interpretation of the results. Especially the single particle results are presented as measured, but connection to the main question (i.e. the mechanism behind the Ca enrichment) is not made clear. I don't think that it is unexpected that Ca and organics are internally mixed in sea spray particles. However, how the organic Ca helps to explain the Ca enrichment is not clear to me.

Thus, I think that there are major revisions necessary before the manuscript can be accepted for ACP.

My comments and concerns are listed in the following:

Author's Response: We would like to express our gratitude to the anonymous reviewer for the thorough review of our manuscript and for providing insightful comments that have significantly contributed to its quality.

To better understand calcium enrichment in sea spray aerosols (SSAs), it is necessary to verify the chemical form of calcium. This is because the current water-soluble estimation of Ca^{2+} enrichment in SSAs may be inaccurate without considering organically complexed calcium. Thus, we believe that single-particle analysis is a crucial aspect of comprehending the mechanism of calcium enrichment in SSAs. In this study, we identified a single-particle type that calcium internally mixed with organics (i.e., OC-Ca). It should be noted that OC-Ca is not equal to organic Ca. Although we cannot directly identify the chemical form of calcium via SPAMS, we rigorously inferred that OC-Ca may be organically complexed calcium based on its specific mixing state and thus be partially water-soluble.

We attempted to explain the mechanisms of calcium enrichment in SSAs by establishing a relationship between IGAC and SPAMS datasets. Initially, we found calcium enrichment in ambient aerosol samples in the Ross Sea, which we hypothesize is associated with several environmental variables, such as sea ice fraction, ambient temperature, and wind speed. Then, we attempted to investigate which particle types of calcareous aerosol contribute to calcium enrichment by comparing the chemical composition (e.g., the peak intensity of Ca), mixing state, and size of individual aerosols using SPAMS, as well as the absolute mass concentration using IGAC. Our results suggested that a single-particle type of OC-Ca (internally mixed organics with calcium) may partially contribute to calcium enrichment in SSAs.

Based on a theory of strong coordination between Ca^{2+} and organic matter and the specific mixing state of OC-Ca observed in the Ross Sea, we further infer that the production mechanism of OC-Ca may be associated with marine microgels. Therefore, a comprehensive understanding of the characteristics of OC-Ca behind the mechanisms of calcium enrichment is conducive to further recognizing the CCN and IN activation in remote marine areas.

Detailed point-by-point responses are as follows:

General comments

1. Manuscript structure:

The main text of the manuscript is rather short. Many of the important and interesting discussions regarding methods and uncertainties are only found in the supplement. This is unusual for an ACP manuscript and make me suspect that the manuscript had been originally submitted somewhere else.

Author’s Response: Thanks for the reviewer’s comment. We would like to clarify that this manuscript has undergone extensive revision before submission to Atmospheric Chemistry and Physics. And we are sorry for the unclear. To improve writing structure and readability, we have incorporated the following parts into the main text, as suggested by reviewer 1# and reviewer 2#.

By incorporating these additions, we believe that the revised manuscript has achieved a more comprehensive and cohesive structure, and we thank the reviewer for their helpful input in this regard.

I recommend moving the following parts of the supplement into the main text:

S1: merge with section 4

Author’s Response: Thanks for the reviewer’s constructive suggestion. We have incorporated Text S1 into Section 2.4.1 Aerosol water-soluble ion constituents, Section 4 Discussion, and Section 5 Conclusions and atmospheric implications.

S2: merge with section 2.3

Author’s Response: We have incorporated Text S2 into Section 2.4.

from S3: lines 123 to 141: move to section 4

Author's Response: We have revised the manuscript as suggested. Please refer to the ending of section 4 Discussion (Lines 475-510).

S6: move to section 3.2

Author's Response: Thanks for the reviewer's constructive suggestion. Some of the content in Text S6 (lines 211-236) has been present in the original main text (lines 267-305 in Section 4). Therefore, we incorporated lines 203-210 into the beginning of Section 3.1.

We propose that both Na^+ and Ca^{2+} in our observations originated from marine sources. The mass concentration of Na^+ exhibited a strong positive correlation with that of Cl^- ($r = 0.99$, $p < 0.001$) and Mg^{2+} ($r = 0.99$, $p < 0.001$) (**Fig. S6**), indicating that they had a common origin (i.e., sea spray). However, it is not surprising that the mass concentration of Na^+ showed a relatively weak correlation with that of Ca^{2+} ($r = 0.51$, $p < 0.001$) (**Fig. S6**). This can be explained by the low water-soluble complexation of Ca^{2+} with organic matter and/or insoluble Ca^{2+} in the form of calcareous shell debris, such as $CaCO_3$. In addition, the potential impact of long-range transport of anthropogenic aerosols and dust contributing to Ca^{2+} may be limited due to the predominance of polar air masses during the observation campaigns (see **Fig. S1**).

S8: move to main text, maybe as an additionally results subsection

Author's Response: Thanks for the reviewer's suggestion. We have carefully considered the results that there is little difference between leg I and leg II regarding the chemical composition, size, and mixing state of OC-Ca particles. Therefore, we hope to keep this part in the supporting information. Also, we give a summary of this part in the end Section 2.4.2 Single-particle analysis.

There was little difference in individual particle analysis regarding chemical composition, size, and mixing state of particle clusters obtained from leg I and leg II (SI Text S3).

Taken together, we believe that these additions have significantly enhanced the clarity and organization of our manuscript and would like to express our appreciation to the reviewer for their helpful suggestion. Please refer to the revised manuscript for more details.

2. Calcium enrichment:

It is known that calcium is enriched in sea spray. The data from the IGAC instrument confirm this nicely. The results show that the highest enrichment factors are found at low temperate, low wind speed and sea ice conditions. This is a solid result, but I am no expert in this field and can not judge whether this is new or not.

Author's Response: Thanks for the reviewer's comments.

Calcium enrichment in SSAs has been compellingly verified in previous studies. We provided a summary of recent advances in calcium enrichment in SSAs in Table S1. These studies indeed demonstrated the presence of calcium enrichment in SSAs, but they have not established a clear relationship between calcium enrichment and various environmental factors.

In this study, we discussed how specific environmental factors affect calcium enrichment through field observations. We believe that these interesting findings could provide a better understanding of the mechanisms behind calcium enrichment in SSAs.

3. Single-particle analysis:

The abstract suggests that the controlling factors of the Ca enhancement wich are still unknown are studied in this manuscript.
It is not clear to me what the results of the mansucript mean for the controlling factors.
Author's Response: We apologize for this misleading. Here "control" may not be appropriate. We would like to express that calcium enrichment in SSAs could be affected by a series of environmental factors. Our results indicated that the enhanced Ca^{2+} enrichment in SSAs was sensitive to the lower temperature, lower wind speeds, and the presence of sea ice. To avoid the potential ambiguities, we have rephrased the abstract as follows:
Abstract: Although calcium is known to be enriched in sea spray aerosols (SSAs), the factors that affect its enrichment remain ambiguous. In this study, we examine how environmental factors affect the distribution of water-soluble calcium (Ca^{2+}) distribution in SSAs. We obtained our dataset from observations taken during a research cruise on the R/V *Xuelong* cruise in the Ross Sea, Antarctica, from December 2017 to February 2018. Our observations showed that the enrichment of Ca^{2+} in aerosol samples was enhanced under specific conditions, including lower temperatures (< -3.5 °C), lower wind speeds (< 7 m s^{-1}), and the presence of sea ice. Our analysis of individual particle mass spectra revealed that a significant portion of calcium in SSAs was likely bound with organic matter (in the form of a single-particle type, OC-Ca). Our findings suggest that current estimations of Ca^{2+} enrichment based solely on water-soluble Ca^{2+} may be inaccurate. Our study is the first to observe a single-particle type dominated by calcium in the Antarctic atmosphere. Our findings suggest that future Antarctic atmospheric modeling should take into account the environmental behavior of individual OC-Ca. With the ongoing global warming and retreat of sea ice, it is essential to understand the mechanisms of calcium enrichment and the mixing state of individual particles to better comprehend the interactions between aerosols, clouds, and climate during the Antarctica summer.

A calcium-dominated OC-Ca particle type is detected. This particle type dominates the Ca-containing particle types, but it is not clear if these particles really represent microgels. The process how the biological organic material and the calcium end up in the same particle can not be identified from SPMS data alone.
Author's Response: We agree with the reviewer's comments regarding the limitations of the SPMS dataset to demonstrate that the particle type of OC-Ca represents microgels.

Based on the specific mixing state of OC-Ca, we infer that the OC-Ca might be marine microgels. As previously reported, on the one hand, Ca^{2+} tends to bind with organic matter of biogenic origin, such as exopolymer substances (EPSs), and subsequently assemble as marine microgels (Verdugo et al., 2004; Gaston et al., 2011; Krembs et al., 2011; Orellana et al., 2011; Verdugo, 2012; Orellana et al., 2021). On the other hand, Leck, Bigg, and their colleagues have reported the presence of microgels in the cloud samples in the polar region (Leck and Bigg, 2005a, b; Bigg and Leck, 2008; Leck and Bigg, 2010; Leck et al., 2013; Kirpes et al., 2019). We cannot accurately identify whether the OC-Ca is microgels. We have clarified it in section 4 to better highlight this limitation. Please refer to lines 630-633.

Notably, the dataset via SPAMS cannot directly identify marine microgels. OC-Ca was likely associated with marine microgels, as calcium and biological organic material were extensively internally mixed. This OC-Ca type has previously been observed in the laboratory simulation of Collins et al. (2014).

4. Particle size range:

The difference in the size rane of the two techniques is only discussed in the supplement. This is an important point when it comes to comparing the results of the two techniques. I suggest to move this part (supplement lines 123 - 141) into the main text (see comments above).

Author's Response: Thanks for the reviewer's constructive suggestion. We have incorporated lines 123 to 141 of Text S3 into the ending of Section 4 Discussion. Please refer to lines 492-501 in the revised manuscript.

Furthermore, it is not only the size range, but also a comparison between number fractions or peak intensities (SPMS) and mass concentrations (IGAC). This should also be discussed.

Author's Response: Many thanks for the reviewer's constructive suggestion. We conducted a comparison analysis between particle count, peak area, and mass concentration, as shown in Table 1. The discussion of this part was also incorporated into Section 4, such as lines 402-404, 414-422, 423-427, etc. Meanwhile, we have moved Table S5 to the main text as Table 1.

The OC-CA particle size distribution as displayed (Fig 3 i) centers around 1 µm, but this may be an instrumental effect (transmission and detection efficieny of the SPAMS). A plot of particle number fractions per size bin versus particle size will better show the contribution of each particle type.

Author's Response: Thanks for the reviewer's constructive suggestion. As mentioned by the reviewer, the particle size distribution may be affected by the transmission efficiency of the SPMS. We have added a subplot of particle number fractions per size bin versus particle size into Fig. 3 (j), as follows:

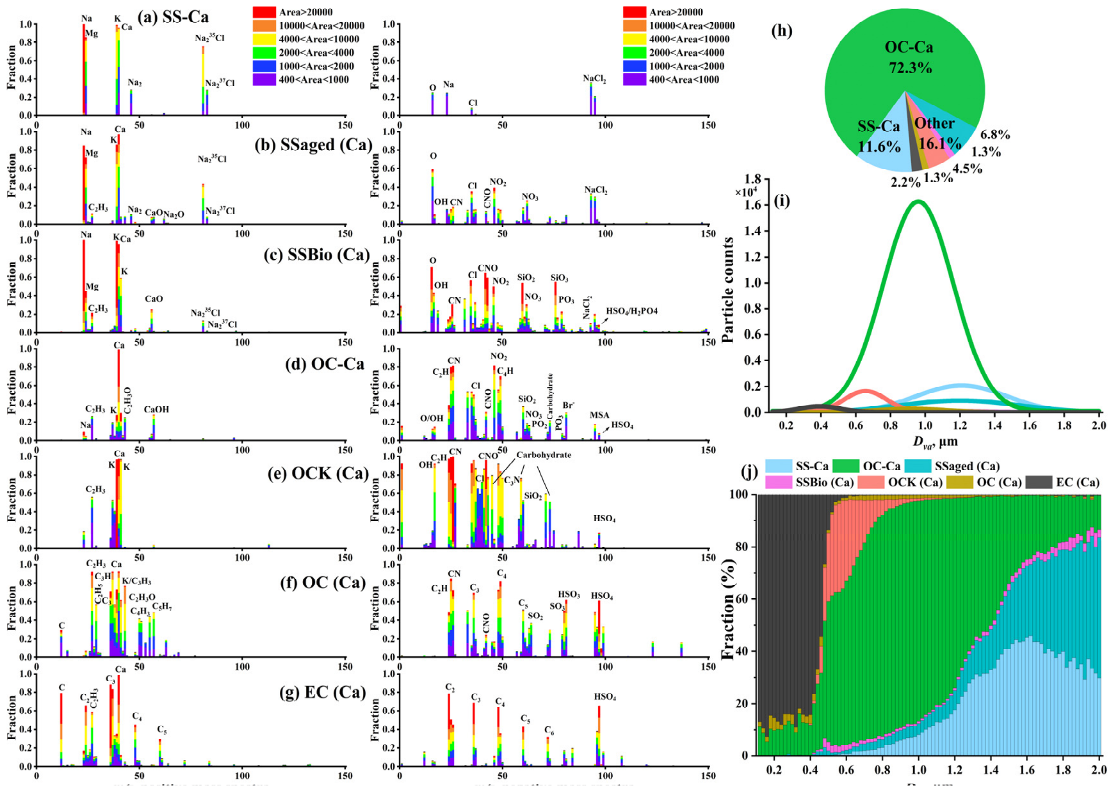


Figure 6

(a) – (g) Average digitized single-particle mass spectra of seven chemical classes of Ca-containing particles. New single-particle types are reclassified with *m/z* 40 [Ca^{2+}] based on previous ART-2a results. (h) Relative proportion and (i) unscaled size-resolved number distributions of single-particle types using Gaussian Fitting. (j) Number fractions of single-particle types per size bin versus particle size.

5. Trajectories:

More trajectories are needed. Either finer time steps (one trajectory per hour) or the "ensemble mode" of HYSPLIT, where many trjectories are calculated per start time with slight differences in the starting conditions. Only through such ensembles one can see the variations between individual trajectories and can judge the reliability of the backward calculation.

Author's Response: Many thanks for the reviewer's constructive suggestion. As suggested, we conducted a 96-hour back trajectory analysis, which includes one trajectory per hour in each starting condition. This analysis covered the selected enhanced calcium enrichment events (Area 1-5) and incorporated surface types such as sea ice, open water, Antarctic land, and chlorophyll-a concentration. Our results indicated that air masses traveling over the ice upon Ross Sea (marginal ice floe/sea ice) and/or Antarctic land were highly associated with enhanced calcium enrichment events. Moreover, the analysis indicated that the long-range transport of dust and open water are unlikely responsible for the observed calcium enrichment in SSAs. The discussion of this analysis has been incorporated into section 3.1 of the main text. We have also supplemented a new plot, Figure 5, to illustrate the results of the 96-hour back trajectory analysis.

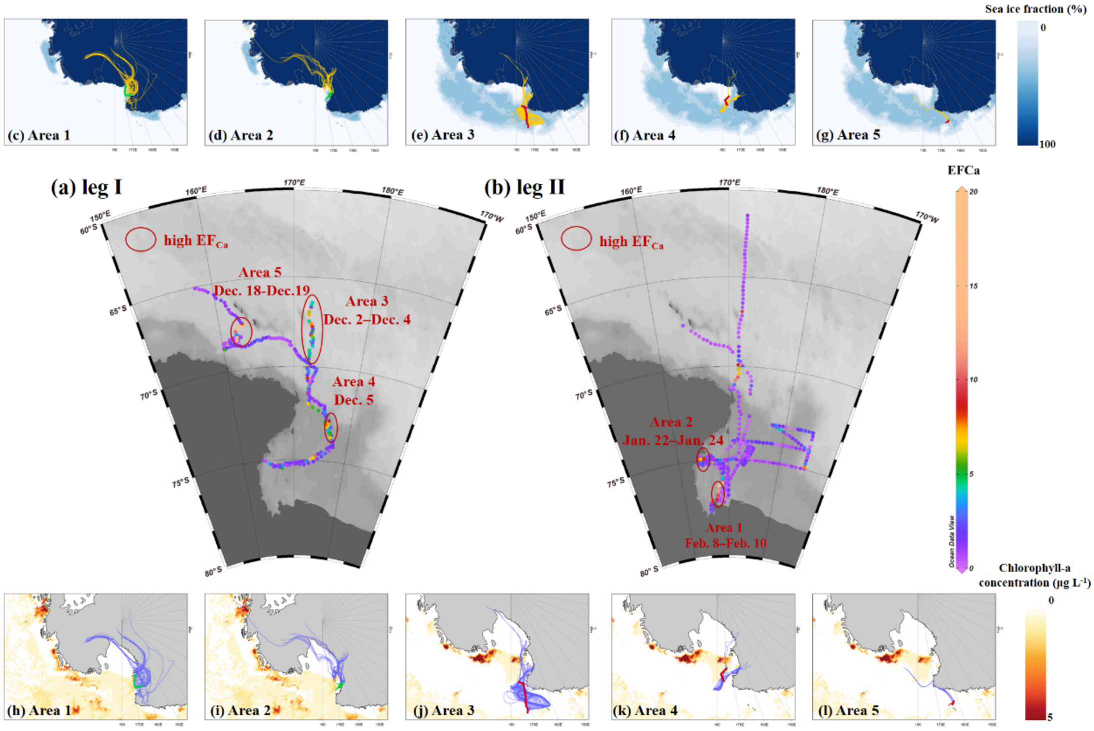


Figure 5

Distribution of EFCa during the (a) leg I and (b) leg II. Five distinct areas with continuous enhanced Ca^{2+} enrichment events, along with 96-hour back trajectories (one trajectory per hour in each starting condition), sea ice fraction (c-g, yellow traces), and chlorophyll-a concentration (h-l, light-blue traces). Lines in red and green referred to ship tracks for corresponding areas during the leg I and leg II, respectively.

Specific points

Section 3.2

(1) What do you mean by "were further refined with an ion signal of m/z 40 [Ca]+."? Was there any threshold applied to the intensity of m/z 40 or were all mass spectra selected that had a signal > 0 at m/z 40? Please explain. >0

Maybe this should be explained already in section 2.3.2 (lines 160-170)?

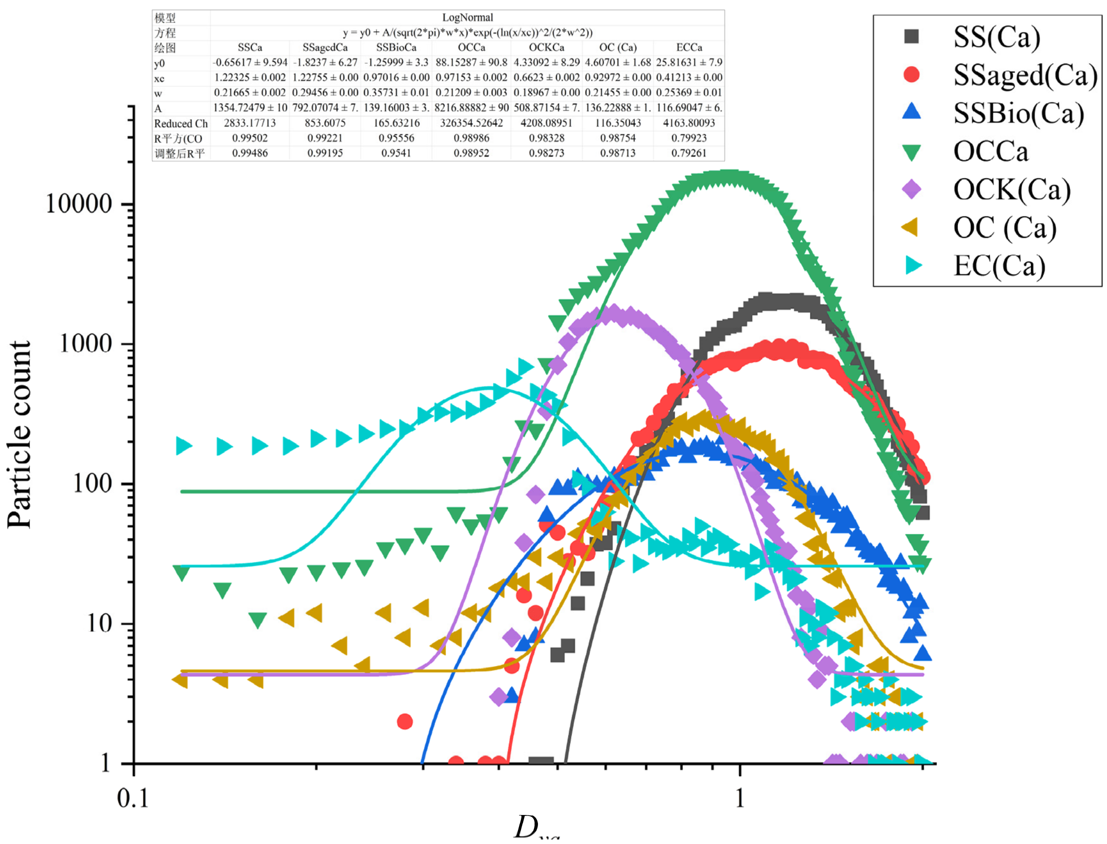
Author's Response: We apologize for any confusion. In the data analysis of SPAMS, we first applied the ART-2a algorithm to cluster the obtained particles into seven groups. We then reclassified the clustered groups by setting a threshold for *m/z* 40 $[Ca]^{+}$ signal (> 0) to obtain individual calcareous particles. This means that all particles that were reclassified contained signals of *m/z* 40 $[Ca]^{+}$. We hope this clears up any misunderstandings and have revised the relevant sentences as follows.

To elucidate the mixing state of individual calcareous particles, we set a threshold of *m/z* 40 $[Ca]^+$ to reclassify all single-particle types that were obtained from the ART-2a algorithm. This means that all reclassified particles contain signals of *m/z* 40 $[Ca]^+$.

(2) Figure 3:

i) the size distributions look like Gauss fits. Please confirm if they are. I suggest using log scales for both axes. For the diameter axis, this is very common in aerosol science, and for the y-axis it will make particle types with low concentrations better visible. On a log scale, the Gauss fits should be replaced by lognormal fits.

Author's Response: Thanks for the reviewer's constructive suggestion. We agree with the reviewer's comment that using a double logarithmic axis is common in aerosol science. However, redrawing the plot using this axis format may not be suitable or visually effective. Therefore, we have followed the above suggestion and created a plot of particle number fractions per size bin versus particle size. We used Gaussian fitting to analyze the size distribution, which we have confirmed in the figure caption.



A plot of size distributions using a double logarithmic axis.

Minor points

(3) Title: remove the "through", e.g.:

Enrichment of calcium in sea spray aerosol: Bulk measurements and individual particle analysis during the R/V Xuelong cruise over the Ross Sea, Antarctica

Author's Response: Thanks for the reviewer's comment. We have revised it accordingly.

(4) Heading of section 2.2:

Meteorological

Author's Response: Thanks for the reviewer's comment. We have revised it accordingly.

References

Bigg, E. K. and Leck, C.: The composition of fragments of bubbles bursting at the ocean surface, Journal of Geophysical Research: Atmospheres, 113https://doi.org/10.1029/2007jd009078, 2008.

Collins, D. B., Zhao, D. F., Ruppel, M. J., Laskina, O., Grandquist, J. R., Modini, R. L., Stokes, M. D., Russell, L. M., Bertram, T. H., Grassian, V. H., Deane, G. B., and Prather, K. A.: Direct aerosol chemical composition measurements to evaluate the physicochemical differences between controlled sea spray aerosol generation schemes, Atmos. Meas. Tech., 7, 3667-3683, https://doi.org/10.5194/amt-7-3667-2014, 2014.

Gaston, C. J., Furutani, H., Guazzotti, S. A., Coffee, K. R., Bates, T. S., Quinn, P. K., Aluwihare, L. I., Mitchell, B. G., and Prather, K. A.: Unique ocean-derived particles serve as a proxy for changes in ocean chemistry, Journal of Geophysical Research: Atmospheres, 116https://doi.org/10.1029/2010jd015289, 2011.

Kirpes, R. M., Bonanno, D., May, N. W., Fraund, M., Barget, A. J., Moffet, R. C., Ault, A. P., and Pratt, K. A.: Wintertime Arctic Sea Spray Aerosol Composition Controlled by Sea Ice Lead Microbiology, Acs Central Sci, 5, 1760-1767, https://doi.org/10.1021/acscentsci.9b00541, 2019.

Krembs, C., Eicken, H., and Deming, J. W.: Exopolymer alteration of physical properties of sea ice and implications for ice habitability and biogeochemistry in a warmer Arctic, P Natl Acad Sci USA, 108, 3653-3658, https://doi.org/10.1073/pnas.1100701108, 2011.

Leck, C. and Bigg, E. K.: Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer, Tellus B, 57, 305-316, https://doi.org/10.1111/j.1600-0889.2005.00148.x, 2005a.

Leck, C. and Bigg, E. K.: Source and evolution of the marine aerosol - A new perspective, Geophys Res Lett, 32https://doi.org/10.1029/2005gl023651, 2005b.

Leck, C. and Bigg, E. K.: New Particle Formation of Marine Biological Origin, Aerosol Sci Tech, 44, 570-577, https://doi.org/10.1080/02786826.2010.481222, 2010.

Leck, C., Gao, Q., Mashayekhy Rad, F., and Nilsson, U.: Size-resolved atmospheric particulate polysaccharides in the high summer Arctic, Atmos Chem Phys, 13, 12573-12588, https://doi.org/10.5194/acp-13-12573-2013, 2013.

Orellana, M. V., Hansell, D. A., Matrai, P. A., and Leck, C.: Marine Polymer-Gels' Relevance in the Atmosphere as Aerosols and CCN, Gels, 7https://doi.org/10.3390/gels7040185, 2021.

Orellana, M. V., Matrai, P. A., Leck, C., Rauschenberg, C. D., Lee, A. M., and Coz, E.: Marine microgels as a source of cloud condensation nuclei in the high Arctic, P Natl Acad Sci USA, 108, 13612-13617, https://doi.org/10.1073/pnas.1102457108, 2011.

Verdugo, P.: Marine microgels, Annual Review of Marine Science, 4, 375-400, https://doi.org/10.1146/annurev-marine-120709-142759, 2012.

Verdugo, P., Alldredge, A. L., Azam, F., Kirchman, D. L., Passow, U., and Santschi, P. H.: The oceanic gel phase: a bridge in the DOM-POM continuum, Mar Chem, 92, 67-85, https://doi.org/10.1016/j.marchem.2004.06.017, 2004.