We thank the reviewers for their detailed and helpful comments. We have added discussions based on reviewers' comments, adjusted multiple figures, and added ternary diagrams in the Supplementary Material. We have also adjusted the structure of the paper. Our responses are below in the italicized font, and the track-changed manuscript and Supplement is attached. Line numbers refer to the revised draft.

Reviewer 1

This manuscript presents an interesting data set on the composition of aerosol sampled during ORACLES and CLARIFY downwind of Africa over the Atlantic Ocean during burning season in 2017 and 2018. Single particle elemental analysis conducted with TEM-EDX provides information about the mixing state (internal versus external), shape, viscosity, and volatility of the collected particles that can provide insight into photochemical, aqueous and heterogenous processing during transport which is not available from techniques measuring bulk aerosol.

The authors suggest that the new data presented in this paper provide important complement to previously published AMS data from the 2 campaigns that will address 3 key questions: 1) do the aerosols in the 2 campaigns differ as a function of the age of the smoke plumes, 2) what are the differences between aerosol in FT and MBL, and 3) what processes caused any differences found while investigating the first 2 questions? Authors also state that determining the mixing state of the aerosol is a motivating question, but I assert that the mixing state is information that may contribute to answering the other questions rather than being of high intrinsic interest by itself. The evolution of smoke advected over the ocean, and how that evolution may be modified by mixing with seasalt aerosol, as well as how seasalt aerosol may be modified by mixing with smoke, have climatic relevance so I was looking forward to hearing the answers to the 3 questions the authors stated they were addressing.Unfortunately, bulk of the paper presents the single particle composition in a large number of ways that are not very well connected to each other, and rarely clearly connected back to the motivating questions. The fact that the conclusions of this manuscript include nothing related to the fact that CLARIFY sampled older smoke than ORACLES, and almost nothing about differences between aerosol in the FT and MBL (just that there was less depletion of Cl in fresh seasalt aerosol in the MBL compared to in the FT) is illustrative. Also, more than a few interesting (sometimes puzzling) observations are pointed out almost in passing, with little attempt at understanding what they may suggest about aerosol processing.

We have removed the mixing state as a motivating question and have tried to more clearly address the motivating *questions, as most sections refer to both the different campaigns and age and BL/FT. We have also rewritten most of the conclusion.*In the following I work through the paper noting sections that could/should be expanded to perhaps develop one or more compelling arguments. Along the way I will also note sections or statements that are not as clear as they might be.

In 3rd paragraph of the introduction the summary of prior work on the extent of coating on BC during CLARIFY (very thick) compared to ORACLES (less thick with some evidence for loss of coating with age) is interesting since the smoke sampled in CLARIFY was significantly older and might therefore have less coating. I assumed this was setting up a major line of investigation based on the TEM-EDX results, but really never found it.

Regarding coating, we found a significant amount of inorganic coating in both campaigns and now emphasize this in the conclusion and line 350. Less organic observed with the TEM in more aged aerosol (CLARIFY) is also consistent with Dobracki et al.'s and Sedlacek III et al.'s findings of loss of organic with plume age, although our TEM results are qualified by loss of volatile organic in the chamber. By less organic found in CLARIFY, this also extends to less coating being present and also less thick than CLARIFY. We discuss this in the OA section (lines 266, 305) and in the conclusion lines 735-755

In second paragraph of section 2.3 it might be helpful to say something about where most of the fires were. Alternatively, modifications to Fig 1 or supplemental Fig 1 might be a way to convey this information (more on that later).

Added that fires were in southern and central Africa (lines 242)

Second paragraph of section 2.4, were there SP2 instruments on both aircraft? If not, which had one and which did not?

Yes, there were SP2 instruments on both aircraft. We have added this (lines 218-220).

Lines 202-203 state that Table 1 includes BC mass/total PM1 but I do not find that. Rather it includes BC mass and the number of BC particles/cm^3.

Thank you, have fixed this (line 230)

Second paragraph of section 3.1 introducing Fig 1. Lot of questions about the trajectories: where were the fires, how far above the fire(s) did given parcel pass (i.e., many trajectories quite high, hence may not have entrained much smoke)? It might be easier for the reader to figure some of this out if there were 4 panels, separating BL and FT samples, with fire hot spots included on the maps.

Figure 1 was introduced for general orientation purposes and doesn't rely on landcover or trajectories to identify if a plume was sampled. Included in text (lines 244-246): Detailed flight information is included in overview papers including whether the flight passed through a plume (Redemann et al 2021). Ancillary data (CO data) will show whether a plume was sampled, with models (Redemann et al. 2021) showing that plumes are often above the cloud.

Line 216 Table 1 shows a filter collected 8/30/17 and 2 on 9/30/18 so "except for two" should be except for three.

Thank you, we have changed this (line 243)

Section 3.2.1 The finding that the organic aerosol in CLARIFY was more volatile (hence lost more quickly when hit by TEM beam) is interesting, and a noteworthy finding. But it is not clear to me that the AMS f44 fully supports this. While there are a few ORACLES samples with high f44 most of the samples in both campaigns cluster from 0.18 to.24 (per right panel in Fig 2). Please explain how the combination of f43 and f44 is, or may not be, consistent with your inference based on single particle analysis.

> *Add (lines 283-286): Most of the variation in filters sampled is in the ORACLES points with higher f44 than the CLARIFY data. As f44 is an indicator of low OOA fraction but not high volatility fraction, the higher ORACLEs points with regard to f44 is consistent with TEM findings of lower volatility organic on ORACLES filters. The f43 spread is similar to differences in instrument baselines and therefore should not be over interpreted.*

The third paragraph in this section is also interesting, using TEM images to assess viscosity and volatility. But there are very few particles shown in Fig 3. Would be much stronger with a numerical summary of how many particles in ORACLES looked like the round one on left compared to the one in the middle, etc.

> *Added (lines 296): Included that more than 80% of particles in ORACLES are rounded/viscous as shown in the left and center images in Figure 3, top panel.*

The loss of tarballs with age is an important finding.

Section 3.2.2 I find the first sentence to be a little confusing, by including internally and externally mixed variants of K-salts. If you counted a particle that was mostly OA, with a little K (or BC with small K crystal attached) as OA (or BC) instead of K would the number fraction of K-salts be much smaller?

> *Added lines (326-328): Only K-salts that looked solid were counted in this number. So, if a particle was OA with K, but without K-salt inclusion, this would not be counted as a K-salt. If a particle was BC with a K-crystal attached, that would be a BC-K salt internally mixed particle*

More important point. Table 2 shows pretty big difference between BL and FT in all three columns, but the sign of all differences is opposite between the two campaigns. Given motivating question 2 (and 3) nearly requires that the authors at least try to explain this.

> *Added lines (347-353) Table 2 shows a difference between BL and FT in all columns, with the sign of the differences being different in the two campaigns. It should be noted that of the three ORACLES filters collected in the BL, two have marine backtrajectories, so BB organic may be underrepresented here. For CLARIFY, cloud processing may remove the more hygroscopic BC containing particles as these are activated and removed by precipitation, and hence the organic/BC ratio is high relative to the FT, but this does not work for ORACLES. The main finding here is that BC with inorganic, as analyzed by TEM, is the most prevalent BC mixing state.*

Section 3.2.3 I am not convinced that it is a good decision to ignore ORACLES in this section. Kind of seems the point of entire paper is to compare and contrast the 2 campaigns, in the framework of looking at old versus very old smoke (and how both kinds of smoke interact with seasalt).

We agree with this. We have added Table 4 to analyze ORACLES filters in the same manner as Table 3's CLARIFY and discuss in section 3.2.3

Line 301. The atomic ratio of Na:Cl in SS is 0.84. Seasalt is not halite.

Change this, thank you, to 0.86:1 based on additional input from Reviewer 2.

Displacement of Cl from seasalt by acids is well established (based on many studies), so need not be emphasized so much here. The Cl rich particles are probably new, hence more interesting.

Lines 348-349 Not convinced that Na in the FT (mixed with BBA) requires mixing BBA into MBL and then modified aerosol back out. Could just mix seasalt into FT and have

Good point, changed sentence to include sea salt mixing into FT (line 435)

On the other hand, the Gold1 filter does support BBA mixing into the MBL (but is this really surprising?)

359-366 As noted above, the Cl rich particle are interesting. But are they important (e.g., what impact on radiative forcing, good CCN)?

We have not found much information on these Cl rich particles in terms of atmospheric importance, but would hypothesize that they are good CCN based on ability to uptake water (lines 459-460)

Section 3.3 last paragraph? Any evidence that the change in the response of K-salts to the electron beam translates to an atmospherically relevant change (like the decreasing viscosity of the sulfur/organic particles in the same samples)

Based on Reviewer 2's input, we have specified that degradation of K-salts may be due to amorphization, dissolution and recrystallization of the salt during processing. (lines 560-562)

We hypothesize that a more amorphous structure may allow for more water uptake and that the salts may be better CCNs or more susceptible for further processing, but have not included in this text because pretty speculative.

Section 3.4 end of second paragraph. Dilution of particles sourced from fires is not unexpected as transport distance increases. Does the similar fraction of the S/K particles in FT and BL during CLARIFY suggest more mixing between the FT and BL (compared to ORACLES). Is there a meteorological reason this might happen (like more convection, as suggested elsewhere based on transition in cloud field)

Added that this may be due to entrainment/detrainment into the lower FT (lines 592-594).

lines 502-505 Case for more S bearing particles in the FT during ORACLES being due to cloud processing is not really supported by Fig 8a and lines 420-425 where it is clear that it was in the MBL that ORACLES samples had more cloud influence.

We have removed "FT"

Lines 507-519 This is a jumpy paragraph that is hard to glean anything from. Not clear that colocation of K, Cl and S requires gas phase HCl condensing on BBA as seasalt contains all 3 of these elements.

Yes this paragraph is very jumpy; we have deleted the paragraph and reworked the entire section 3.4.

Section 4 (Conclusions) See opening comment regarding lack of connection to motivating questions.

We have reworked the conclusion to try to more clearly address differences in campaigns due to aging, as well as potential processing and SSA-BBA interaction and coating/organic

Lines 528-530 Given the loss of OA in the TEM, the large fraction of internally mixed K and BC is artificially inflated, perhaps by a lot in CLARIFY samples.

This is true and we have added this.

Line 539-540 First sentence of next paragraph has no real point

This is true; we have deleted the sentence.

Lines 553-554 see comment above on lines 507-519

We have mostly rewritten this paragraph.

Reviewer 2

General Comments

In their manuscript "Biomass burning and marine aerosol processing over the southeast Atlantic Ocean: A TEM single particle analysis," the authors Dang et al. present a series of analyses on aged biomass-burning and marine aerosols collected during the CLARIFY and ORACLES field campaigns sampling biomass-burning aerosol and biomass-burning impacted marine air masses originating from central Africa. The paper focuses on the transmission electron microscopy analysis of collected particles and the insights that can be gained from this analysis. The analysis is wide-ranging, the paper is overall well written, interesting results are presented, and the geographic area and emission timescale covered by the field-collected samples address a significant current measurement gap. However, there are several sections of the data presentation and discussion where I feel that the authors need to include more detail, either to support the conclusions that are drawn, to cover other possible explanations for the observations, or to address the results of prior work. I believe the manuscript will be suitable for publication in *Atmospheric Chemistry and Physics* after the questions and issues below are addressed.

1. The authors discuss the atmospheric processing of BBA in detail, but I'm not certain I agree with all aspects of the discussion and conclusions. The authors conclude with "Due to the considerable processing of organic aerosol and the noted effects of the MBL on BBA, it appears that aqueous processing, photolysis, and interaction with the MBL are the key drivers in physical and chemical properties such as mixing state and elemental composition of very aged BBA, rather than source" (page 16, lines 584-586).

The conclusion that fuel type is not a major factor in affecting composition and morphology of aged BBA appears to be based on observations that BBA becomes mixed with other inorganic salts through atmospheric and cloud processing and therefore the initial BBA composition is of lesser significance. This conclusion may be reasonable for BBA originating in the currently studied geographic region but does not seem generally applicable to BBA where interaction with marine air masses will not necessarily occur in the days following emission. Additionally, as the authors note, fuel type has a substantial influence on the relative and absolute prevalence of salt and chloride phases in BBA (e.g., Jahn et al. 2021; Goldberger et al. 2019; Liu et al. 2017; Levin et al. 2010) and salt phases will influence the ability of particles to uptake water and act as CCN (e.g., Gomez et al. 2018; Semeniuk et al. 2007; Pósfai et al. 2003). The present work suggests that cloud and/or aqueous processing can significantly impact BBA aging, so would the ability of fresh BBA to uptake water and act as CCN (which is strongly influenced by inorganic salt content and therefore fuel type) not be a potentially major driver in affecting how atmospheric aging proceeds?

> *This is a great point, thank you. We have incorporated the potential importance of inorganic salt content in fresh BBA mixing into the conclusion (765-771) as well as in the abstract. Further we have added that gas phase oxidation of NOx leading to formation of NO_3 is a significant pathway for further addition of inorganic salt.*

The processing of organic aerosol is discussed in terms of organic ratios (Org_{tot}, BC, f44, f43) derived from AMS (and SP2?) measurements and from TEM observations on particle viscosity and volatility. The description of f44 and f43 in section 2.4 does not appear to be consistent with the cited work (Ng et al. 2011). Ng et al. stated that "m/z 44 is thought to be mostly due to acids… or esters" (not diacids or organic peroxides, page 5 line 190) and that "m/z 43 is predominantly due to non-acid oxygenates" (not acids, page 5 line 187). The authors mention derivation of f60 in section 2.4 but do not utilize this organic fraction during later analysis. Recent work (Hodshire et al. 2019) has highlighted the usage of the ratio f60:f44 to analyze BB plume aging in a number of studies: could such a comparison be useful in the present work as well? The authors seem to focus more on photolysis and fragmentation (in addition to aqueous processing) as ways that BBOA evolves during atmospheric aging and less on oxidation of organics (in either the gas or particle phase), mentioning oxidation specifically only once (page 16, line 574). Oxidation increases the AMS oxidized mass fractions (f44 and f43), leads to oxidative fragmentation, and can change molecular photoabsorption cross sections. Photoxidation of laboratory-generated BBA has also been observed to alter BBOA volatilization behavior (Jahn et al. 2021) and physical properties (Jahl et al. 2021). I think the authors should address in more detail the role that oxidation may play in altering BBOA, in addition to photolysis, evaporation/condensation, and aqueous processing.

We have changed to the m/z 43 and m/z44 descriptions to account for acid/esters and non-acid oxygenates as stated by Ng et al. (2011). (lines 211 and 214)

Based on conversations with colleagues, using f60 is challenging since it is close to background based on m60 values in clean and BB plume conditions. We have removed the f60 reference (line 208)

We have included more information on oxidation throughout the manuscript (lines 306-311,755-760).

2. Can the authors provide more detail on sample collection? Was any size segregation performed during particle sampling? From the TEM images in the manuscript, it looks like many particles are in the submicron range; is this characteristic of all the particles that are included in the tabulated data and statistics? How long were individual filter sample collection times? Is it possible that particle morphologies or compositions were altered during collection, and if so could this affect aspects of the discussion on particle mixing state? For example: could particle impaction alter particle morphology due to, e.g., the spreading of organic material around other particle constituents or the lacey carbon framework; or could inorganic material undergo chemical reactions following collection as the aircraft passes into new airmasses?

We have included text to say (lines 153-164): Size segregation was not performed during particle sampling. Most observed particles are in the submicron range. It is possible that morphologies or compositions were altered during collection, as in other aerosol TEM studies. For example compositions of hydrate sulfates have been suggested to change in the TEM chamber or during processing (Buseck and Pósfai 1999),with acidic particles containing more water spreading more on a TEM grid than neutral species. Andreae et al. (1986) suggest that CaSO4 observed on filters without sea salt ions in the marine atmosphere could be from breakup up sea salt particles containing a gypsum crystallite. A sodium chloride core and magnesium chloride coating has been suggested to be due to efflorescence of a particle after collection (Ault et al. 2013). Posfai et al. suggest that an interesting crystalline rod morphology may be due to water loss within the TEM chamber. Generally, the particles we observed were separated from other particles on the filter and so agglomeration and aggregation did not influence organic mixing with adjacent particles. Samples were collected, on average, for approximately ten minutes and in dry conditions, which may limit any chemical reactions the particles are subject to as the aircraft passes into new air masses.

3. I think the authors need to include more detail when describing the composition of different particle populations, specifically what's shown in Table 3 and Figure 11. Table 3 lists average ratios of Na:Cl and Na:S across CLARIFY filters but it's difficult to tell how much heterogeneity exists within the filter populations as a whole. Relatedly, Figure 11 illustrates the extent to which S, Na, K, and Cl are co-located within the ORACLE and CLARIFY samples but doesn't communicate anything about the elemental ratios, which makes it difficult to draw conclusions on particle composition, mixing state, and population-level compositional heterogeneity. I suggest the authors construct a series of ternary diagrams (either for the main text or SI) to more clearly show the ratios of these elements within particles, which will better allow the reader to understand and visualize the composition, mixing state, and heterogeneity of each filter's particle population. I think this would also make it easier for a reader to follow the discussion in section 3.0—Results and evaluate the conclusions in section 4—Conclusions.

Na-S-K and Na-S-Cl ternary diagrams are included in the Supplementary Material. They show, broadly, more Na for below cloud samples in ORACLES and higher Na for both above below and above cloud samples in CLARIFY than ORACLES.

Specific comments

Page 3, lines 84-85: I realize that this summary of the conclusions of Posfai et al (2003) is modeled after what's stated in the abstract of that work, but I don't believe that this is the most complete way to represent the conclusions of that work. Posfai et al. wrote "Even if the carbonaceous part of organic particles were water insoluble, the inorganic K-salt inclusions should make the mixed particle hydrophilic. Thus, organic particles with inorganic inclusions are likely responsible for the high cloud-nucleating potential of biomass smoke particles." Posfai et al. discussed the high degree of mixing between inorganics and both organics and soot, and in the abstract emphasized that observations on internal mixing informed their hypothesis on the cloud nucleus constituents of smoke. Thus, I think the authors of the present study should also emphasize that inorganic material was theorized to be important for BBA hygroscopic behavior in Posfai et al. Related to this, I would like to suggest another reference relevant for this discussion: the related work of Semeniuk et al. (2007), who analyzed the hygroscopic behavior of SAFARI BBA through TEM and concluded that inorganic particle components were the main driver behind particle water uptake and hygroscopic behavior.

Included in lines 87-90: They determined that organic particles with inorganic inclusions likely contribute to the high cloud nucleating capability of biomass burning particles, and Semeniuk et al. (2007), using environmental TEM, found that the inorganic phases of SAFARI particles took up water while soot and tar balls did not; therefore they determined that the inorganic content of mixed organic-inorganic particles determined the hygroscopic properties of BBA.

Page 3, line 110: "very" is used to describe the degree of aging here and elsewhere; please be more quantitative when describing the degree of aging, either highlighting time since emission, time in cloud, and/or estimated radical exposure levels (or the ranges of these quantities, if more than one sample is being discussed).

We have changed/removed "very" here and in other instances throughout the paper and replaced it with the age in days.

Page 7, lines 242-244: what time period does each data point in Figure 2 (right) represent? What CO values would be considered typical of BB-influenced air vs relatively pristine marine air?

We have added (lines 275-278) ORACLES filters (triangles) are 2-7 days and CLARIFY (squares) are 4-15 days aged. A CO cutoff value of over 120 ppbv is used to denote BB-influenced air, based on overall campaign data and Figure 17 in Haywood et al. (2021), which shows the Ascension Island CO frequency distribution and that 120 is at the upper end of the Gaussian distribution of the clean air data.

Page 7, line 249: I'm not sure what "groups" refers to in this sentence: individual particles? Different samples? Please clarify.

Thank you, this was a confusing sentence. Changed to "particles." (line 290)

Page 8, lines 266-275: the observations and discussion on tar balls here is interesting. Can the authors comment on any potential reasons (differences in fuel or fire conditions, differences in other parameters measured during sampling, etc.) for why tar balls may have been observed in these two fresh samples but not others? Additionally, can the authors comment on any potential removal or transformation mechanisms?

> *This suggests a removal process, potentially through deep precipitation near the coast, as they are advected west over the ocean.*

Page 8, lines 285-288: do the authors intend to describe the mechanism by which BC is coated with inorganics? Prior work (Jahn et al. 2020; Li et al. 2003; Gaudichet et al. 1995) has described the formation and prevalence of inorganic phases in BBA as resulting (in part) from the volatilization-deposition of inorganic elements present within the biomass fuel, which can theoretically deposit to any particles generated in the BB plume.

> *We have added (lines 331-336): Inorganic salts in BBA can result from volatiles from the burning source depositing inorganics onto particles in the BB plume (Jahn et al., 2020; Li et al., 2003; Gaudichet et al., 1995). Different salts will indicate different processes; K-salts will form due to evaporation of potassium in the fire and subsequent near field condensation onto the BC; while this will occur with some S and N as well, co-emitted SO_2 and NO_2 can oxidize and condense and lead to additional coating in the far field.*

Page 8, lines 288-289: was BC mixed with both organics and salt a mixing state that was observed at all?

> *We did not observe this.*

Page 9, line 304: Prior electron microscopy work has indicated that there can be significant deviation from the nominal Na:Cl atomic ratio in sea spray aerosol, which is ~0.86:1 (not 1:1) and which also varies as a function of particle size (Krueger et al. 2003, see Figure 7). I suggest that the authors potentially consider additional metrics or ratios to use to examine the aging of sea spray aerosol, or at least discuss the natural variability that can be present.

> *We added that natural variability can be present, with Krueger et al. (2003) finding that Cl/Na atomic ratio increases with particle diameter. (lines 378-380)*

Page 9, line 305: please provide a reference for the sea spray aerosol processing timeline. Is this timeline mostly universal for sea spray aerosol or does it vary by region or with influencing air masses?

> *We have added lines (377-381) However, Na and Cl in the sea salt aerosol rarely are in a 0.86:1 ratio as would be expected from freshly emitted SSA, indicating that the particles have been processed. Natural variability can be present, with Krueger et al.(2003) finding that Cl/Na atomic ratio in sea salts increases with particle diameter. The aging timescale of sea salt also varies depending on the production of NO_2 and SO_2 and its conversion rate to H_2SO_4 and HNO_3 since these acids displace the Cl, and these rates will vary by location.*

Page 9, line 306: please provide citation(s) for the statement on SO_2 oxidation, as there are several mechanisms by which this can occur.

We have provided Sievering et al. 1991 and Miller et al.(1987) as references. (lines 383-384)

Page 9, lines 307-308: Cl would be volatilized as a gaseous molecule, not in its atomic form. Cl gases can also partition to existing Na-free aerosol and do not necessarily need to be involved in the process by which new particles form.

Removed sentence

Page 9, line 308-309: please provide citations for the statement on determining SSA aging, as (I assume) this methodology has been described and used in prior work.

Cl/Na ratios for relative aging have been use for example in Kirpes et al. (2018), Hand et al. (2010) and Young et al. (2016). (lines 385-386)

Page 9, line 320: I don't know how significantly this will affect the overall sea spray aging discussion, but I think it's worth acknowledging that prior work has observed significant variation (<1-13%) in the atomic % of S in fresh sea spray particles (Ault et al. 2013).

Have added this reference (line 391)

Page 9, line 324: specify the Na:Cl ratio on Gold 23.

Specified, as 20.2

Page 9, line 335: explain the rationale behind the 120 ppbv CO cutoff: is this based on other measurements from these field campaigns or prior literature?

As mentioned in a previous answer, based on overall campaign data; Figure 17 in Haywood et al. (2021) showing the Ascension Island CO frequency distribution and 120 is at the upper end of the Gaussian distribution of the clean air data.

Page 10, lines 345-346: are the high amounts of NOx based on measurements during the current campaigns or prior literature? Please specify and provide citations.

Prior literature, referenced Jin et al. (2021) for high levels of NOx in BB plumes (line 433)

Page 10, lines 347-348: could the BC-$NaNO_3$ particle originate from biomass burning rather than sea spray? It is difficult to tell the size of the Na region(s) in Figure 6e. Please also specify in the text here that the proper TEM image is Figure 6e.

We have specified that the TEM image is Figure 6e and also that possible this may be sea spray mixing into the FT with BC. (lines 436-437)

Pages 10-11: I have several questions related to filters Gold 14, 15, and 18 and the discussion here.

- Gold 8 was noted to have several Cl-rich particles and was described as having other markers for mixing between the boundary layer and free troposphere; could the Cl-rich particles on Gold 8 be related to those on Gold 14, 15, or 18 in any way?

> *Yes, the Cl rich particles in Gold 8 have a similar morphology to those in Gold 14,15,18 so could be related. However 30% of the particles on Gold 8 has the presence of Na, so is different from the Gold14, 15, 18 filters, which did not have any Na present. (lines 409-411)*

- The composition of particles on Gold 14 (N and Cl) suggests that these may be composed of NH4Cl, and the discussion of the HNO3-NH3-NH4NO3 system seems to imply that the authors consider this possibility; do the authors think it's likely that the observed N-Cl particles are NH4Cl? If so, please state this directly.

> *The presence of ammonium in the FT and Cl in the samples, as well as strong Cl and N peaks in the EDX spectra suggest that these particles may be NH4Cl. (lines 479-480)*

- Based on the EDX data, the identity of the Cl^- counterion appears to be unclear in most of the Gold 15 particles; is this correct? Do the authors have any hypotheses regarding the Cl phase? Is it possible this is NH4Cl but the N signal is relatively weaker compared to Gold 14 and is therefore not visible?

> *The lack of an observable counterion in the EDX spectra of Gold 15 particles may be due to a weaker N signal than in Gold 14, or potentially Cl dispersed within a sol-gel network. (lines 489-490)*

- The composition of particles on Gold 18 (Mg/Ca and Cl) seems like it could suggest particles of a marine origin, as particles of similar composition (relatively enriched in Mg or Ca) and morphology appear to have been observed in prior work (Kirpes et al. 2018; Prather et al. 2013). Is the elemental composition of these particles homogeneous across each whole particle? If these particles originate from sea spray without additional processing, would that change the discussion in this section?

> *Possibly, this is interesting. We did not perform EDX mapping but the composition appears homogenous across the whole particle, and we did not observe any distinct coatings.*
>
> *Prather et al. (2013) observed that long chain bioorganic species as well as Ca and Mg form stable collapsed structures as sol-gels, and potentially particles from Gold 15 and Gold 18 may be sol-gel with Ca and Mg dispersed within a sol gel structure. (lines 487-488)*

- Gold 18 has CO levels below 120 ppbv listed in Table 4 (119 ppbv), does this mean that this sample was not influenced at all by BB air as would be suggested based on the previously mentioned 120 ppbv cutoff? 120 vs 119 ppbv is obviously a small difference, but it illustrates the difficulties of using a sharp cutoff value.

> *We agree the cutoff is rather sharp and 119 may well be BB influenced air.*

- The authors propose that new particle formation occurred before/during flight C042, but this does not appear to be a period where new particle formation was discussed in the work of Wu et al. (2020) cited earlier in this section. Can the authors provide similar evidence (SMPS size distributions) for the assertion in the present work as was used in Wu et al. (2020)? Looking at Figure 7 it appears to me that very little time was spent in the altitude range 2250-2800 m and from Table 1 it appears that there is no AMS or SP2 data for this time period either; given the lack of data, is it reasonable to speculate on the composition and formation mechanisms of these particles? Or, are there alternative explanations to the one given in the manuscript?

> *We have changed the graph as the sampling time indicates a shorter time period than was indicated in the Gold 14 figure. It is now F2 in the Supplementary Material.*
> *We do not have SMPS size distributions for this time period, and CN data shows around 1437 particles/cm^3, which although high, is not definitive. . As such we will also include primary SSA aerosol as a potential mechanism.*

- I disagree with the characterization of ammonium nitrate as semivolatile: ammonia and nitrate (as nitric acid) are volatile/semivolatile, but ammonium nitrate salt is not semivolatile.

> *Makes sense, thank you. We have removed semivolatile from the text.*

- With the reported RH measurements, the authors seem to be implying that (at least some) aerosols are expected to be deliquesced; if this is the case, please state so directly. Prior work (Jahn et al. 2021; Semeniuk et al. 2007) has also observed BBA to take up water in this RH range.

> *Relative humidity at filter collection times according to backtrajectories is in the 60-70% range, which would facilitate aerosol deliquescnce and the subsequent uptake of HCl. (lines 473-475)*

- The work of Gunthe et al. (2021) concluded that high levels of ammonia were necessary to drive HCl partitioning to the aerosol phase. Are there any measurements during this or similar time periods that point towards what could potentially drive HCl to condense and react? I realize this may be beyond the scope of the current work, but can thermodynamic modelling (e.g., Pye et al. 2020) during this or similar periods be used to constrain the likelihood and conditions under which HCl could partition to the aerosol phase (e.g., how much HCl would need to condense to generate the observed particles, and is this amount reasonable given ambient sources and concentrations)?

> *There are no ammonia measurements from the campaign, but AMS ammonium measurements from other filters from the campaign range from 0.1 to 3 ug/cm^{-3}. Unfortunately, we do not have AMS NH4 data for the Gold 14, 15 and 18 filters. We think that thermodynamic modelling is a great idea regarding HCl partitioning.*

- The inorganic/crustal elements observed on filters Gold 14, 15, and 18 (Si, K, Ca, Mg) have all been observed in BBA during prior work (Li et al. 2003); if the authors believe these signatures are from SSA and not BBA please make that clear.

> *The presence of the elements Si, K, Ca and Mg are hypothesized to be from SSA rather than biomass burning based on the unique morphology and composition of the particles on these filters. (lines 459-461)*

- The authors posit (page 11, lines 389-391) that condensation of Cl-species gives rise to the particles observed on filters Gold 14, 15, and 18. Prior work examining sea spray aerosol suggests that sea spray composition is heterogeneous and can vary episodically depending on the aerosol generation mechanism and other conditions (Ault et al. 2013; Prather et al. 2013; Krueger et al. 2003). Is there a possibility that some of the particles on Gold 14, 15, and 18 are primary?

> *Yes, potentially they are primary, we were assuming that they were secondary based on the lack of Na present. We have added: The particles could also originate from sea spray without additional processing, and as primary particles may be sol gel structures of bioorganics and as observed in Prather et al. (2013). (lines 501-502)*

Page 12, line 420: my understanding of cloud microphysics is somewhat limited; is cloud processing intensity a generally used metric? If so, please include a citation, and if not, please explain the rationale. My understanding of droplet coalescence is that the overall size distribution is relevant for predicting coalescent collisions and that clouds with high aerosol loading can have high cloud water content but a low rate of coalescence.

> *Cloud processing intensity is a novel metric described in detail in Che et al. (submitted). (lines 525-526)*

Page 12, line 432: please provide a citation (e.g., a recent review article) that provides some background on cloud droplet coalescence processes.

> *Grabowski et and Wang (2013) has been added. (line 536)*

Page 13, Figure 10/discussion before section 3.4: over what area is the elemental wt% measured in each particle? If possible, please note the area over which EDX was performed, as in Figure 9. Do the EDX wt% values listed include all non-C elements? For the particles shown in the top panel, do the authors have before/after EDX data to inform what phases volatilized from the particle during analysis? The authors write that these are K-phases, but it also looks like crystalline material remains after EDX on RF5_Filter1_47. Can the authors clarify what they mean by "degradation of the K-salt during cloud processing"? Is this chemical reaction to form mixed K-phases, some degree of amorphization originating from hydration/dissolution and recrystallization, or something else? Some salt phases (some nitrates and sulfates, for example) have also been observed to be unstable upon electron beam exposure following exposure to water vapor and/or acid gases without aqueous processing (e.g., Jahn et al. 2021; Hoffman et al. 2004), offering an alternative explanation for the behavior observed here.

> *We do not have the specific area over which EDX was performed, other than areas where there is a clear hole in the particle- that is where the EDX beam was, for example RF5_Filter1_47. The beam was centered on a large and central part of each particle for this analysis. The EDX wt% includes all non-C elements. While it would have been very useful to have before/after EDX data to inform the phases of what happened after beam exposure, we do not have this data. For example RF5_Filter1_47, the electron beam created a hole in the particle, so the crystalline part which remains was outside of the electron beam. We have clarified degradation of K-salt to include amorphization from hydration, dissolution and recrystallization, as suggested, and have also included the references regarding water vapor and acid gases. (lines 562-564)*

Pages 13-14, section 3.4: I found the discussion in this section a little difficult to follow. The paragraphs list a lot of percentages that are difficult to mentally keep track of and I ended up rereading this section a couple times. I would consider reorganizing some of this material to start a paragraph/section with a conclusion statement and then go through the numbers that support it; for example, starting the paragraph at page 13, line 476 with the idea that BBA is more diluted on CLARIFY than ORACLES filters and then explaining the numbers that support this.

We have reorganized and rewritten most of section 3.4.

Page 14, line 504: consider emphasizing that aqueous formation pathways for sulfate in cloud water are generally predicted to be faster than-gas phase formation pathways.

We have emphasized this in the text (lines 597-598)

Page 14, line 512: In a preceding paragraph the authors suggested a marine influence for the Cl in CLARIFY aerosol, and in the preceding section (3.2) and later in this paragraph the authors discuss the mixing/coalescence of sea spray and BB particles and the fact that sea spray aerosol may contain some amount of K. Therefore, I'm wondering why co-located K/S+Cl implies Cl condensation to BBA in CLARIFY aerosol rather than mixing of sea spray and BBA or simply the presence of sea spray aerosol? Or is the condensation of Cl implied solely for the filters described in Table 4?

We have reworked this section to include the possibility of primary sea spray aerosol.

Page 15, lines 528-529: I don't say this to lessen the relevance and importance of the present work, but Posfai et al. (2003) did observe a large degree of internal mixing between BC and salts.

Changed this to note that Posfai et al. (2003) as well as our work show a large amount of mixing between black carbon and salts. (lines 671-672)

Page 15, lines 539-540: consider rephrasing this sentence, as it implies (to me) that CLARIFY/ORACLES weren't focused on BBA and that SAFARI didn't attempt to examine the noted particle constituents (which they did).

Removed sentence

Page 15, line 547 and page 16, line 558: consider combining these paragraphs, as they appear to discuss the same phenomenon.

Paragraphs combined

Technical Comments

References to Dobracki et al. (2021), Sedlacek et al. (2021), and Che et al. (2021) are included in numerous locations throughout the manuscript but are not included in the list of references. Even if these manuscripts are not published, a bibliographic entry is needed for each with the author list, working title, and preparation status.

References have been added/updated for these papers

The word “collocate” is used in various places in the manuscript; I believe the authors intend to use the word co-locate (alternatively colocate), as collocate is a separate word

Thank you, we have changed this throughout the document.

Page 2, line 53: “BBA aerosol” is redundant

Fixed to remove “with BBA”

Page 4, line 125: include the product ID# for the holey (lacey?) TEM grids and nuclepore filters

Fixed Ted Pella, Inc, Product # 01881 and WhatmanTM WHA10417112

Page 5, line 206 (and potentially elsewhere): “above cloud samples” ⍰ “above-cloud samples”

Thank you, we have fixed this.

Page 10, line 369: add that Wu et al. (2020) is also based on the CLARIFY campaign to emphasize the relevance to the discussion here

Fixed

Page 10, line 372: add the CPC to the instrumentation listed in the Methods section

Added this

Page 12, line 417: there’s an extra “spent”

fixed

Page 13, line 459: “about” ⍰ “amount”

Fixed

General Table and Figure comments: please try to increase the size of axis labels, legends, and in-figure labels, as these were overall difficult to read. I also urge the authors to use a, b, c… labelling for figure panels to enable clearer references to specific panels within the manuscript. As many of the TEM images in tables are too small to see clearly, consider including larger images in a supplementary file.
Page 25, Figure 5: three numbers are present in the ratio above the left-most TEM image but the order and identity of the third number isn’t listed

It’s a ratio of 1.4:1 for page 25, Figure 5. Increased size/ changed Figures 4, 7, 9, 10,

Page 26, Table 3 caption: “forum” ⍰ “from”

Fixed

Page 30, Figure 11: The ORACLES and CLARIFY labels within the figure are switched from the caption

Fixed

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Figure S4 Na-S-Cl ternary diagrams for A) ORACLES below cloud B) ORACLES above cloud C) CLARIFY below cloud and D) CLARIFY above cloud. Note that the lack of particles in A) and B) are due to the majority of particles having no Cl as well as most Cl-containing particles not containing Na or S.

Biomass burning and marine aerosol processing over the southeast Atlantic Ocean: A TEM single particle analysis

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Abstract

This study characterizes single particle aerosol composition from filters collected during the ObseRvations of Aerosols above CLouds and their intEractionS (ORACLES) and CLoud–Aerosol–Radiation Interaction and Forcing: Year 2017 (CLARIFY-2017) campaigns. In particular the study describes aged biomass burning aerosol (BBA), its interaction with the marine boundary layer and the influence of biomass burning (BB) air on marine aerosol. The study finds evidence of BBA influenced by marine boundary layer processing as well as sea salt influenced by BB air. Secondary chloride aerosols were observed in clean marine air as well as in BB-influenced air in the free troposphere. Higher volatility organic aerosol appears to be associated with increased age of biomass burning plumes, and photolysis or oxidation may be a mechanism for the apparent increased volatility. Aqueous processing and interaction with the marine boundary layer air may be a mechanism for the presence of sodium on many aged potassium salts. By number, biomass burning potassium salts and modified sea salts are the most observed particles on filter samples. The most commonly observed BC coatings are inorganic salts. These results suggest that atmospheric processing such as photolysis, oxidation and cloud processing are key~~, rather than BB fuel type, has a major role~~ drivers in the elemental composition and morphology of aged BBA. Fresh BBA inorganic salt content, as it has an important role in the particles' ability to uptake water, may be a key driver in how aqueous processing and atmospheric aging proceeds~~.~~

1. Introduction

With Africa producing almost a third of the Earth's biomass burning aerosol (BBA) (Roberts et al., 2009), two aircraft campaigns, ObseRvations of Aerosols above CLouds and their intEractionS (ORACLES) and CLoud–Aerosol–Radiation Interaction and Forcing: Year 2017 (CLARIFY-2017) were focused on understanding African biomass burning aerosol interaction with clouds and radiation in the southeast Atlantic (Haywood et al., 2021; Redemann et al., 2021). The CLARIFY campaign was based near Ascension Island in 2017 and ORACLES was based offshore of Namibia in 2016-2018. CLARIFY findings detail a complex vertical structure in aerosol ~~which may be due to a temperature inversion which~~ with a temperature structure inhibiting ~~inhibits~~ mixing between layers (Haywood et al. 2021). Over Africa, mixing is inhibited by stable layers at the top of the continental boundary layer (CBL) (Garstang et al., 1996), and over the southeast Atlantic the BBA in the residual CBL moves over the marine boundary layer (MBL) as the air is transported west (Haywood et al. 2021). However, BBA aerosol is more often affected by the MBL than previously accounted for, ~~with BBA~~ reaching the MBL through pathways that are not fully articulated (Zuidema et al., 2018), ~~and~~ with entrainment processes through the clouds potentially ~~affect~~ altering aerosol properties further. An example of this is the low single scattering albedo in the boundary layer compared to the free troposphere (Zuidema et al., 2018; Pistone et al., 2019). Both campaigns report that a more detailed aerosol process-level understanding including the properties of black carbon, organic carbon and inorganic compounds and how they vary as a function of mixing state and altitude is needed, as is knowledge of properties of the aerosol as they age from emission to deposition and the degree of mixing of BBA into the MBL (Haywood et al. 2021; Redemann et al. 2021).

While in-situ instruments provide data over large temporal and spatial scales, the instruments which analyzed chemical composition in the ORACLES and CLARIFY campaigns analyzed bulk aerosol; detailed off-line single particle analysis can offer valuable information to complement these online measurements. The principal in-situ instrument used in these campaigns to determine aerosol chemical composition is the Aerosol Mass Spectrometer (AMS). The AMS can detect organic and non-refractory inorganic mass at high time resolution. There are limitations on the size range of aerosols detected depending on the inlet system employed, with no detection above one micron and a decreasing efficiency above 700 nm. Salts do not vaporize easily and tend to recombine with oppositely charged ions and make quantification of salts in the mass spectra difficult, if not impossible (Nash et al., 2006). The mixing state of organic and inorganic constituents can only be determined with offline analysis of collected samples rather than in-situ bulk aerosol measurements. Transmission electron microscopy (TEM) coupled with energy dispersive X-ray (EDX) is suited to understand physical and chemical properties of individual particles including shape, elemental composition, mixing state, volatility and viscosity, and it is particularly useful for complex aerosol which have been processed (Signorell and Reid, 2011; Reid et al., 2018; Li et al., 2003). Therefore TEM-EDX is a useful method for understanding processes affecting aged BB aerosol as well as marine salts which are pervasive over the ocean.

Previous work of African BBA from the Southern African Regional Science Initiative (SAFARI-2000) showed that the aerosols were primarily composed of black carbon, potassium salts, and organic/sulfur (Liu et al. 2000; Pósfai et al. 2003; Li et al. 2003). The SAFARI campaign was mostly focused on BBA that were less aged than particles in CLARIFY and ORACLES. SAFARI results showed that KCl particles occur in young smoke more often while K_2SO_4 and KNO_3 particles occur more in aged biomass burning aerosol (Li et al. 2003). This is due to gas phase oxidation of NO_x and SO_2 and the displacement of HCl by the stronger acids HNO_3 and H_2SO_4 during plume transport. The authors theorized that aging caused sulfate to accumulate on organic and soot particles due to the large amount of internally-mixed soot/sulfate and organic/sulfate in haze (Pósfai et al. 2003). Based on the location and composition of the particles, Pósfai et al. (2003) concluded that organic and soot particles were the main CCN constituents of BBA. They determined that organic particles with inorganic inclusions likely contribute to the high cloud nucleating capability of biomass burning particles, and~~.~~ Semeniuk et al. (2007), using environmental TEM, found that the inorganic phases of SAFARI particles took up water while soot and tar balls did not; therefore they determined that the inorganic content of mixed organic-inorganic particles determined the hygroscopic properties of BBA. SAFARI-2000 samples were taken in stratus clouds that capped the boundary layer, distinct from the BB haze layer in the FT, and these samples were dominated by sea salt particles (Pósfai et al. 2003). CLARIFY and ORACLES online observations also show an aerosol population dominated by coated black carbon (BC), organic, and sulfates, consistent with the SAFARI TEM findings of BBA. CLARIFY noted a thick inorganic or organic coating around BC (Taylor et al. 2020); while ORACLES noted a less thick coating around BC as well as a decreasing amount of coating with plume age (Sedlacek et al., in prep~~ 2021~~). ORACLES AMS data also noted a decrease in organic with plume age (Dobracki et al., 2022). As the single particle soot photometer, used to detect coatings on BC, does not differentiate between organic and inorganic material, TEM can help elucidate the type and source of coating on BC.

Sea salt aerosol, generated through a bubble bursting process on the sea surface (Lewis and Schwartz, 2004), have implications for radiative effects (Murphy et al., 1998) and cloud condensation nuclei (CCN) activity (King et al., 2012). Sea salt aerosols are modified when they react with sulfate, nitrate, and organic acids, resulting in a Na-rich and Cl-depleted aerosol and emission of gaseous HCl (Gard et al., 1998). There have been studies on the interaction of urban and anthropogenic sources with marine aerosol (Adachi and Buseck 2015), but single particle studies of sea salt aerosol and variations due to mixing with BB air are scarce. Coastal areas near urban sites show sea salt particles being modified by anthropogenic sources. Adachi and Buseck found that sea salt particles were modified by H_2SO_4 and HNO_3 by acid displacement of Cl (2015) and sea salt particles have also been shown to be Cl-depleted by organic acid displacement (Laskin et al., 2012; Kerminen et al., 1998). Pósfai et al. (1995) performed TEM analysis of marine aerosol as part of the Atlantic Stratocumulus Transition Experiment/ marine Aerosol and Gas Exchange (ASTEX/MAGE) campaign and found that polluted continental air affected sea salt aerosol processing, heterogeneity, and mixing with sulfates and nitrates.

With both biomass burning salts and marine salts being major contributors to aerosol in the southeast Atlantic region, a technique that can detect salts is important to accurately represent the aerosol in the region. Further, the plumes sampled during the CLARIFY and ORACLES campaigns are ~~very aged~~aged up to 15 and 7 days, respectively, according to back trajectories of filter sampling times. This~~, which~~ is different from previous campaigns such as SAFARI-2000, which was deployed closer to the burning source, and so TEM results can provide information on processing of ~~very~~ aged (2-15 days from emission) BBA. This paper will describe the single particle analysis in context of the ancillary data including AMS measurements, back trajectories, cloud processing, time from source and time in the MBL. Our main questions are as follows: (1) what are the dominant aerosols in the region and do CLARIFY and ORACLES aerosol differ from each other based on differences in BB plume age, (2) what are the ~~are~~ differences observed between MBL and FT aerosol, and (3) ~~what are the mixing states of the aerosol, (4)~~ what are the proposed processes which have acted on the aerosol. We proceed with a description of filter sampling and analysis methods, describe the region's aerosol types during the two campaigns while comparing and contrasting between the two. Then, we compare aerosol composition and state in the MBL and FT, and discuss possible processing during transport.

2.0 Method

2.1 Filter Sampling

Aerosol sampling was performed with the NASA Ames Research Center (ARC) aerosol filter system (AFS), installed on the P3, and the filter system operated on the UK Bae-146 aircraft operated by the Facility of Airborne Atmospheric Measurement (FAAM). ~~Holey~~ Lacey carbon TEM grids (Ted Pella, Inc, #01881) were attached to 400 nm hole size polycarbonate nucleopore 400 nm hole size (WhatmanTM WHA10417112) filters.   The Bae-146 has been used for filter analysis for single particle analysis (Chou et al., 2008), as well as bulk analysis (Sanchez-Marroquin et al., 2019; Hand et al., 2010; Andreae et al., 2000).   The AFS was composed of a filter holder manifold with five separate filters, connected to the aerosol in situ suite inlet during ORACLES 2017 and 2018. A vacuum pump connected to a flow meter to maintain flow of 30 liters per minute was used for sampling, with five manually controlled valves that were used to switch the sampling to filter holders. The filter manifold was pre-loaded before each flight with filters. Samples for both campaigns were deposited on TEM grids at the locations, sampling times, and total flow volumes listed in Table S1 of the Supplementary Material.

After sampling, the ORACLES 2017 and CLARIFY 2017 filters were sealed in polycarbonate filter holders and wrapped in parafilm paper and aluminum foil and transported together with ice packs in a cooler and placed in a designated freezer immediately at University of Manchester. The ORACLES 2018 filters were sealed in the same manner and transported with ice packs and stored in a designated freezer at Tel Aviv University. A preliminary set of TEM analysis was conducted on the ORACLES and CLARIFY 2017 filters at the University of Manchester, and then sealed and transported together with ice packs in a cooler for analysis at Tel Aviv University. Care was taken to maintain similar handling, storage, transport, and analysis of all filters in both campaigns. All data included in this study are from the Tel Aviv University analysis.

Size segregation was not performed during particle sampling. Most observed particles are in the submicron range. It is possible that morphologies or compositions were altered during collection, as in other aerosol TEM studies. For example compositions of hydrate sulfates have been suggested to change in the TEM chamber or during processing (Buseck and Pósfai, 1999),with acidic particles containing more water spreading more on a TEM grid than neutral species. Andreae et al. (1986) suggest that $CaSO_4$ observed on filters without sea salt ions in the marine atmosphere could be from breakup up sea salt particles containing a gypsum crystallite. A sodium chloride core and magnesium chloride coating has been suggested to be due to efflorescence of a particle after collection (Ault et al., 2013). Posfai et al. suggest that an interesting sulphate crystalline rod morphology may be due to water loss within the TEM chamber. Generally, the particles we observed were separated from other particles on the filter and so agglomeration and aggregation did not influence organic mixing with adjacent particles. Samples were collected, on average, for approximately ten minutes and in dry conditions, which may help to limit any chemical reactions the particles are subject to as the aircraft passes into new air masses.

2.2 Transmission Electron Microscopy – Energy Dispersive X-Ray Analysis (TEM-EDX)

A JEOL™ JEM-2010F FEG-TEM with a ThermoNoran™ energy dispersive X-ray detector (EDX) was used at Tel Aviv University's Exact Sciences' electron microscopy laboratory to analyze 14 filters from CLARIFY (2017) and 16 filters from the ORACLES (2017, 2018) campaigns. TEM analysis was performed at 200 KeV accelerating voltage, a take-off angle of 15.9 degrees for X-ray emission from the sample, with an electron beam dwell time of no more than 30 seconds and spot size 3. The filter was scanned visually and representative particles near the center of the TEM grid were analyzed. EDX spectra was collected for each particle and elemental weight percentage and atomic percentage were found per particle and normalized to 100% using NSS software with Cliff-Lorimer Absorbance correction method. C and O are considered semiquantitative due to the contribution from the Formvar film of C and O from the TEM grid. Ratios of elements such as Na/S and Na/Cl were found by obtaining the either the weight or atomic values for individual particles, finding the ratio of interest, and averaging the ratio per filter.

2.3 Back-trajectory analysis

Back trajectories of each sample were generated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015), with the time step set to one hour. Filter sampling lasted up to approximately ten minutes per filter, and back trajectories were calculated as an ensemble of each minute of filter sampling time. To improve the accuracy of the trajectory, we used the hourly high-resolution ERA5 reanalysis data (fifth-generation atmospheric reanalysis data) to drive the calculation. The ERA5 data is on 0.25° × 0.25° horizontal resolution and includes 37 pressure levels. We ~~collocate~~colocated the cloud liquid water content of ERA5 to the coordinates of trajectories, with a threshold of 0.001 g/kg to detect clouds on the trajectory. Two collocations were performed: one with the 4-D coordinates of the trajectory (time, longitude, latitude, altitude) and another one with 3-D coordinates (time, longitude, latitude). Thus, the cloud liquid content points and profiles at the trajectory are provided, and the mean time of trajectory inside the cloud (cloud liquid water content >0.001 g/Kg), and under clear sky (no cloud liquid water above the trajectory) are calculated accordingly. For each sample, we calculated the back trajectories for 1, 2, 3, 5, 7 and 10 days, and the in-cloud and clear sky time correspondingly.

To determine fire locations, fire radiative power (FRP) data was measured by the spinning enhanced visible and infrared imager (SEVIRI) from the geostationary satellite Meteosat-8. The FRP is produced with a 15-min repeat cycle for pixels which contain active burning (Roberts et al., 2005); hourly data was used to match the time step of the trajectory. The age of the BB aerosol is then estimated as the time in days when the trajectory first intercepts the FRP points, similar to the method used by Vakkari et al. (2018). The BBA 7-day backtrajectory overlaid with MODIS landcover classifications is included in the Supplementary Material Figure S1.

2.4 Aerosol Mass Spectrometer~~ and~~ , Single Particle Soot Photometer and Cloud Droplet Probe

The non-refractive chemical composition for submicron particles was measured using two Aerodyne Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS, Aerodyne Research Inc.), a compact version (C-ToF-AMS) used in CLARIFY (Wu et al., 2020) and a high-resolution (HR-ToF-AMS) used during ORACLES (~~(~~Dobracki et al., 2022~~)Dobracki et al. in prep~~; Redemann et al. 2021). The mass concentrations of organic, sulfate, nitrate, and ammonium were provided. Organic aerosol fractions including f43~~, f44 and f60~~ and f44 were also derived from the mass spectra obtained during both campaigns. f43 is the fraction of the measured organic mass at m/z 43 relative to the total organic aerosol (OA) mass concentration and is indicative of ~~aliphatic carbon chains (C_3H_7+) and oxygenated fragments (C_2H_3O+)~~non-acid oxygenates (Ng et al., 2011) common of fragments of aldehydes, ketones, and acid functionalities. Likewise f44 is the fraction of the measured organic mass present at mz44 relative to the total OA mass concentration. The m/z 44 mass ~~is particularly useful in AMS analysis since it is a result of thermal decomposition of the diacid and organic peroxides on the heater to form CO_2+~~is due to acids or esters (Ng et al., 2011). Since these compound classes are commonly associated with low volatility organic fractions, a high f44 has been associated with low volatility aerosol (Aiken et al., 2008).

The mass concentration of the refractory black carbon (rBC) of particles ranging from 80 – 650 nm was obtained in both campaigns by~~ the~~ single-particle soot photometerrs~~r~~ (SP2, Droplet Measurement Technologies, Boulder, CO) using laser-induced incandescence. Detailed information on SP2 measurements can be found in Taylor et al. (2020). Cloud droplet probes (CDP) (Droplet Measurement Technologies, Boulder, CO) was used in both campaigns to measure cloud droplet number concentration.

3.0 Results

3.1 Overview of observations

Table 1 shows the conditions in which the filters were collected along with ancillary indicators including latitude and longitude, collection above or below cloud, and AMS data including organic, SO_4 NO_3, and NH_4 ~~and BC~~ mass and fraction of PM1 as well as BC mass and number concentration. Time in-cloud in the 24 hours prior to filter collection and time from fire provide additional context for the sampled aerosols. The gaps in the AMS values are due to quality assurance checks which determined that the data for specific filters are unreliable. In the "time from fire" column, if back trajectory analysis did not show interception with fire but rather a marine source, "marine" is noted in the column. There are more samples taken above-~~-~~cloud, and generally, BC mass values are higher in above-~~-~~cloud samples. 6/14 CLARIFY filters and 3/16 ORACLES filters were sampled in the MBL, with the remainder sampled in the FT. The ORACLES 2017 and CLARIFY 2017 filters were sampled from mid-August to early September, while the ORACLES 2018 filters were collected late September through October. The ORACLES samples, in general, represents aged BBA and CLARIFY samples represent extremely aged BBA.

Figure 1 indicates the location of filter sampling as well as back-trajectories including altitude per filter. As shown by the back trajectories, the filter samples covered different BB sources such as savanna, forest and grasses, with fires focused around central and southern Africa. CLARIFY sampling was more centered around Ascension Island whereas ORACLES sampling was closer to the African coast with most filters, except for ~~two~~three, sampled during October 2018. Detailed information on ORACLES flight and sampling conditions, per flight can be found in Redemann et al (2021), which provides ancillary data such as CO which will show whether a plume was sampled, with models (Redemann et al. 2021) showing that plumes are often above-cloud.

3.2 Aerosol classifications

The TEM filters showed a heterogeneous aerosol population with variations in mixing for organic, NaCl salts, potassium salts, and black carbon. ~30-70 particles on each filter were analyzed to determine composition and particle type. The main particle types including potassium salts, sea salt, black carbon and organic aerosol will be described along with the main findings in the following sections.

3.2.1 Organic Aerosol

The AMS data corresponding to filter collection times show that 35% to 70% of CLARIFY and 18% to 68% of ORACLES PM1 is organic, by mass; therefore in-situ data indicates that a substantial amount of PM1 aerosol is organic in both campaigns. While TEM results show organic aerosol for both CLARIFY and ORACLES filters, there is significantly more organic aerosol present on the ORACLES filters. We hypothesize that this is due to differences in the volatility and viscosity of the organic material. Figure 2, left panel, shows a comparison of the fraction of particles, by number, with organic on each filter and the AMS organic fraction, by mass, for the corresponding filter. The majority of CLARIFY filters do not have any particles with organic material, while the majority of ORACLES filters have some particles which contain organic material. This extends to any organic coatings as well; ORACLES organic coatings are largely more thick than organic coatings present on CLARIFY filters. As AMS data shows a significant amount of organic aerosol present in both campaigns (Wu et al. 2020; Redemann et al. 2021), the differences in visible organic material on filters can be attributed to loss of volatile organics in the TEM chamber. It is known that volatile species will be lost from particles in a TEM chamber (Pósfai et al. 2003; Hudson et al. 2004) and preferential loss of organic would indicate a comparatively volatile material.

For context, Figure 2, right panel, shows the f43 vs f44 space for the entire ORACLES and CLARIFY campaigns, with filter data overlaid and marked by filter collection below cloud as well as the CO values marked in the colorbar to denote whether the sample is from a BB plume. ORACLES filters (triangles) are 2-7 days and CLARIFY (squares) are 4-15 days aged. A CO cutoff value of over 120 ppbv is used to denote BB-influenced air, based on overall campaign data and Figure 17 in Haywood et al. (2021), which shows the Ascension Island CO frequency distribution and that 120 is at the upper end of the Gaussian distribution of the clean air data. Low volatility oxygenated organic aerosol will typically have a lower f43 and higher f44 than semi volatile oxygenated organic aerosol (SV-OOA) (Ng et al., 2010, 2011). ~~Both campaigns show a high f44 typical of highly aged organic aerosol, and the ORACLES data show a slightly lower f43 which is associated with low volatility oxygenated organic aerosol (LV-OOA), although the difference is quite small.~~ ~~Low volatility oxygenated organic aerosol will typically have a lower f43 and higher f44 than semi-volatile oxygenated organic aerosol (SV-OOA) (Ng et al., 2010, 2011).~~ Most of the variation in filters sampled is in the ORACLES points with higher f44 than the CLARIFY data. As f44 is an indicator of low OOA fraction but not high volatility fraction, the higher ORACLEsS points with regard to f44 is consistent with TEM findings of lower volatility organic on ORACLES filters. The f43 spread is similar to differences in instrument baselines and therefore should not be over interpreted.

TEM has been used to differentiate ~~groups into~~ high and ~~contact angle and~~ low contact angle ~~groups~~ particles where viscosity and volatility of each particle can be qualitatively determined from the particle image. While factors such as surface tension and adhesion forces influence particle shape, viscosity and volatility can still be qualitatively measured on a comparative basis by using electron microscopy images (Reid et al. 2018). Figure 3, top panel, shows a progression from left to right of increasingly volatile organic as imaged by the TEM. The presence of more rounded, viscous organic (Figure 3, top panel, left image) in ORACLES samples compared to CLARIFY's low contact angle organic (Figure 3, top panel, right image) on the filters is also indicative of relatively higher volatility of organic in CLARIFY filters. More than 80% of ORACLES organic has a rounded morphology, as shown in the left and center panels of Figure 3, top panel.

Figure 3, bottom panel, shows the reduction in Org/BC and Org44/BC mass ratios, based on AMS measurements, for both CLARIFY and ORACLES filters as age from biomass burning source is increased. Filters where backtrajectories did not indicate a BB source are included in the "marine" category. It appears that increased age reduces the organic to BC fraction, similar to the findings of Dobracki et al. (~~submitted~~2022) which found organic aerosol to black carbon mass ratios decreasing from 14 to 10 as the aerosol aged over the Atlantic~~, indicating a loss in organic aerosol in the BB plumes with age~~. UV exposure can work to break down oligomers and low-volatility components in organic (Wong et al., 2015; Lignell et al., 2014) and may account for lower amounts and/or higher volatility of organic present on CLARIFY filters. Photooxidation can also lead to fragmentation of organic chains and oxidation has been observed to change BBOA volatility in laboratory studies (Jahn et al., 2021) as well as physical properties (Jahl et al., 2021) . Our results of less organic present for aged samples are consistent with ~~(~~Dobracki et al.~~,~~ (2022) and Sedlacek II et al.'s (in prep) findings of loss of organic and organic coating with age, although TEM results are caveated by preferential loss of volatile organic.

Tar balls are a type of round organic aerosol unique to biomass aerosol and as of now, the only way to identify tar balls has been through microscopy. Tar balls are estimated to contribute up to ~30% of BB aerosol mass (Sedlacek III et al., 2018). They are highly spherical, high viscosity, and largely resistant to electron beam damage. SAFARI found a considerable number of tar balls (Pósfai et al., 2003) as well as the Biomass Burning Observation Project (BBOP) (Sedlacek III et al., 2018). Adachi et al. (2019) observed tarball formation, likely from primary organic particles, within three hours of emission, with the processing of tar balls possibly~~e~~ related to oligemerization of OA. We did not find many tar balls in the CLARIFY and ORACLES campaigns, with the exception of filters corresponding to RF10 and RF11, which were aged for 1 and 2 days, respectively. RF10 had very viscous aerosol but was mixed with considerable amounts of nitrogen and sulfur. This suggests a removal process, potentially through deep precipitation near the coast ~~for tar balls in very aged BB plumes as they~~as tarballs are advected west over the ocean.

3.2.2 Potassium salts and black carbon

More than 60% of particles, by number, from the two campaigns were potassium salts, either externally or internally mixed. Only K-salts which appeared solid were counted in this number. If a particles was OA with K present, but without a visible K-salt inclusion, this would not be counted as a K-salt. If a particle was BC with a K-crystal attached, this would be counted as a BC-Ksalt internally mixed particle. ~~(Jahn et al., 2020; Li et al., 2003; Gaudichet et al., 1995)~~This is consistent with findings from (Li et al., 2003) where organic particles and potassium salts were the predominant particle types in the smoke. The salts were often mixed with black carbon, organic, or sulfates. Inorganic salts in BBA can result from volatiles from the burning source depositing inorganics onto particles in the BB plume (Jahn et al., 2020; Li et al., 2003; Gaudichet et al., 1995). Different salts will indicate different processes; K-salts will form due to evaporation of potassium in the fire and subsequent near field condensation onto the BC; while this will occur with some S and N as well, co-emitted SO_2 and NO_2 can oxidize and condense and lead to additional coating in the far field. One ~~very~~ common particle type was potassium salt internally mixed with BC, where the K-salt encapsulates the black carbon in a core-shell configuration. EDX analysis can ablate the salt and leave the refractory black carbon core intact. Another common particle type was organic aerosol with interstitial salts. These two common K-salt mixtures are shown in Figure 4. The coating of BC gives rise to absorption enhancements as discussed by Taylor et al. (2020), where they found universally thickly coated BC, and almost no externally mixed BC. The source of the coating is not described in that paper; the~~, and -~~TEM results show that a common coating type is a hygroscopic salt, with implications for both absorption enhancement and enhanced CCN capability of the particles.

The three common black carbon mixing states, BC with salt, BC with organic, and externally mixed BC are shown as a fractional amount that exists in each campaign and BL/FT in Table 2. Internal mixing refers to a particle which has two or more separate components, whereas externally mixed particles contain one component per particle. The predominant mixing state is BC internally mixed with salt, however, BC mixing with organic is likely underestimated due to volatization of organic in the chamber. Table 2 shows a difference between BL and FT in all columns, with the sign of the differences being different in the two campaigns. It should be noted that of the three ORACLES filters collected in the BL, two have marine backtrajectories, so BB organic may be underrepresented here. For CLARIFY, cloud processing may remove the more hygroscopic BC containing particles as these are activated and removed by precipitation, and hence the organic/BC ratio is high relative to the FT, but this does not work for ORACLES. The main finding here is that BC with inorganic, as analyzed by TEM, is the most prevalent BC mixing state.

3.2.3 Marine aerosol

~~The predominant aerosol on CLARIFY filters are either marine salts or BBA which have been influenced in some manner by the marine atmosphere. The analysis here will focus on CLARIFY aerosol as they show more marine influence than ORACLES. Most CLARIFY filters have sea salt aerosols (SSAs) with Na and/or Cl present in varying ratios in the particles, as presented in Table 3. There are also minor amounts of Ca, Mg, K, as would be present in seawater.~~

CLARIFY and ORACLES aerosol were both influenced by the marine atmosphere. Most CLARIFY filters have sea salt aerosols (SSAs) with Na and/or Cl present in varying ratios in the particles, as presented in Table 3. There are also minor amounts of Ca, Mg, K, as would be present in seawater. Table 4 lists the ORACLES particle percents for Na and Cl as well as ratios. Both Table 3 and Table 4 list altitude, CO, and time from fire source to provide context as to whether the air mass is BB influenced. As a measure of aging and sea salt conversion, Tables 3 and 4 list Na:Cl and Na:S weight percent ratios for particles which have those elements present, averaged per filter. A comparison of Table 3 and Table 4 shows that for ORACLES filters, average Na and Cl wt% is less, per particle, and there is a larger variation in % particles per filter containing Na and/or Cl than in CLARIFY. In ORACLES, Na/Cl per filter is higher than CLARIFY due to the low Cl wt% particle average, and Na/S ratio is generally lower due to the lower Na wt%. ~~However, Na and Cl in the sea salt aerosol rarely exist in a 1:1 atomic ratio, as would be expected from freshly emitted SSA, indicating that the particles have been processed. (Krueger et al., 2003)~~

A schematic of the SSA lifecycle, with representative particles from several CLARIFY filters and example mechanisms for Cl depletion, is provided in Figure 5. Briefly, freshly emitted sea salt, generated from ocean bubbles bursting, has Na and Cl present in a 0.86:1 atomic ratio. However, Na and Cl in the sea salt aerosol rarely are in a 0.86:1 ratio as would be expected from freshly emitted SSA, indicating that the particles have been processed. Natural variability can be present, with Krueger et al.(2003) finding that Cl/Na atomic ratio in sea salts increases with particle diameter. The aging timescale of sea salt also varies depending on the production of NO_2 and SO_2 and its conversion rate to H_2SO_4 and HNO_3 since these acids displace the Cl, and these rates will vary by location. The aerosols are ~~quickly~~ processed in the atmosphere, ~~within the span of hours,~~ with nitrates and sulfates replacing Cl. S is removed from the atmosphere through oxidation of SO_2 in water associated with sea salt particles (Sievering et al., 1991; Miller et al., 1987) as well as cloud processing (Beilke and Gravenhorst, 1978), and N species like HNO_3 and NO_2 are also available for reactions with sea salt. Variations of Na:Cl, then, can help to determine ~~degree of~~ relative aging for SSA, as has been used for example in Kirpes et al. (2018), Hand et al. (2010) and Young et al. (2016). For context, Na and SO_4 weight percent in sea salt, based on the composition of sea water, are 60.31 and 7.68, respectively (Seinfeld and Pandis, 2012). Using the atomic weights of sulfur and oxygen, this leaves an expected Na:S ratio of approximately 16:1 in sea salt. A lower than 16:1 ratio indicates Cl displacement by S and is and indicator of aerosol aging, therefore based on the ratios in Table 3, our samples are aged sea salt. Prior work has shown variation of up to 13% in the atomic percent of S in fresh SSA (Ault et al., 2013).

~~4 details three filters consisting of Cl-rich aerosol. Both Table 3 and Table 4 list altitude, CO, and time from fire source to provide context as to whether the air mass is BB influenced. As a measure of aging and sea salt conversion, Table 3 lists Na:Cl and Na:S weight percent ratios for particles which have those elements present, averaged per filter. Table 4, as it is based on Cl aerosol without Na present, does not list these ratios. Table 3 also lists the percent of particles per filter which contain Na or Cl, as well as average weight percent of Na or Cl in the particles, averaged per filter. For context, Na and SO_4 weight percent in sea salt, based on the composition of sea water, are 60.31 and 7.68, respectively (Seinfeld and Pandis, 2012). Using the atomic weights of sulfur and oxygen, this leaves an expected Na:S ratio of approximately 16:1 in sea salt. A lower than 16:1 ratio indicates Cl displacement by S and is and indicator of aerosol aging, therefore based on the ratios in Table 3, our samples are, on average, very aged sea salt. (Ault et al., 2013)~~

~~All~~ For CLARIFY, all SSA on~~in the~~ filters collected in the MBL have NaCl with varying levels of Cl depletion. The presence of Na colocated with Cl on all below-cloud filters and in only 2/7 of the above-cloud filters suggests the particles are less aged in the BL samples compared to the FT samples. Gold 23, a filter sampled in the FT, has a high Na:Cl ratio of 20.2 for particles with both Na and Cl, and this suggests that these salts are aged due to the Cl depletion. The other filter sampled above-cloud with Cl, Gold8, has mostly Cl-only particles and a also crystals of Na:Cl which appear freshly emitted with a cubic NaCl structure. Gold 8 has particles similar in morphology to Cl-rich particles present on filters Gold 14, 15, and 18 which will be described in a later section, the difference being that Gold 14,15 and 18 filters did not have any Na-containing particles present. Cl-only particles in the FT suggests mixing of the MBL and FT, as it shows that Cl ~~from the ocean~~ has reached the FT through turbulent mixing at the top of the MBL. ~~Unprocessed NaCl particles in the FT implies a rapid mixing (within hours as this is the average processing time of NaCl) of MBL and FT air associated with the Gold 8 samples.~~ Both Gold8 and Gold23 filters have backtrajectories which show airmasses from the continent which are entirely within the FT.~~, therefore supporting the top-of-BL mixing with FT hypothesis rather than sea salt being present due to airmass transport through the MBL~~. As deep convection does not occur in this region, marine salts which are observed more than a few hundred meters above the BL height in the Ascension Island region of approximately 2250m (Haywood et al., 2021) may be brought in from outside the region.

In the above-cloud CLARIFY samples, all particles were subject to BB influenced air based on CO values, where we choose 120 ppbv as a CO level indicating BB influenced air above background levels. In the FT, Cl was mostly not present or depleted. ~~There was~~ BC often mixed with sodium sulfates, Cl, and nitrate, as well as K-salts mixed with $NaSO_4$.

Filter Gold 24, interestingly, shows sodium nitrate mixed with black carbon. N can be difficult to detect in EDX spectra as it is between the C and O peaks and can be difficult to deconvolute; therefore the presence of N in the EDX spectra indicates that there is a substantial amount in the particles. Gold 24 was collected above-cloud and in highly BB-influenced air (331 ppbv of CO; 1.9 $\mu g/cm^{-3}$ NO_3). Gold 9, also collected above-cloud in BB influenced air (329 ppbv of CO; 3.1 $\mu g/cm^{-3}$ NO_3), also has sodium nitrate but to a lesser extent than Gold 24. As these are the two above-cloud CLARIFY filters with the highest CO levels, and are also the two filters which show some presence of sodium nitrate, this suggests that BB air may influence the sea salt conversion from NaCl to $NaNO_3$. This is likely due to the ~~significant amount~~emissions of NO_X in ~~the initial~~ BB plumes (Jin et al., 2021) to form HNO_3 and drive Cl out of the sea salt aerosol. There is also an influence of marine air on BC. For example, the bottom center image in Figure 6e shows a black carbon particle mixed with sodium nitrate from the Gold 24 filter, collected in the FT. The presence of the Na in the FT suggests BB entrainment into the MBL and subsequent mixing of marine air into the FT, as alternate explanation, sea spray mixing into the FT with BC.

There were different morphologies and compositions of the marine salts due to different salt conversion processes: some large rounded NaCl over 1.5 micron in diameter and Ca, Mg, and Na sulfates and chlorides. Figure 6 shows a few examples of the many different morphologies of marine salts found on ~~the~~ CLARIFY filters. Figure 6 ~~image~~ F is from Gold 1 which was collected in the MBL, and the particle is BC encapsulated in sodium sulfate; this may be due to aqueous processing where sodium sulfate forms around a BC core. This suggests that while in the FT there is BC and K-salts mixed with sodium, BC, if entrained in the MBL, can also be significantly affected by sea salts and mixed with sodium nitrates and sulfates.

Na and Cl are collocated on individual particles in 5/13 above-cloud filters and 2/3 below-cloud filters. All below cloud filters had BC present. RF2_1 BC is not mixed with Na or marine salts. RF5_2 and RF7_2 filters have BC mixed with salts containing Na,S and K, We did not observe clear crystalline sea-salt morphologies in either above-cloud or below-cloud samples as are observed in CLARIFY filters, and also did not observe Cl-dominant particles.

Three filters from CLARIFY, Gold 14, 15 and 18 were dominated by Cl particles which do not have Na present. Table 54 shows the three Cl dominant filters along with altitude at filter exposure, CO levels, and time from fire, and SI Figure ~~7~~ S2 provides ~~flight tracks including~~ altitude and particle counts during the filter exposure time. The Cl-rich filters are interesting because of the high spatial density as well as the uniformity of the particles on the filter. The uniform particle composition and morphology of the particles suggests that, per filter, the particles have been subject to similar atmospheric processing. Gold 14 was collected in the FT and backtrajectories show interception with biomass burning six days prior to filter collection. Backtrajectories for filters Gold 15 and 18, both collected in the MBL, show that they do not intercept with the fires and are not as influenced by BB air as Gold 14. The presence of the elements Si, K, Ca and Mg are hypothesized to be from SSA rather than biomass burning based on the unique morphology and composition of the particles on these filters. The atmospheric implications for the Cl-rich particles are not clear, although their ability to uptake water may be conducive to their ability to act as CCN.

Gold 14 was collected above-cloud, with 47/47 of the particles having strong Cl and N peaks, and some of the particles show very minor amounts of Si. Wu et al. (2020)'s analysis of the CLARIFY campaign noted an increase in nitrate mass concentration with increasing altitude, and found that the nitrate aerosol mostly existed as ammonium nitrate in the FT. They suggest that the increased levels of nitrate in the FT may be due to colder temperatures at high altitudes which would help partition the HNO_3-NH_3-NH_4NO_3 system into the aerosol phase (Wu et al. 2020). Particle counts from the condensation particle counter (CPC) show a particle count average of 1437 particles/cm^{-3} ~~a large increase in particle numbers when the flight C042 increased in altitude from 2250m to 2800 m, which may signify an area of newly formed ammonium nitrate as the nitrate partitions into the aerosol phase~~. As ammonium nitrate is a ~~semi-volatile~~ hygroscopic inorganic salt which can dissolve into the aqueous aerosol phase, we hypothesize that the Cl aerosols are from HCl in the gas phase which partitions into the aerosol water and ammonium nitrate aerosol. Relative humidity at filter collection times according to backtrajectories is in the 60-70% range, which would ~~also help the~~facilitate aerosol deliquescnce~~become aqueous~~ and the subsequent uptake of HCl. Previous work (Semeniuk et al., 2007; Jahn et al., 2021) has also shown BBA to uptake water in this RH range. Hydrochloric acid partitioning into aerosol water has also been inferred in urban atmospheres, where the highly water absorbing and soluble chloride in the aqueous phase enhances aerosol water uptake through co-condensation and particle growth, causing haze to form (Gunthe et al., 2021). The presence of ammonium in the FT and Cl in the samples, as well as strong Cl and N peaks in the EDX spectra suggest that these particles may be NH_4Cl.

Gold 15 was collected below cloud at 329 meters and 21/21 of the analyzed particles were composed predominantly of carbon and chlorine with small amounts of silicon and potassium; the particles appeared ~~very~~ similar across the filter so EDX on additional particles was not performed. These may be HCl gas uptake onto sea spray aerosol. Gold 18 was collected below cloud at 332 meters. 32/32 particles sampled on the TEM filter were either $CaCl_2$ or $MgCl_2$ with silicon and may have formed through chlorine reacting with Ca and Mg in aerosolized sea water. Prather et al. (2013) observed that long chain bioorganic species as well as Ca and Mg form stable collapsed structures as sol-gels, and potentially particles from Gold 15 and Gold 18 may be sol-gel with Ca and Mg dispersed within a sol gel structure. The lack of an observable counterion in the EDX spectra of Gold 15 particles may be due to a weaker N signal than in Gold 14, or potentially Cl dispersed within a sol-gel network.

The high density of the chloride particles on the filters, compared to the other TEM filters, along with the uniform composition and morphology of these particles, suggests either condensation onto new particles formed in the FT or condensation onto marine particles formed from spray in the MBL. While the prevailing view is that new particle formation rarely occurs over open oceans, work by Zheng et al. (2021) shows new particle formation in the remote MBL occurs frequently after the passage of a cold front, with factors such as removal of existing particles by precipitation, vertical transport of reactive gases from the ocean and cold temperatures facilitating new particle formation. Iodine species can also form new particles in pristine regions (He et al., 2021). These conditions do not characterize our sample, however, these studies are part of a growing area of work which supports new particles formation in the remote MBL; if the newly formed particles are aqueous, they can support HCl uptake and may explain the Cl-dominant aerosol observed. The particles could also originate from sea spray without additional processing, and as primary particles may be sol gel structures of bioorganics and as observed in Prather et al. (2013).

The filters were collected in both above and below cloud conditions, which suggests a mixing of the MBL and FT, as Cl, either in the gas or aerosol phase, reached the FT after having being emitted from the ocean; air exchange at the top of the BL due to turbulent mixing may be for the cause of this, particularly as there is a transition from stratocumulus to cumulus near Ascension Island, and a corresponding increase in convection (Gordon et al., 2018). We hypothesize that Cl in the FT may be from HCl in the BL which gets taken up into cloud droplets, and on their evaporation at cloud top is re-released onto more neutral aerosol such as ammonium nitrate.

3.3 Marine boundary layer and aqueous phase processing

The MBL had a large effect on BB aerosols and as well as processing of sea salt aerosols. A comparison of cloud processing and time in the FT and MBL for the aerosol collected during the filter sampling time is provided in Figure ~~8~~7. The filters are segregated by collection in the MBL and FT and the fractional time spent in each environment is shown in Panels B (collected in BL) and D (collected in FT). Panel D shows that aerosols collected in the FT, irrespective of campaign, have spent nearly all their time in the FT. Panel B shows that of filters sampled in the BL, CLARIFY aerosols have spent more than 80% of the fractional time ~~spent~~ in the BL in the day before filter sampling compared to ORACLES' 45%.

The cloud processing intensity, which is the mean cloud liquid water content multiplied by the mean in-cloud time, in the days prior to the airmass reaching the downwind filter collection location is provided, in Figure 8 Panel A. Cloud processing intensity is a metric described in detail in Che et al. (submitted). Aerosols collected in the MBL were subject to more cloud processing than those collected in the FT, as the aerosols would need to be entrained into BL. ORACLES aerosol, on average, spent slightly more time in-cloud and with clouds with a higher liquid water content than CLARIFY aerosol, particularly apparent for those filters collected in the MBL.

In sea salt, K weight percent is 1.1, assuming sea salt has the composition of seawater and ignoring atmospheric processing (Seinfeld and Pandis, 2012). The K-salt from BB has a significantly higher weight percent than the minor amounts of K found in seawater and sea salt. The fraction of K-salt mixed with sodium increases with age, as shown in Figure 7~~8~~ Panel C. This implies that the K-salt from biomass burning is processed in a way which allows Na incorporation into the particle. As Na is not volatile at atmospheric pressures, we hypothesize that the mechanism is processing by particle mixing, either by cloud drop coalescence (Grabowski and Wang, 2013) or drizzle wash out of aerosol and evaporation.

The interaction of the MBL with BBA and the effect of BB air on marine aerosol has been shown in previous sections, and we hypothesize the mixing of Na salts with BBA to be due to aqueous processing and particle mixing through, for example, cloud drop coalescence. An aqueous K-salt particle from CLARIFY's Gold 9 filter is presented in Figure ~~9~~8. It has varying Na:K ratios by weight percent, designated in the red circles, and there is no Cl in the particle. We assume that the Na present is from marine sources because the area with an 11:1 ratio has 13 wt% Na but only 1.2 wt% K; this is a higher Na wt% than would typically be expected from BBA. However, it should be noted that Na may also be from biomass burning, as sodium has been noted in BB fuel, with the type influencing the amount of Na in particles (Hudson et al., 2004). The image shows that Na mixes with K-salts, organic and sulfur in varying degrees throughout a single aqueous particle and therefore this is a potential mechanism for Na incorporation into existing K-salts.

Single particle structure and morphology is important as it affects aerosol optical properties and ability to act as cloud condensation nuclei. Figure 9~~10~~ shows BC + K-salt (top panel) and BC + (organic/sulfur) mixtures as a function of time in cloud encountered one day before sampling. The spherical nodules are black carbon and the more reflective white areas in the bottom panel are the sulfur/organic mixture. Each particle ID shows the TEM image and associated time in cloud (hours) in the day before sampling, the mean liquid water content of the clouds (g/kg) in the day before sampling, and the weight percent of all elements other than carbon in the particle. From left to right, the time in-cloud increases. If the electron beam visibly altered the particle, an "after" image is shown along with an "before" image to indicate the particle's response to the electron beam. In each particle, the black carbon is insoluble and appears unaffected by increased cloud processing; however, both the K-salts and the sulfur/organic appear affected by increased time in cloud. In the left most panel for Figure 10, top panel, the K-salt is completely unaffected by exposure to the electron beam. The other images in Figure 10 show electron beam damage, indicating that these K-salt structures are more susceptible to volatilization and degradation due to the electron beam; this may be due to degradation of the K-salt during cloud processing and the amorphization from hydration, dissolution, and recrystallization of the salt during processing~~.~~ As an alternative explanation, nitrates and sulfates have been shown to be affected by electron beam exposure after exposure to acid gases or water vapor (Jahn et al., 2021; Hoffman et al., 2004). The K-salt particles on the right, which were subject to the most time in cloud, have a less distinct morphology which may indicate periods of water uptake and loss. In Figure ~~10~~9, bottom panel, the sulfur-organic constituent of the aerosol which was subject to the least ~~about~~ amount of time in-cloud appears to have high viscosity, and was unaffected by the electron beam. After more time in cloud, the sulfur/organic on these particles appear to have a lower viscosity, to be more flat, and also to be more affected by the electron beam. Although these are only a few particles, the images imply that cloud processing can affect certain constituents of mixed aerosols more than others; the structure of the K-salt and the viscosity of the sulfur/organic mixture appear to be more affected by aqueous processing compared to BC.

3.4 Elemental mixing in individual particles

EDX of individual aerosol particles can provide information on elemental mixing across the entire ORACLES and CLARIFY sample sets. Figure 10~~1~~ shows the elemental mixing of CLARIFY and ORACLES samples collected in the free troposphere and boundary layer, designated in separate columns, with each row of pie charts indicating whether a set of two elements are ~~collocated~~ colocated on individual particles for all particles of the specified particle set. All percentages are based on particle numbers rather than mass. The elements S, Na, Cl and K were chosen for elemental mixing analysis as they are the elements which most commonly appear in the EDX spectra. C and O are found in the spectra of almost all particles, and so these elements are not included in this analysis. Supplementary Information, Figures S3 and S4, also includes BL and FT Na-S-K and Na-S-Cl ternary diagrams for additional context, showing that there is more Na and Cl in the CLARIFY samples, particularly the BL.

BBA is more diluted on CLARIFY than ORACLES filters, and S/K particle fractions in the BL/FT suggest increased mixing due to detrainment and entrainment for CLARIFY samples. A higher fraction of ORACLES aerosol contains S, 80%, compared to CLARIFY's 40%. ~~Three quarters of CLARIFY particles which contain S also contain Na, while most ORACLES particles contain S without Na present.~~ S is mixed with K in 34% of CLARIFY and 73% of ORACLES aerosols. This suggests that ORACLES S is predominantly from biomass burning as it is ~~collocate~~colocated~~d~~ with K, and potassium is frequently used as a marker for BBA, consistent with the high amounts of K-salts observed in TEM samples. 76% of ORACLES FT aerosol contain ~~collocate~~colocated~~d~~ S + K, compared with 59% of ORACLES BL aerosol. In comparison, 35% and 33% of CLARIFY FT and BL aerosols have ~~collocate~~colocated~~d~~ S+ K, respectively, implying a dilution of BBA in the CLARIFY aerosol population collected on filters~~,~~ in comparison to ORACLES. The similar fraction of S/K particles in the FT and BL during CLARIFY as compared to ORACLES may be due to the transition over the ocean and the increased entrainment and detrainment across the BL top. Higher fractions of S-containing particles in ORACLES may also be related to cloud processing (Ervens et al., 2018), and aqueous formation pathways for sulfate in cloud water are predicted to be faster than gas-phase formation pathways.

More CLARIFY than ORACLES particles show evidence of marine influence as evidenced by the presence of Na and Cl. 70% of CLARIFY aerosols and 33% of ORACLES aerosol contain some combination of Cl and/or Na. Of ORACLES aerosols containing Na, only ~~a minor fraction~~2% is mixed with Cl, compared with 20% of CLARIFY particles~~ containing both Na and Cl~~. Cl can be found in fluids of some vegetation and so can be present in BBA (Liu et al. 2000), thus while ORACLES Cl may be due to either biomass burning or a marine influence, it is likely that the high fraction of CLARIFY particles with Cl present, relative to the ORACLES population, is indicative of a marine influence for particles in the BL and lower altitudes in the FT. This is also supported by the difference in CLARIFY Cl in the BL (75% of particles) versus the FT (31% of particles), as well as CLARIFY filters Gold 14, 15 and 18 which were dominated entirely by Cl particles.

Cl particle mixing differences between BL/FT dominate in CLARIFY aerosol, but not in ORACLES, as evidenced by K+Cl and S+Cl mixing. Cl is present in 6% and 47% of ORACLES and CLARIFY particles, respectively. K+Cl is present in 3% and 8% of ORACLES FT and BL particles, and 10% and 42% of CLARIFY FT and BL particles, respectively. S+Cl is present in 3% and 4% ORACLES FT and BL particles, and 8% and 27% of CLARIFY FT and BL particles, respectively. CLARIFY Cl is mixed with K or S three to four times more in the BL than in the FT, while the BL does not have as much of an influence on Cl mixing with K or S for ORACLES particles. The increased Cl mixing with S/K in the CLARIFY BL may be due to secondary processes which deposit Cl onto BBA, or a high fraction of primary SSA which also includes S and/or K.

~~81% of ORACLES and 54% of CLARIFY aerosols have K present. 22% of CLARIFY aerosol contain collocated K and Cl, while Cl is present, with or without K, in only 3% of ORACLES aerosol. S mixed with Cl is present in 15% of CLARIFY and 3% of ORACLES aerosol. ORACLES aerosols contain a much lower fraction of Cl-containing particles than CLARIFY.~~

The reverse trend is observed for Na, with Na particle mixing differences between BL/FT more apparent in ORACLES than CLARIFY, as evidenced by K+Na and S+Na mixing. 44% of CLARIFY aerosol contains Na compared to 30% of ORACLES aerosol. K+Na is present in 22% and 50% of ORACLES FT and BL particles and 35% and 43% of CLARIFY FT and BL particles, respectively. S+Na is present in 24% and 46% of ORACLES FT and BL particles and 28% and 32% of CLARIFY FT and BL particles, respectively. Thus while Na is slightly more likely to be mixed with K or S in the CLARIFY BL compared to FT, Na is mixed with S or K about two times more in the ORACLES BL than FT. This may be due to increased BL/FT entrainment and detrainment for CLARIFY samples, and in-cloud aqueous processing and particle mixing for ORACLES samples which can deposit Na onto BBA in the BL.

~~38% of CLARIFY aerosols have Na collocated with K, versus 26% of ORACLES particles. 56% and 17% of ORACLES and CLARIFY aerosols contain K but no Na, respectively. Following trends pointed out earlier, Na is present in relatively more CLARIFY aerosol than ORACLES.Three quarters of CLARIFY particles which contain S also contain Na, while most ORACLES particles contain S without Na present.~~

~~The higher number of particles with S present in ORACLES samples, particularly the FT, may indicate a higher fraction of BBA (because it is collocated with K) compared to CLARIFY, or more sulfate aerosol formation via cloud processing. Studies have shown formation of sulfate to be related to cloud processing (Ervens et al., 2018), and ORACLES samples were subject to higher amounts of cloud processing than CLARIFY samples.~~

~~The high amounts of Na and Cl, both separate and collocated in CLARIFY samples, particularly the BL, suggests a high amount of marine boundary layer influence and marine salts. While the majority of particles in both CLARIFY and ORACLES contain K, K largely exists independently of Cl in the ORACLES samples, while it is mixed with Cl for a substantial fraction of CLARIFY particles particularly in the BL where 42% of particles contain collocated K + Cl. Similarly, S exists largely without Cl in ORACLES particles but is collocated with Cl in 27% of CLARIFY particles. This implies gas phase Cl condensation onto BBA, particularly K-salts, in CLARIFY aerosol. There is also a substantial difference in the amount of Na collocated with K in the FT and BL for both ORACLES and CLARIFY campaigns: CLARIFY FT 35%, BL 43%; ORACLES FT 22%, BL 50%. The majority (59%) of ORACLES FT particles contain S independent of Na; however, of the ORACLES samples collected in the BL, 46% of the particles contain S collocated with Na. This implies, again, a marine boundary layer influence in the increased Na-containing particles in the BL for both campaigns. Assuming that BBA is in the FT and then becomes entrained in the BL, this transition could help facilitate aqueous processing and particle mixing through droplet coalescence in cloud and evaporation, which would incorporate Na onto the BBA.~~

4.0 Conclusions

As CLARIFY sampled older smoke than ORACLES, this study, by comparing the two campaigns in the FT and BL, shows ways in which African BBA smoke is affected by SSA and the marine air, and reciprocally how SSAs may be affected by mixing with BB plumes.

~~This work combines online field measurements and TEM analysis of two campaigns with disparate aging of BBA aerosol. Detailed s~~Single particle analysis revealed considerable heterogeneity in the mixing and processing ~~in the aerosol population~~ of CLARIFY and ORACLES ~~filters in terms of mixing of elements and processing of individual particles~~aerosols. The main aerosols are BBA and SSA. We ~~find~~ found similarities to the previous major campaign which analyzed African BBA, SAFARI-2000, in that we ~~find~~ observed an abundance of potassium salts, black carbon, and organic carbon with interstitial potassium salts (Pósfai et al., 2003; Li et al., 2003). ~~While SAFARI noted an~~

~~abundance of potassium salts, our TEM analysis shows for the first time in the region that a large fraction of BC is internally mixed with potassium salts.~~ Posfai et al. (2003) as well as our analyses show considerable internal mixing between black carbon and salts; therefore, this suggests that the thick coating on CLARIFY and ORACLES BC as measured by the SP2 (Wu et al. 2020; Redemann et al 2021) is often due to inorganics rather than organics. This has implications for radiative effects due to lensing, as well as CCN capability ~~due to the hygroscopicity of the salt~~as the inorganic salts internally mixed with BC would increase the particle's hygroscopicity. This is important as it suggests that the salts formed in the fire via evaporation and recondensation drive the mixing of the carbon aerosol as the secondary inorganic condenses, and that the organic fraction is separate. This is consistent with findings regarding emissions of BC and K-salts and other salts in the flaming phase of a fire, while organic emissions occur during the pyrolysis or smoldering phases (Haslett et al., 2018). These findings are caveated due to the loss of organic in the TEM chamber, which would artificially increase the internally mixed and salt-BC fraction, particularly for CLARIFY samples.

While SAFARI analysis ~~found abundan~~found ~~t~~a large number of KCl salts near source, both the CLARIFY and ORACLES campaigns ~~are in areas measuring much~~sampled much more aged aerosol, and did not find~~and our results show~~ many ~~that~~ KCl particles ~~was not widely found~~. This is presumably because replacement of Cl by nitrates and sulfates has occurred prior to ORACLES and CLARIFY BBA sampling. ~~Near Ascension Island, Cl, likely from marine sources rather than biomass burning, was present on a large number of particles.~~ While the SAFARI campaign and other recent biomass burning campaigns ~~note a considerable amount of~~ found tar balls, our TEM analysis did ~~not observe~~ not find ~~many~~ tar balls other than on filters RF10 and RF11, which were aged for approximately 1 and 2 days, respectively. T~~ORACLES and CLARIFY aerosol are generally very aged, and so t~~his finding implies a reduction in tar balls in aged African ~~very aged~~ BB plumes.

~~SAFARI was near source and focused on BBA, and online AMS and SP2 analysis for CLARIFY and ORACLES was focused on nitrates, sulfates, organic, BC and ammonium. Our TEM analysis extends this data set through the finding of an abundance of marine salts with varying levels of processing. In general, s~~There were differences observed between FT and BL aerosol. More BBA was found in the FT, and more SSA was found in the BL, as would be expected; as BBA aerosol aged, there was increased entrainment into the BL for the CLARIFY samples relative to the ORACLES samples. SSA~~ea salt aerosol collected in the MBL~~ ~~were~~ in the MBL was less aged than those sampled in the FT, as measured~~evidenced~~ by Cl depletion. ~~Cl was mostly, but not always, depleted in the FT compared to aerosols found in the MBL which had higher levels of Cl.~~ The presence of Cl and, on some filters, freshly emitted NaCl in the free troposphere suggests ~~mixing~~ exchange of the MBL and FT in some regions~~, likely through convection and~~ through turbulent mixing at the top of the BL. For ORACLES, S-containing and K-containing particles were much more likely to be mixed with Na in the BL as compared to the FT. These BL/FT differences with Na-S and Na-K particles were not as evident in CLARIFY. In CLARIFY, the largest composition changes between the FT and BL were that S-containing particles were more likely to be mixed with Cl in the BL as compared to the FT, and similarly, K-containing particles were more likely to be mixed with Cl in the in the BL compared to the FT. These Cl trends were not as clear in ORACLES, and only a minor fraction of ORACLES particles contain Cl. This may suggest that for ORACLES, aqueous processing is a key driver in depositing Na onto BB particles, for example by droplet coalescence in clouds and drizzle evaporating before it reaches the surface. For CLARIFY, secondary processes may be important in depositing Cl onto BB particles.

We found evidence of BBA interaction with the MBL as well as marine salts affected by BB air, which has not been ~~as of now reported~~ reported to date in these~~in these~~ campaigns. Mixing of marine air with BB air affects sea salts because of Cl replacement by nitrate, as ~~the~~ BB plumes ~~had~~ have elevated levels of NOx which replaces the ~~to drive~~ Cl in~~out of the~~ SSA. Reciprocally, BBA was influenced through, for example BC mixing with sodium sulfates and sodium nitrates and the presence of Na and Cl on large number of BB particles. There is considerable mixing of Na with BBA through what we believe is aqueous processing of particles, through, for example either cloud drop coalescence or drizzle washout of aerosol and subsequent evaporation. Na and Cl were present in a higher fraction of particles in CLARIFY samples as compared to ORACLES. TEM particles show evidence of aqueous processing, with varying ratios of soluble components throughout a single particle. Particle morphology also show evidence of cloud processing, with soluble components more significantly affected by time in cloud than insoluble components such as black carbon.

~~We found high levels of Cl collocated with K and S in CLARIFY aerosol, particularly those collected in the MBL, and this suggests Cl gas species condensation or HCl uptake onto BB K-salts.~~ The uniformity and ubiquity of Cl-containing aerosol particles on three CLARIFY filters suggests that particles on these filters have been uniformly processed and the existence of areas dominated by Cl aerosol. Further, the high density of Cl spatially on these filters implies HCl condensation onto existing particles which have been recently formed and processed uniformly. Another explanation may be that these are primary particles such as solgel organic particles with Ca, Mg and Cl dispersed. The presence of Cl rich particles are interesting as they may act as good CCN due to their ability to uptake water. ~~There is considerable mixing of Na with BBA through what we believe is aqueous processing of particles, through, for example either cloud drop coalescence or drizzle washout of aerosol and subsequent evaporation. TEM particles show evidence of aqueous processing, with varying ratios of soluble components throughout a single particle. Particle morphology also show evidence of cloud processing, with soluble components more significantly affected by time in cloud than insoluble components such as black carbon.~~

TEM analysis indicates either a loss of organic, including as an organic coating, with plume age, or an increase in ~~organic aerosol~~OA volatility with BB plume age. The reduced amount of organic observed in CLARIFY compared to ORACLES may be due to less organic being present, a more volatile organic which evaporated in the TEM chamber, or both. ~~based on the higher fraction of organic which evaporated in the TEM chamber in CLARIFY compared to ORACLES.~~ Che et al. (submitted) noted SOA formation in the first ~70 hours of BB aging for ORACLES; our results suggest that the secondary organic which forms may be more volatile than the initial organic emitted from biomass burning. There have been different explanations for the vertical structure of single scattering albedo near Ascension Island, with Taylor et al. (2020) and Wu et al. (2020) suggesting a partitioning of inorganic ammonium nitrate onto existing particles at colder temperatures, and ~~(~~Dobracki et al., (2022) hypothesizing that the ~~SSA~~ single scattering albedo differences are due to scattering organic material that is lost from BBA. Sedlacek et al. (~~2021~~in prep) also found a loss of organic material coating BC with plume age in ORACLES; further the authors define different regimes for BBA where organic coating on black carbon increases in the first few hours after emission, the coating mass then plateaus after a several hours to several days when there are competing chemical physical processes such as photochemistry, SOA production, fragmentation and oxidation, and after several days of aging there is material loss due to cloud processing, volatility, and bleaching of brown carbon. While there are different explanations for the vertical structure of single scattering albedo near Ascension Island as well as mechanisms for organic loss with age, our results indicate that higher volatility organic is associated with aging; therefore we hypothesize that ~~photolysis and~~ fragmentation of carbon chains, either through photolysis or oxidation ~~in~~ of the organic, is the predominant mechanism for the apparent higher volatility of aged organic. Our results are compatible with Dobracki et al.'s (2022) and Sedlacek et al.'s (submitted) findings of a loss of organic with age. Increasing oxidation of BB with age, as noted by Wu et al. (2020), and more volatile organic or loss of organic as observed with TEM results implies fragmentation of carbon chains.

~~While studies on combustion types show differences in primary particle types in terms of mixing, amount of organic and elemental composition, for example for particles formed in the flaming and smoldering phase (Liu et al. 2017), these studies are for fresh particles, unlike the very aged combustion aerosol found in ORACLES and CLARIFY.~~ Due to the ~~considerable processing of~~changes in organic aerosol and the noted effects of the MBL on BBA, it appears that aqueous processing, oxidation, photolysis, evaporation, condensation, ~~-~~and interaction with the MBL are ~~the~~ key drivers in physical and chemical properties such as mixing state and elemental composition of ~~very~~ aged BBA. ~~, rather than source.~~ Studies on combustion from different fuel and burn phases show differences in primary particle types in terms of mixing, amount of organic and elemental composition, for example for particles formed in the flaming and smoldering phase (Liu et al. 2017). Our results imply that due to the cloud and aqueous processing that African BBA is subject to, the salt phases present in the BBA will affect the ability of the particles to uptake water, act as CCN, and undergo aqueous and cloud processing. Therefore the inorganic salt content of fresh BBA, fuel type and burning conditions, as well as gas phase oxidation of NOx leading to formation of NO_3 as a significant pathway for further addition of inorganic salts, are key components for the atmospheric aging of BBA in these regions.

Data Availability

Data are publicly available at the ORACLES and CLARIFY archives: http://data.ceda.ac.uk/badc/faam/data/2017 and https://espo.nasa.gov/oracles/archive/browse/oracles/id14. Data not on ~~this~~ these websites can be provided by request.

Author contribution

MS, H. Coe, and CD designed the research. JH, H. Coe, JR, PZ, AN are PIs of the campaigns. JT, MSR, PW, SP, PZ, AN performed field work or provided support for filter collection. CD performed laboratory analysis. CD and H. Che provided figures. CD, H. Che, MS and LZ analyzed data sets. CD led the paper writing, and all co-authors contributed to ideas and writing.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1 Filter IDs, ancillary online aerosol data, location, altitude, backtrajectory-based time from fire as detailed in the text, and in-cloud time over previous 24 hours

Campaign and year	Filter	Date	Particles analyzed	Latitude (°)	Longitude (°)	Altitude (m)	Org (µg/cm^{-3})	SO4 (µg/cm^{-3})	NO3 (µg/cm^{-3})	NH4 (µg/cm^{-3})	BC (µg/cm^{-3})	BC (particles /cm^{-3})	CO (ppbv)	Cloud time in 24hrs (hours)	Above or Below cloud	Time from fire (days)
ORACLES 2017	RF11Filter5	8/30/2017	47	-9.47	5	3505	20.5	1.5	3.1	1.3	3.8	1162	395	0	Above	2
ORACLES 2018	RF02_1	9/30/2018	23	-7.64	5	894	1.1	0.5	0.1	0.1	0.2	56	110	9.35	Below	5
	RF02_2	9/30/2018	35	-7.82	5.03	2606	6.6	0.9	0.3	0.2	0.9	273	210	6.55	Above	1
	RF03	10/2/2018	59	-7.67	5.5	982					1.2	346	156	18.08	Above	6
	RF04	10/3/2018	65	-6.75	7	1195	0.5	0.4	0.0	0.1	0.3	117	120	6.58	Above	6
	RF05_1	10/5/2018	55	-9.5	6.17	943	0.7	0.5	0.1	0.2	1	297	154	11.29	Above	6
	RF05_2	10/5/2018	64	-9.5	6.21	378	0.2	0.2	0.0	0.1	0.5	119	106	8.42	Below	marine
	RF05_3	10/5/2018	37	-9.5	6.11	3247	6.4	1.2	0.5	0.4	0.9	294	210	0	Above	1
	RF06_1	10/7/2018	49	-8.91	5	2444	6	1.1	0.4	0.4	1.3	421	248	0	Above	2
	RF06_2	10/7/2018	39	-6.86	5	2570	2.3	0.6	0.1	0.2	0.5	193	173	0	Above	2
	RF07_1	10/10/2018	43	-12.77	5.01	1091	0.6	0.3	0.0	0.1	0.5	159	121	2.59	Above	6
	RF07_2	10/10/2018	29	-7.39	5	159	0.3	0.2	0.0	0.0	0.4	108	123	0.18	Below	marine
	RF09	10/15/2018	56	-11.35	5	1307	1.2	0.5	0.1	0.1	1	265	158	0.5	Above	7
	RF10	10/17/2018	66	-7.18	10.5	1986	18.5	3	2.6	1.4	2.3	807	417	2.25	Above	1
	RF11	10/19/2018	62	-7.95	9	3027	3.7	0.6	0.3	0.2	0.9	292	190	0.08	Above	2
	RF13	10/23/2018	33	-5.01	-0.68	1127	0.1	0.1	0.0	0.0	0.1	42	118	6.94	Above	4
CLARIFY 2017	Gold_1	8/17/2017	49	-8.8	-11.52	323	4.1	1.9	0.2	0.7	0.5	195	108	0	Below	marine
	Gold_8	8/22/2017	27	-8.46	-13.43	3902	6.9	1.3	1.4	1.0	1.2	380	204	20.77	Above	7
	Gold_9	8/23/2017	39	-5.67	-12.42	2813	18.8	2.9	3.1	2.0	3	934	329	0	Above	4
	Gold_10	8/24/2017	42	-8.37	-15.24	2918	3.9	0.6	0.3	0.3	0.8	232	158	0	Above	5
	Gold_11	8/24/2017	54	-7.7	-13.85	319	0.3	0.3	0.0	0.1	0.1	17	70	0	Below	15
	Gold_14	8/28/2017	47	-8.26	-13.74	2845						683	262	0	Above	6
	Gold_15	8/28/2017	22	-8.28	-13.66	329					1	287	158	0.3	Below	marine
	Gold_18	8/29/2017	32	-8.69	-12.47	332					0.5	174	119	0	Below	marine
	Gold_19	8/30/2017	57	-8	-17.08	1969	5.7	1.6	0.9	0.8	1.8	535	212	0.38	Above	7
	Gold_20	8/30/2017	30	-8.03	-17.3	329	3.6	1.2	0.2	0.5	0.7	225	130	0	Below	marine
	Gold_21	9/7/2017	43	-8.32	-18.48	2357					1.5	436	177	0	Above	6
	Gold_22	9/2/2017	43	-5.66	-13	2139	2.1	0.6	0.2	0.3	0.7	208	128	0	Below	9
	Gold_23	9/2/2017	44	-6.14	-13.52	3500	12.2	1.3	2.4	1.3	2.5	750	273	0	Above	4
	Gold_24	9/4/2017	24	-7.91	-12.72	1950	13.4	2.3	1.9	1.4	3.6	968	331	7.84	Above	4

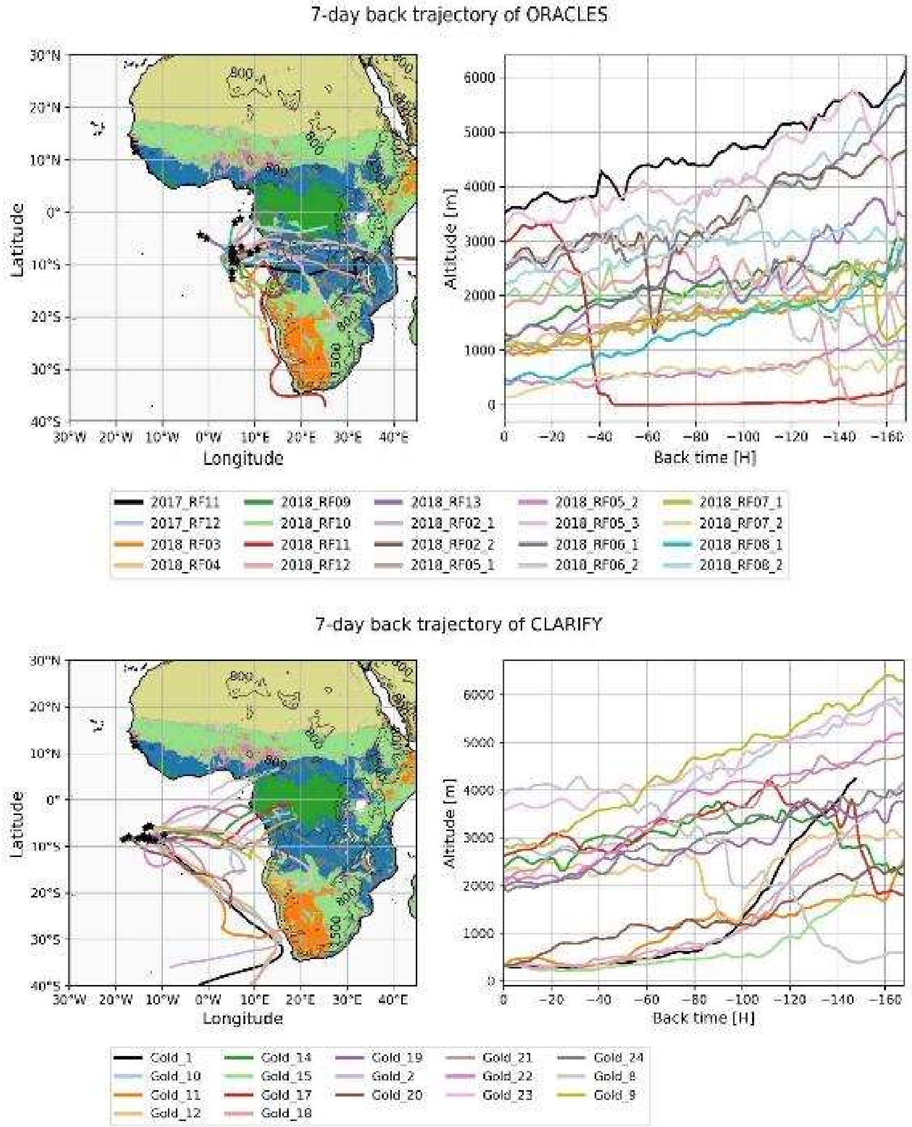


Figure 1 The location of filter sampling and back trajectories related to each filter, including altitude for ORACLES 2017-18 (upper panel), and CLARIFY 2017 (lower panel). Map colors relate to MODIS land cover types.

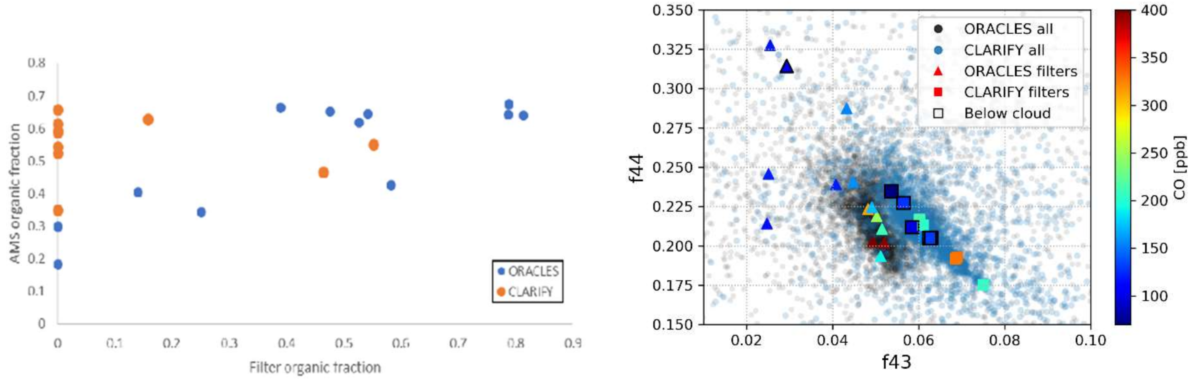


Figure 2 (left) AMS organic fraction vs filter organic fraction and (right) f44 vs f43 space for ORACLES and CLARIFY campaigns with filters marked as triangles for ORACLES and squares for CLARIFY. Colors of the marks denoting filter sampling represent CO concentration, as shown in the colorbar. Samples collected below-cloud are outlined with a black border.

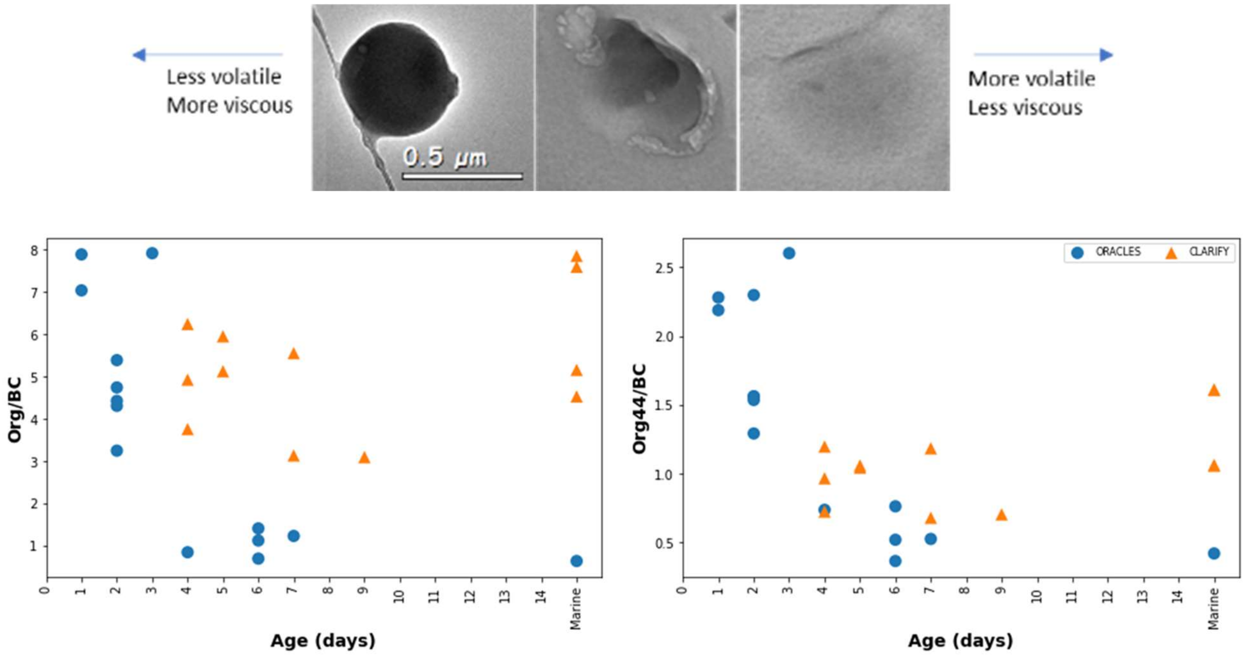
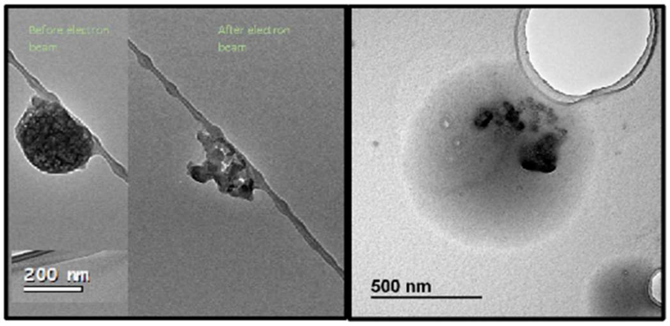


Figure 3 Example of different viscosity/volatility organic aerosol (top panel) showing more round and viscous particles for ORACLES (on the left), and more volatile for CLARIFY (middle and right top panels) and Org/BC and Org44/BC ratios with time from fire source (bottom panel)



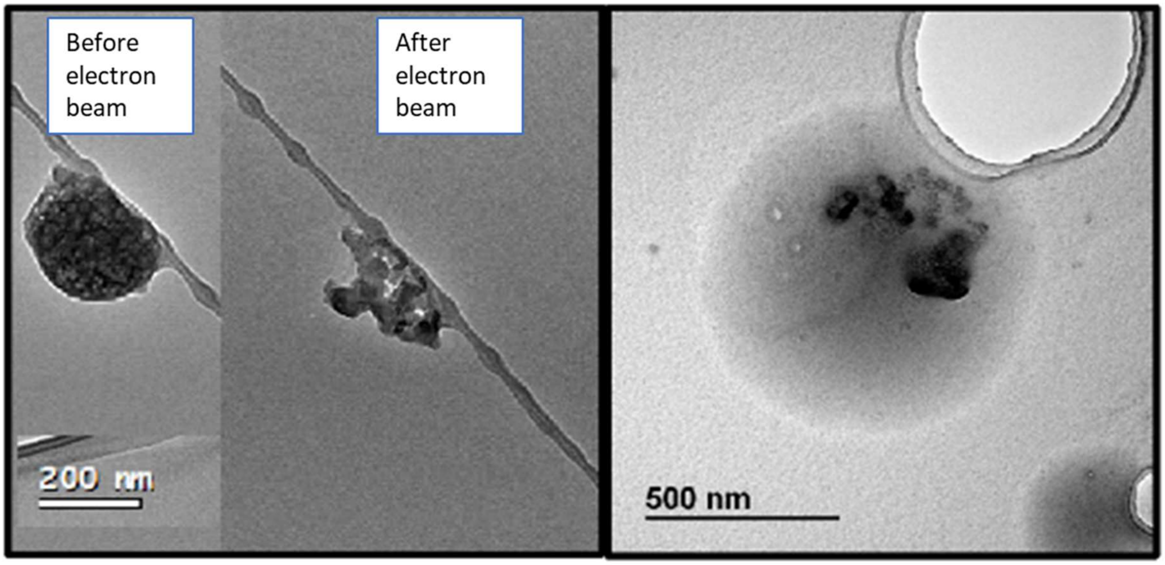


Figure 4 Potassium salt in a core-shell morphology around a refractory BC core (left) and organic with interstitial K-salt (right). Note the difference in scale between the two images.

Table 2 Black Carbon Mixing State by campaign. FT/BL, BC-Salt and BC-Organic refer to internally mixed particles

	BC – Salt	BC – Organic	BC - external
ORACLES BL	0.78	0.00	0.22
ORACLES FT	0.53	0.31	0.16
CLARIFY BL	0.50	0.29	0.21
CLARIFY FT	0.67	0.07	0.26

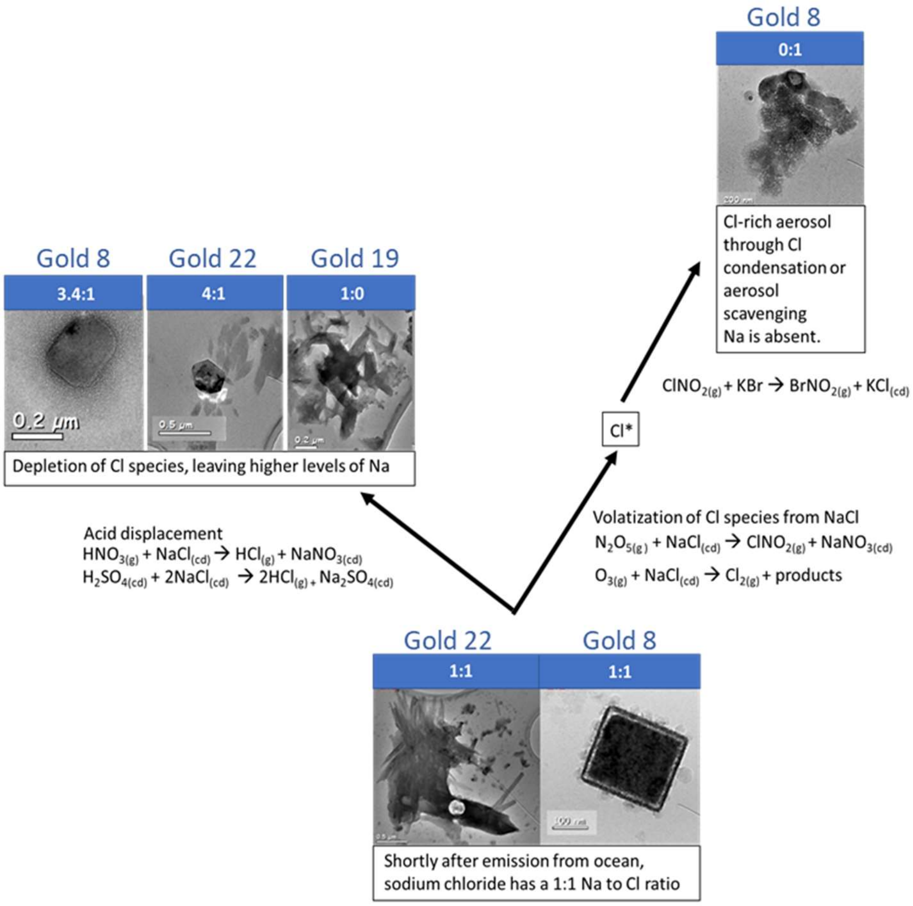


Figure 5 Schematic showing different stages of sea salt conversion with example mechanisms. The particles are from CLARIFY filters and range from sea salts which have been freshly emitted to Cl-depleted particles containing nitrates and

sulfates. Cl aerosol formation is also shown. Na:Cl ratios showing depletion of Cl with sea salt conversion are shown in the bar above each particle image.

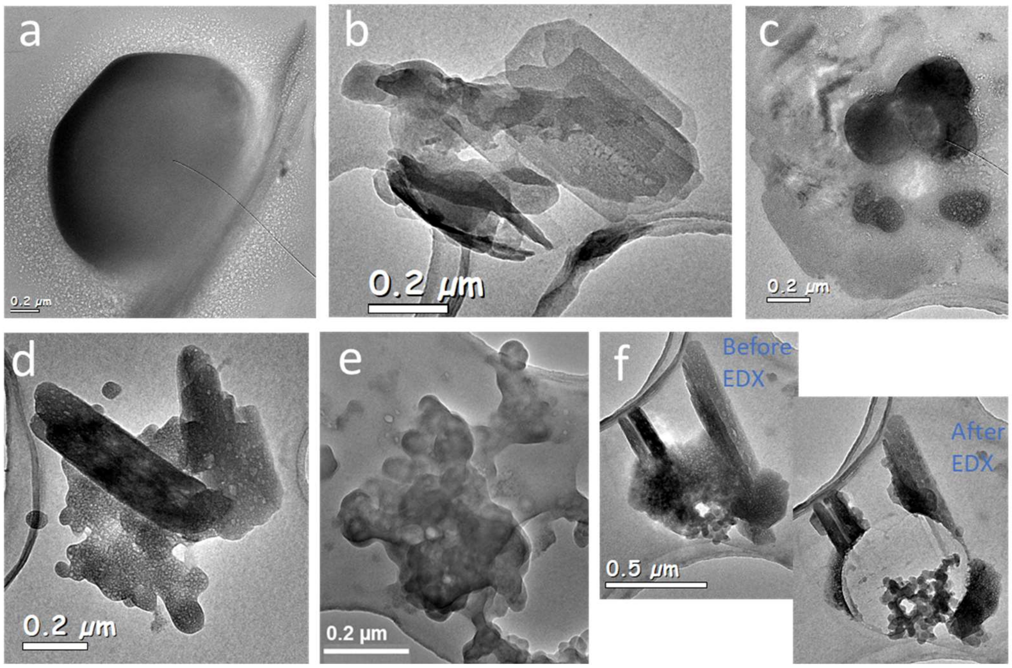


Figure 6 Assorted sea salt particles. (a) ~1.5 micron rounded NaCl; Gold 1 (b) CaSO$_4$; Gold 1 (c) NaCl and Mg; Gold 1 (d) Na$_2$SO$_4$ with K; Gold 1 (e) NaNO3 mixed with BC; Gold 24 (f) BC encapsulated in Na$_2$SO4 with K ; Gold1

Table 3 Na dominant aerosols on CLARIFY filters with sampling location, CO levels, time ~~forum~~ from source, and percentage of particles on the filter with either Na or Cl. The ratios represent the weight percent ratio per particle, averaged across all particles with the elements of interest on each filter.

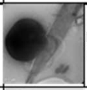
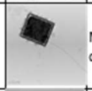
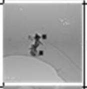
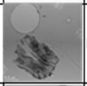
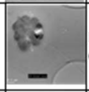
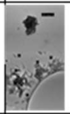
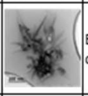
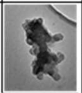
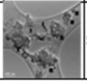
	Altitude (m)	Above/ Below cloud	CO (ppbv)	Time from fire (days)	Particles with Na or Cl (%)	Avg Na wt%	Avg Cl wt%	Na/Cl	Na/S	Representative particle and filter summary	
Gold_1	323	Below	108	marine	98	10.6	10.7	7.2	5.2		Na and Cl with vary levels of Cl depletion; some Na with S; large NaCl particles, BC mixed with NaSO4
Gold_8	3902	Above	204	7	100	13.7	12.6	4.3	NA		Mostly Cl particles without Na although some NaCl 1:1 crystals
Gold_9	2813	Above	329	4	37	5.8		NA	13.1		No Cl prsent; Na mixed with BC and BB salts, sodium nitrate
Gold_10	2918	Above	158	5	74	5.4		NA	5.4		No Cl present; sodium sulfate, BC mixed with Na
Gold_11	319	Below	70	15	80	19.2	4.7	6.1	8.1		NaCl, ammonium chloride, sodium sulfate, Na with depleted Cl all present
Gold_19	1969	Above	212	7	29	3.7		NA	2.0		Na sulfate, BC mixed with Na sulfate; no Cl, BC with Na, P, S, K, Ca
Gold_20	329	Below	130	marine	90	3.4	0.6	12.0	3.5		BC mixed with Na; NaS crystals; NaCl but most particles Cl depleted
Gold_21	2357	Above	177	6	36	1.1		NA	0.8		Trace amounts of sodium, no marine salts noted
Gold_22	2139	Below	128	9	77	12.5	8.7	3.9	3.3		Na_2SO_4, NaCl
Gold_23	3500	Above	273	4	63	7.6	0.5	20.2	3.7		Low levels of Cl, BC mixed with Na, S, K
Gold_24	1950	Above	331	4	77	2.3		NA	1.9		Sodium nitrate mixed with BC

Table 4 Na dominant aerosols on ORACLES filters with sampling location, CO levels, time from source, and percentage of particles on the filter with either Na or Cl. The ratios represent the weight percent ratio per particle, averaged across all particles containing the elements.

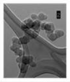
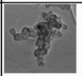
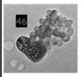
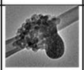
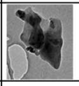
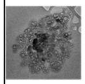
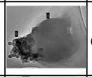
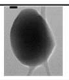
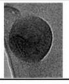
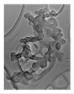
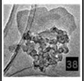
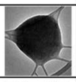
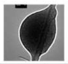
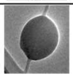
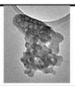
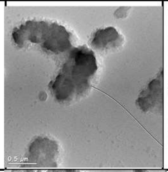
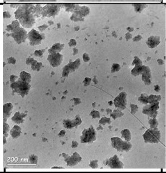
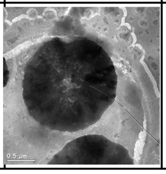
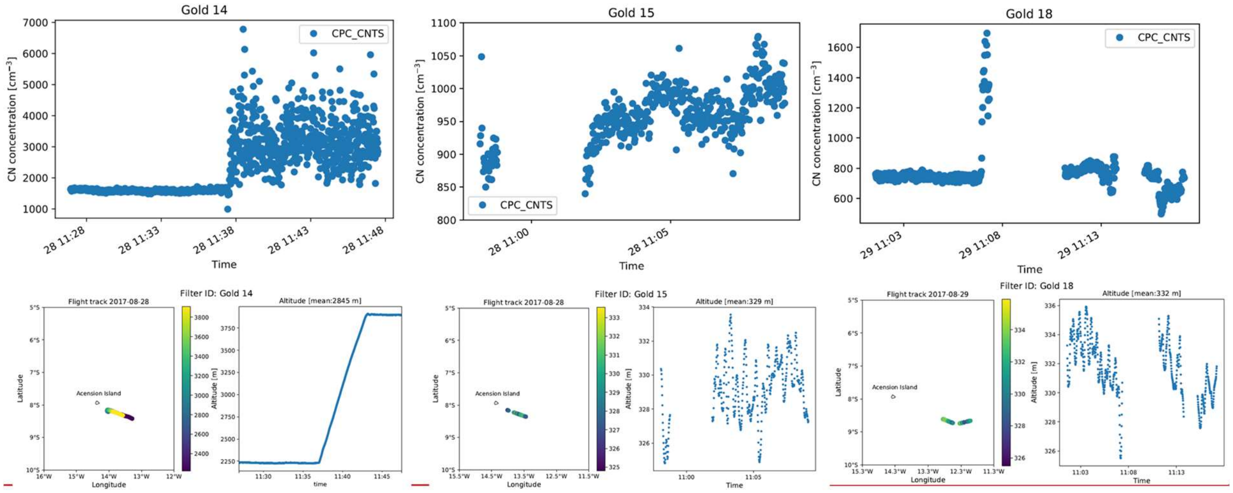
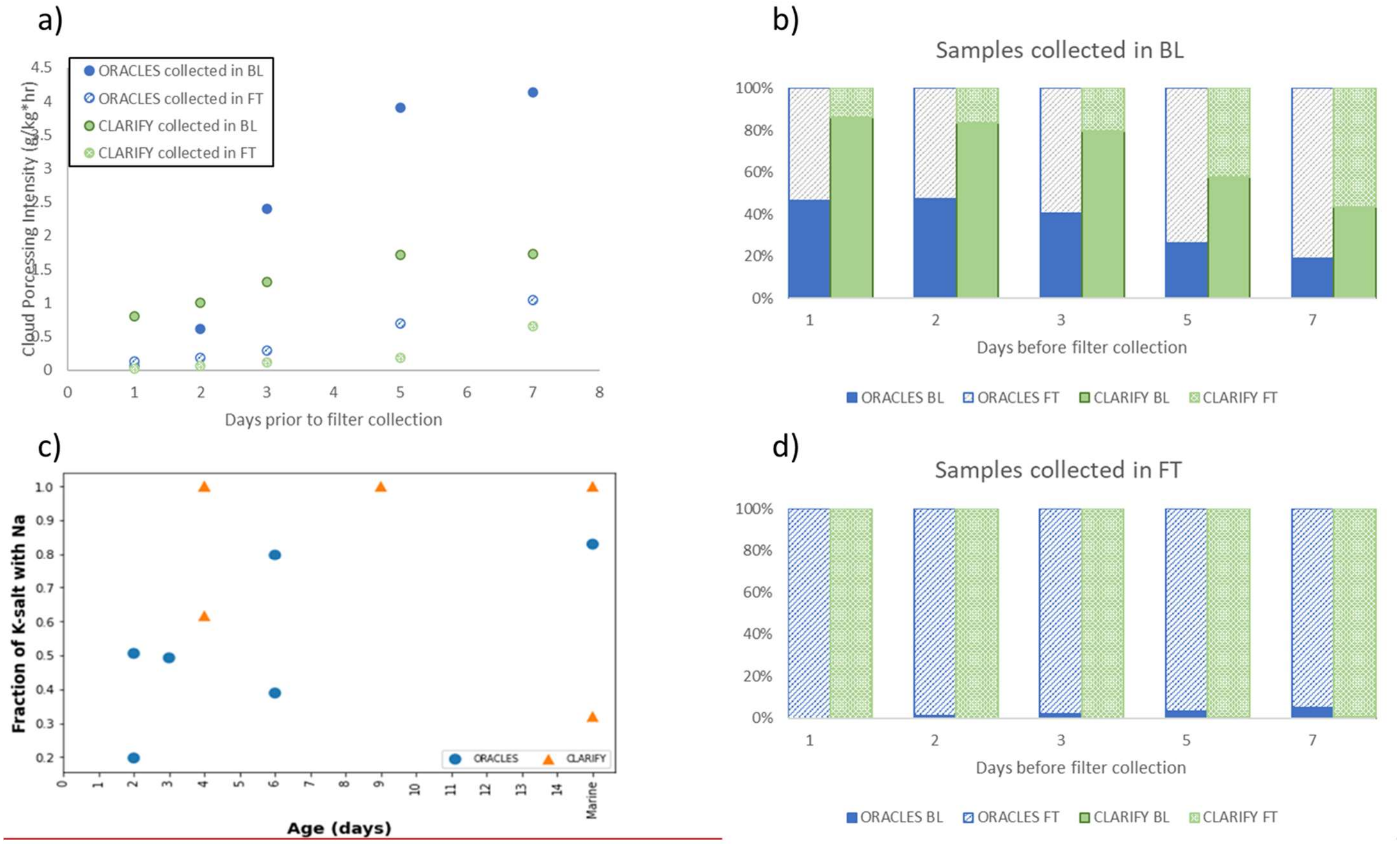
	Altitude (m)	Above/ Below cloud	CO (ppbv)	Time from fire (days)	Particles with Na or Cl (%)	Avg Na wt%	Avg Cl wt%	Na/Cl	Na/S	Representative particle and filter summary	
RF11Filter5	3505	Above	395	2	45	2.2			1.1		
RF02_1	894	Below	110	5	22	0.4	0.7		0.3		BC, K-salt, Ca bearing
RF02_2	2606	Above	210	1	49	1.1	0.5	2.0	0.8		BC, Ca bearing
RF03	982	Above	156	6	0						BC mixed with salts and sulfates
RF04	1195	Above	120	6	35	1.8	1.5	15.2	1.1		BC with K-salt, K salts, sulfates
RF05_1	943	Above	154	6	75	3.4	0.6		2.3		BC mixed with NaSK salts, Ca bearing, Silicates
RF05_2	378	Below	106	marine	76	2.7	0.3	23.5	1.6		NaSK salts, often mixed with BC
RF05_3	3247	Above	210	1	39	0.7			0.2		organic, sulfate mixed with BC
RF06_1	2444	Above	248	2	17	1.9	9.5	19.3	1.4		organic, organic with KS inclusions
RF06_2	2570	Above	173	2	53	5.9	1.2	38.9	4.0		organic, organic/salt mixtures
RF07_1	1091	Above	121	6	53	7.1	5.9	15.4	3.1		BC with K salts, OM, salts
RF07_2	159	Below	123	marine	52	7.0	0.6	20.8	3.6		BC with silicate, Ca bearing, Al silicates
RF09	1307	Above	158	7	11	1.2			0.2		organic with NSK salts, BC in fractal pattern
RF10	1986	Above	417	1	0						externally mixed BC, and internally mixed with viscous sulfur coating.
RF11	3027	Above	190	2	5	0.8	0.2		0.9		ammonium sulphates, OM mixed with salts, externally mixed BC
RF13	1127	Above	118	4	13	1.9			0.3		BC with K salt, OM, salts

Table ~~4~~ 5 Cl dominant aerosol on CLARIFY filters

Filter ID	Altitude (m)	Above/ Below cloud	CO (ppbv)	Time from fire (days)	Particle image & description	
Gold_14	2845	Above	262	6		N and Cl dominant spectra; uniform particles across filter
Gold_15	329	Below	158	marine		C and Cl particles with small amount of K; uniform particles across filter
Gold_18	332	Below	119	marine		Ca and Mg with Cl; uniform particles across filter



~~Figure 7 (upper panel) particle count concentration during filter collection time for the three Cl dominant filters, Gold14, Gold15, and Gold18, as detailed in Table 4, and (lower panel-left column) flight track, and (lower panel-right column) altitude~~


a)
Cloud Porcessing Intensity (g/kg*hr)
ORACLES collected in BL
ORACLES collected in FT
CLARIFY collected in BL
CLARIFY collected in FT
Days prior to filter collection
b)
Samples collected in BL
Days before filter collection
ORACLES BL
ORACLES FT
CLARIFY BL
CLARIFY FT
c)
Fraction of K-salt with Na
Age (days)
Marine
ORACLES
CLARIFY
d)
Samples collected in FT
Days before filter collection
ORACLES BL
ORACLES FT
CLARIFY BL
CLARIFY FT

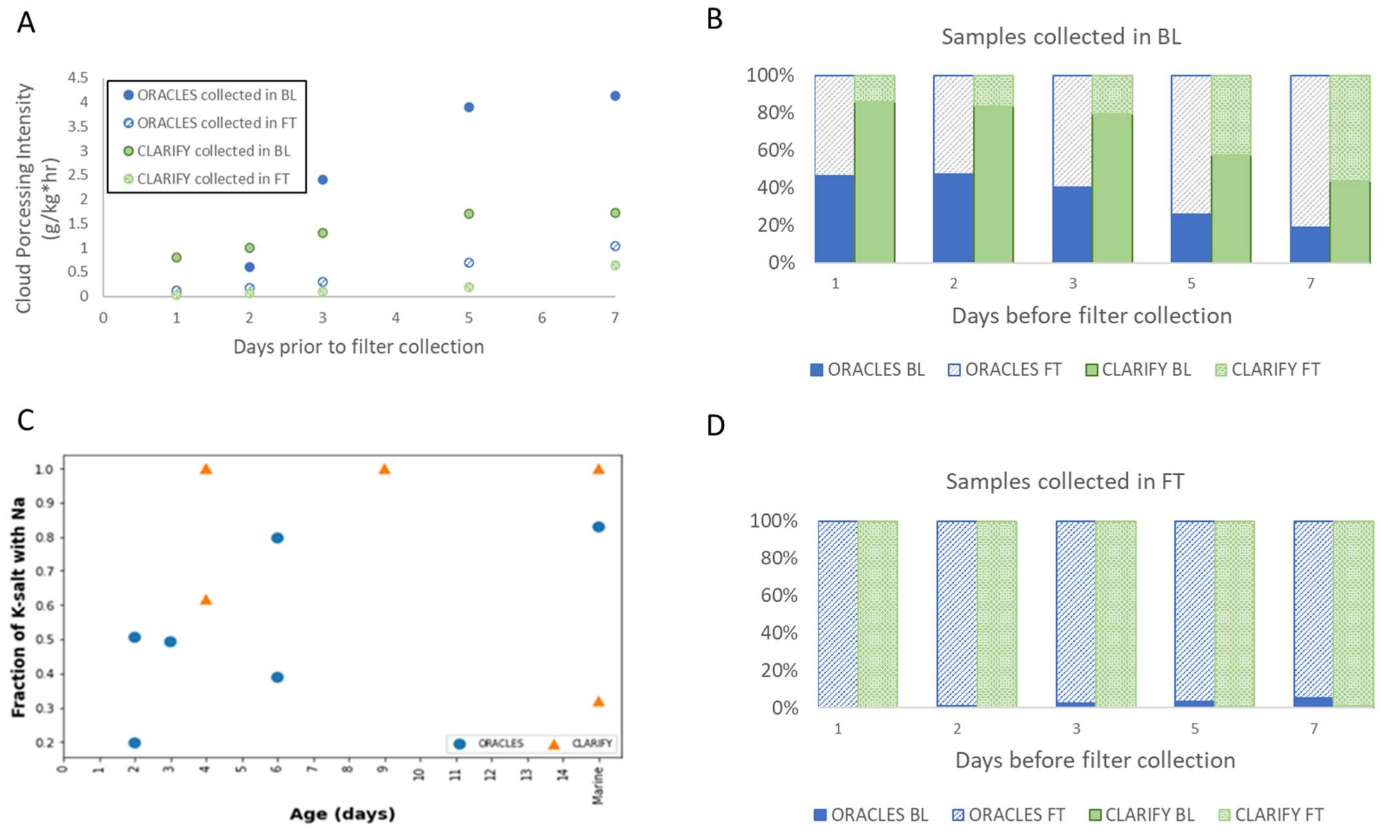


Figure ~~8~~ 7 Panel A~~a~~) BL and FT ORACLES and CLARIFY cloud processing intensity B~~b~~) Time spent in BL and FT for samples collected in the BL in the days prior to filter collection C) Fraction of K-salt, per filter, mixed with Na D~~d~~) Fractional time spent in BL and FT for samples collected in the FT in the days prior to filter collection

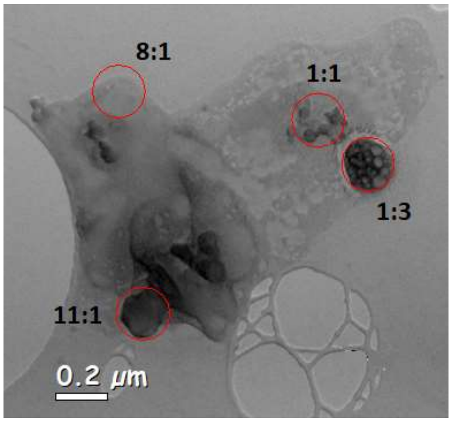


Figure ~~9~~ 8 Aqueous K-salt particle with varying levels of Na throughout particle, with Na:K weight ratio designated in red

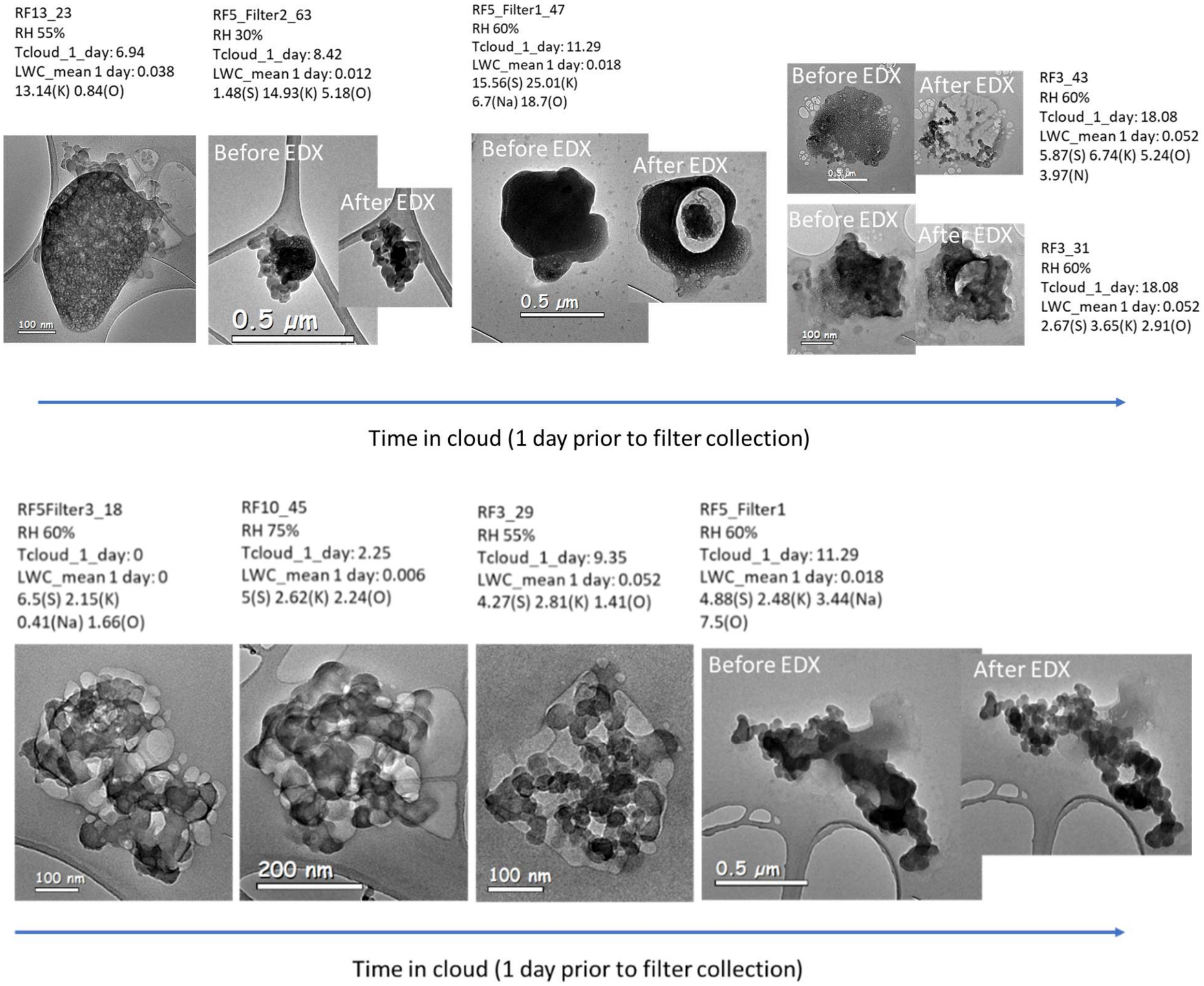
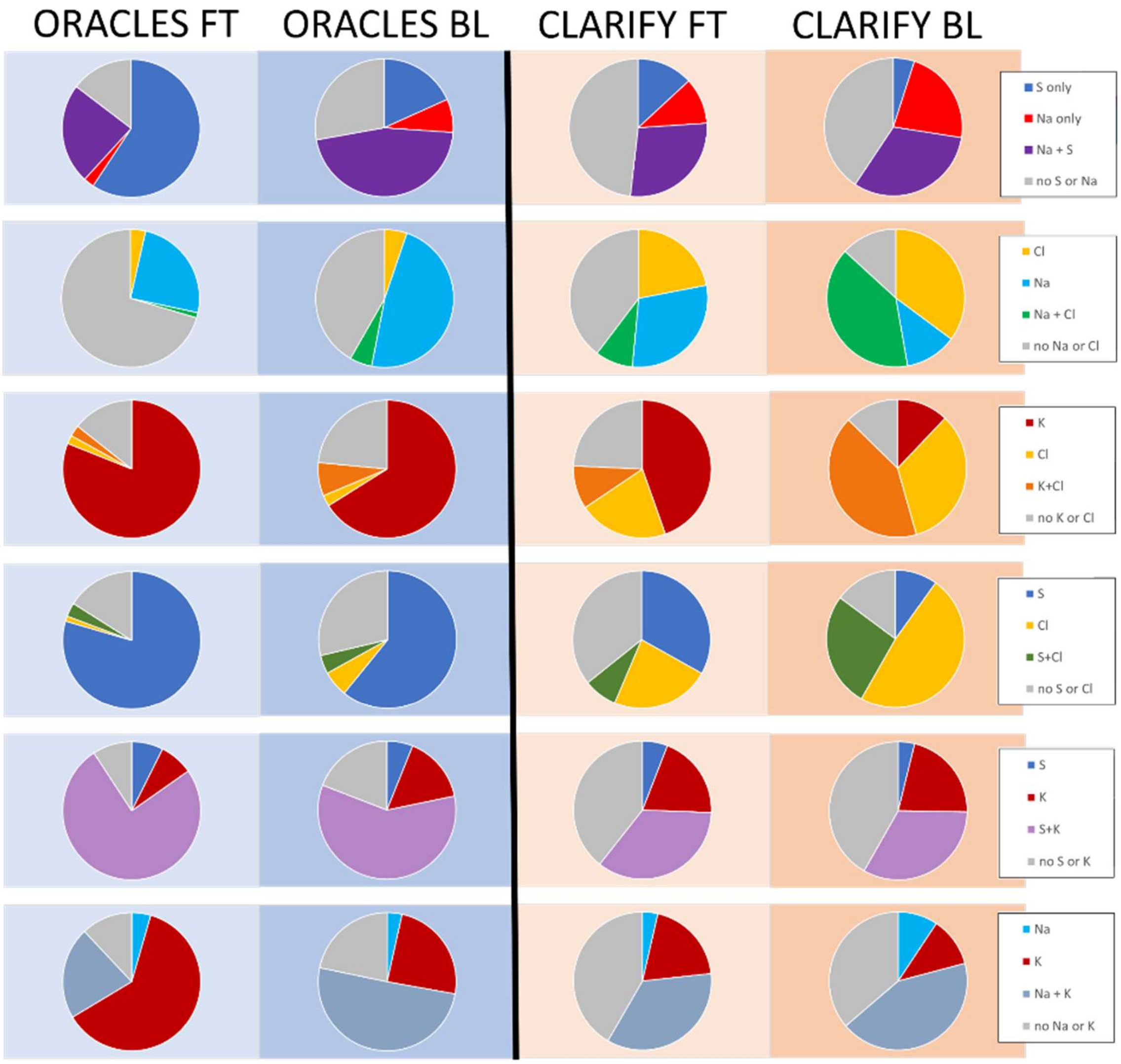


Figure ~~10~~9 Potassium salt mixed with BC (top panel) and sulfur-organic and BC (bottom panel) as a function of time in cloud in the 24 hours prior to filter collection.


ORACLES FT
ORACLES BL
CLARIFY FT
CLARIFY BL
S only
Na only
Na + S
no S or Na
Cl
Na
Na + Cl
no Na or Cl
K
Cl
K+Cl
no K or Cl
S
Cl
S+Cl
no S or Cl
S
K
S+K
no S or K
Na
K
Na + K
no Na or K

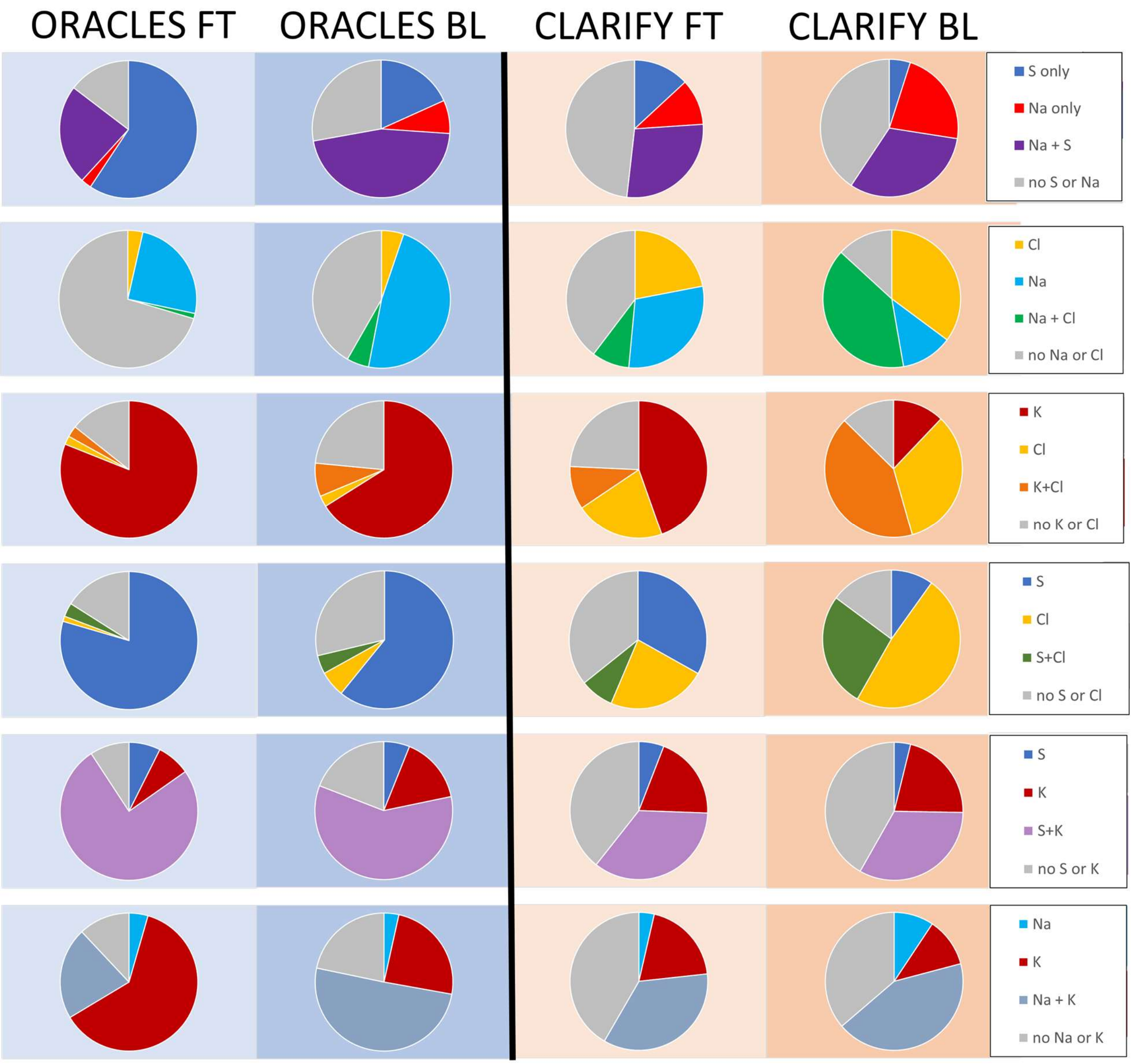


Figure ~~11~~ 10 Elemental mixing states for select elemental pairs for ~~CLARIFY~~ ORACLES (two left columns) and ~~ORACLES~~ CLARIFY (two right columns), separated by filter collection in the free troposphere and boundary layer

Supplementary Material

Table S1 Filter samples, flight and particles analyzed

Sample name	Flight	Date	Start time	End time	Particles Analyzed	Total Flow (L)
Gold 1	C030	8/17/2017	15:19	15:24	49	198
Gold 8	C033	8/22/2017	12:09	12:21	27	66
Gold 9	C035	8/23/2017	16:52	17:01	39	152
Gold 10	C037	8/24/2017	13:58	14:08	42	157
Gold 11	C036	8/24/2017	9:43	9:48	54	229
Gold 14	C042	8/28/2017	11:26	11:36	47	180
Gold 15	C042	8/28/2017	10:58	11:09	22	279
Gold 18	C044	8/29/2017	11:01	11:17	32	315
Gold 19	C046	8/30/2017	9:59	10:11	57	271
Gold 20	C046	8/30/2017	10:43	10:57	30	536
Gold 21	C055	9/7/2017	16:06	16:27	43	325
Gold 22	C049	9/2/2017	10:08	10:19	43	520
Gold 23	C049	9/2/2017	11:56	12:12	44	289
Gold 24	C050	9/4/2017	15:08	15:33	24	720
RF02_1	RF02	9/30/2018	10:05:00	10:15:34	23	317
RF02_2	RF02	9/30/2018	11:22:17,11:45:22	11:27:24,11:49:16	35	297
RF03	RF03	10/2/2018	13:16:59, 13:21:10	13:18:29,13:30:20	59	315
RF04	RF04	10/3/2018	10:01:52	10:13:00	65	334
RF05_1	RF05	10/5/2018	7:34:19	7:44:30	55	305
RF05_2	RF05	10/5/2018	8:09:30	8:19:50	64	310
RF05_3	RF05	10/5/2018	9:06:21	9:18:10	37	355
RF06_1	RF06	10/7/2018	11:43:09	11:48:45	49	168
RF06_2	RF06	10/7/2018	13:22:50	13:33:40	39	325
RF07_1	RF07	10/10/2018	10:25:05	10:34:52	43	293
RF07_2	RF07	10/10/2018	12:05:41	12:15:49	29	304
RF09	RF09	10/15/2018	11:11:52	11:20:26	56	257
RF10	RF10	10/17/2018	9:59:04	10:06:58	66	237
RF11	RF11	10/19/2018	10:23:38	10:35:27	62	355
RF13	RF13	10/23/2018	10:44:57, 10:50:10, 10:54:46, 11:02:56	10:47:09, 10:51:55, 10:58:28, 11:12:03	33	501
RF11Filter5	RF11	8/30/2017	10:29	10:41	47	360

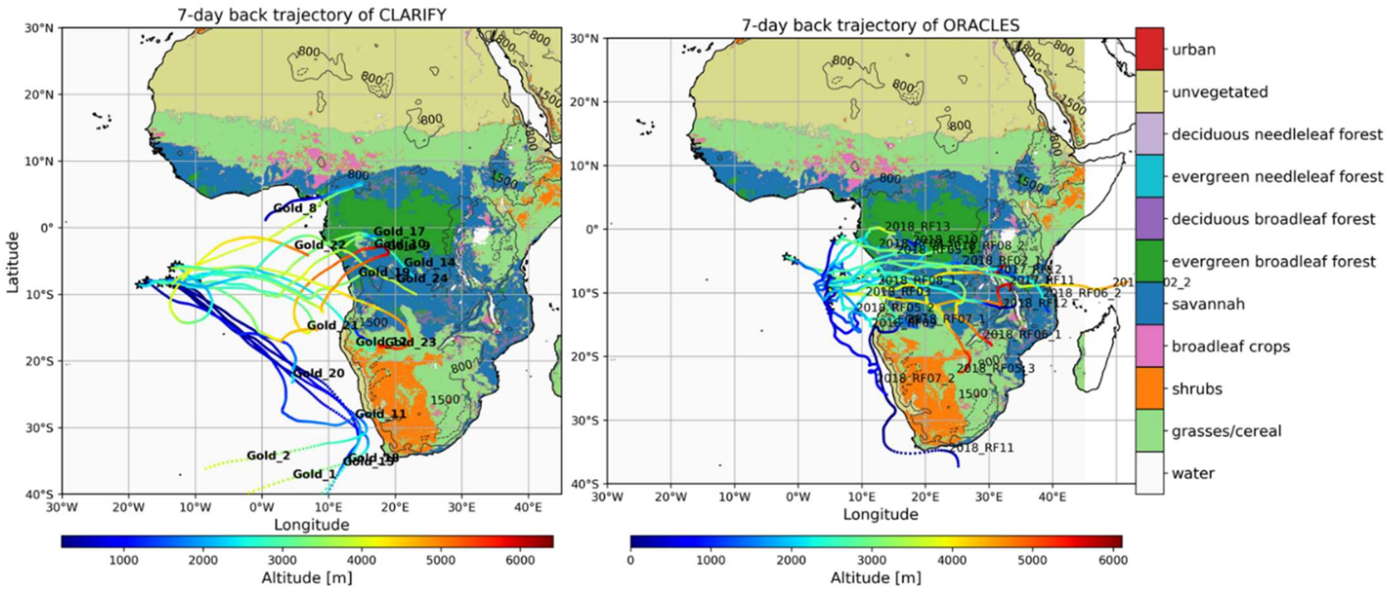


Figure S1 7-day back trajectories and sources of collected filters. The colors represent different broadleaf forests, urban, unvegetated areas, savannah, crop, grasses, and shrubland as denoted by the MODIS land use vegetation classifications.

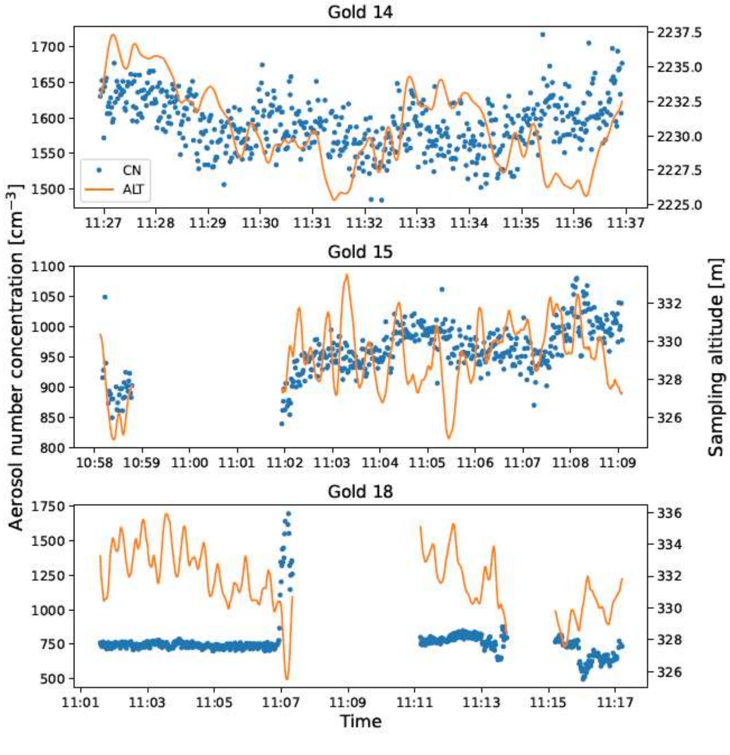


Figure S2 Particle count and altitude for Cl-dominant filters Gold 14, Gold 1, and Gold 18 during filter exposure times

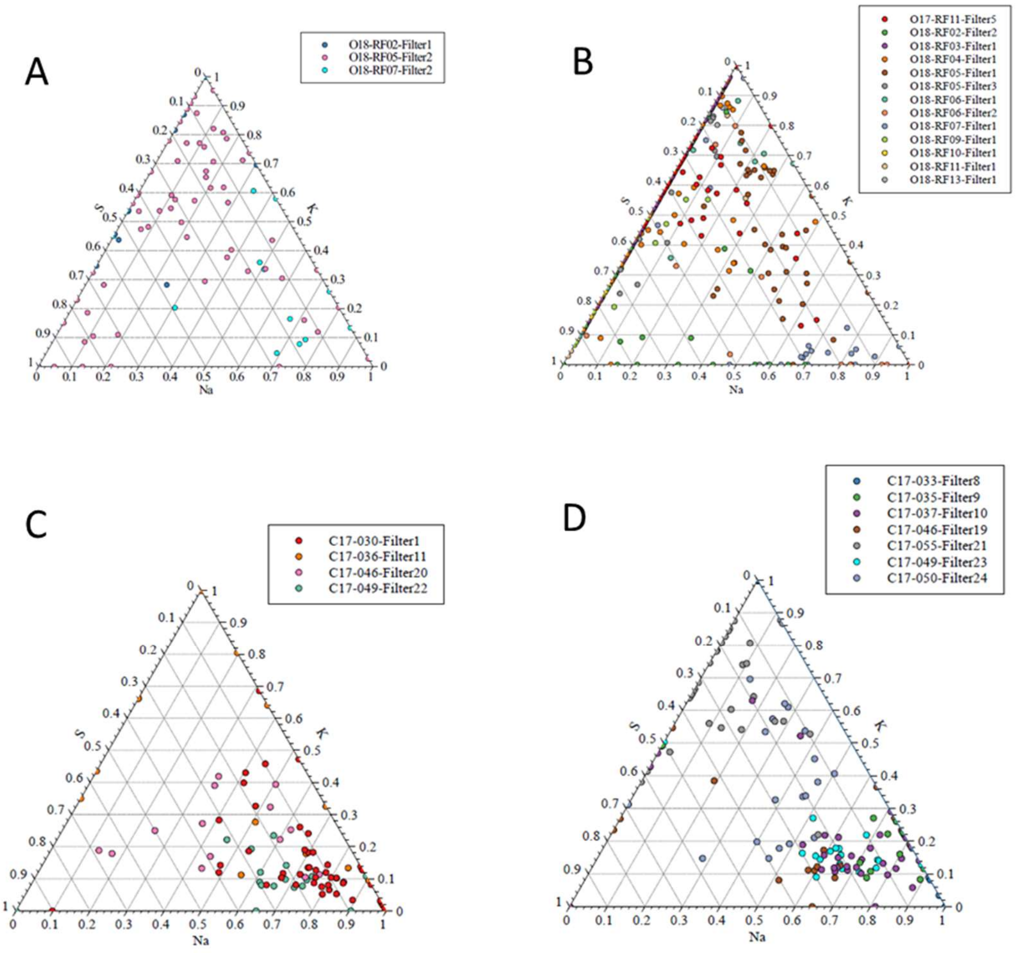


Figure S3 Na-S-K ternary diagrams for A) ORACLES below cloud B) ORACLES above cloud C) CLARIFY below cloud and D) CLARIFY above cloud.

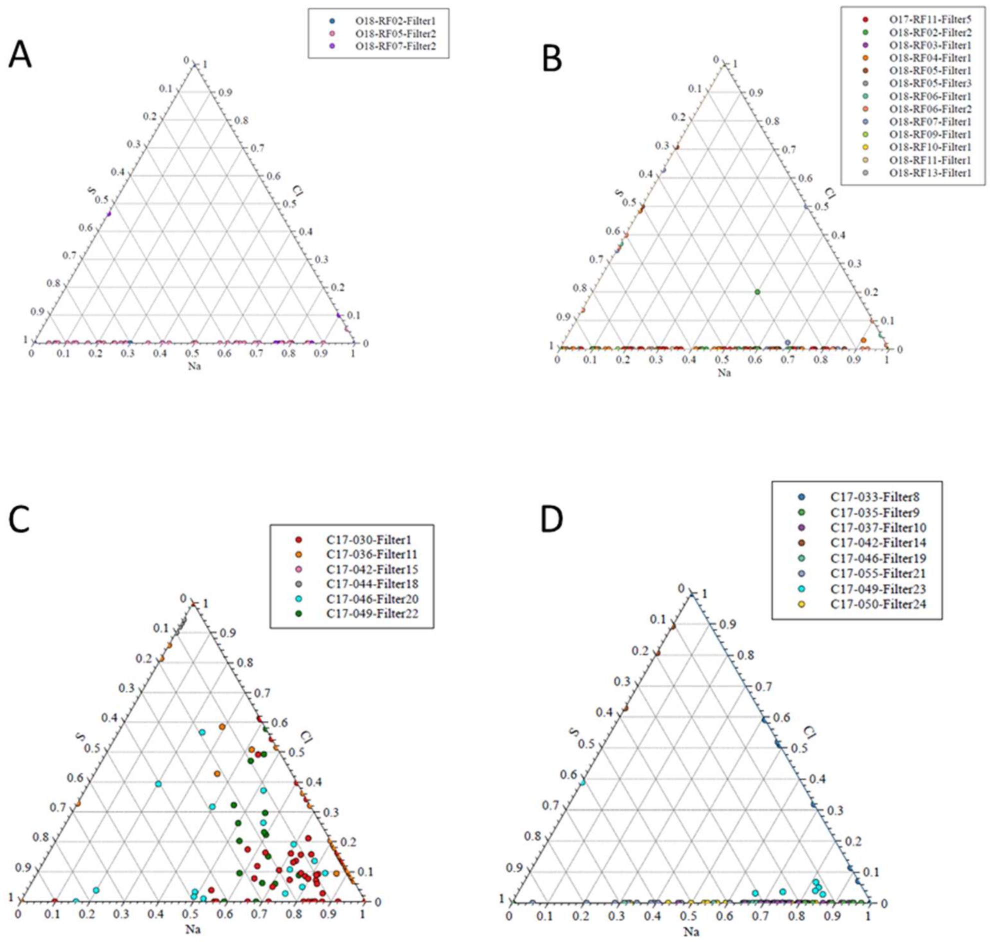


Figure S4 Na-S-Cl ternary diagrams for A) ORACLES below cloud B) ORACLES above cloud C) CLARIFY below cloud and D) CLARIFY above cloud. Note that the dearth of particles in A) and B) are due to the majority of particles having no Cl as well as most Cl-containing particles not containing Na or S.