RC1: 'Comment on egusphere-2024-3656', Anonymous Referee #1, 05 Mar 2025 reply

Comments to Carbonate content and stable isotopic composition of aerosol carbon in the Canadian high arctic

I am a scientist who specialize more in the area of radiocarbon instrumentation and the analytical method.

Thank you for reviewing of submitted manuscript. Responses to individual comments and their addressing is provided separately below. Comments are in black, our answers are in blue.

Introduction

The claim of line 62-63 is too strong or even false about the influence of carbonates on the atmosphere in the Arctic of not been studied yet. Just go to Google scholar and type arctic carbonate aerosol and you will get several publications.

Based on this comment, we reviewed the literature again. There is a large number of publications on the topic of "Arctic aerosols" or "carbonates in the Arctic". Articles on carbonates in the Arctic usually deal with their content in the soil or in the sea/ocean water. In terms of atmospheric aerosols and carbonates, we have added the following relevant study - (Mukherjee et al., 2020). In this context, we have added following new sentence to introduction: ”In addition to dust, it is hypothesized that a source of carbonates in summer Arctic aerosols may be marine microorganisms from sea spray as reported by Mukherjee et al. (2020) based on calcium analyses.”

However, we could not find a study that systematically address a carbonate content in Arctic atmospheric aerosols for more than one year. In contrast, carbonates are not mentioned as a potential aerosol species in terms of their current or future occurrence in the Arctic (Schmale et al., 2021). From this perspective, the significance of this manuscript is novel. If the reviewer has a specific tip for a systematic study on atmospheric aerosol carbonates in the Arctic, we would be happy to receive it.

Finally, to make it clear that this work concerns analyses of atmospheric samples, we made a small change in the manuscript's title as follows: “Carbonate content and stable isotopic composition of atmospheric aerosol carbon in the Canadian High Arctic”

The claim in line 73-74 is misleading. There are many publications that attribute the higher delta13C values to carbonates in the Artic.

Similar to the previous comment, the publications concerning $\delta^{13}C$ content in Arctic carbonates are mostly related to seawater or sediment samples. There is no specific study that addresses changes in $\delta^{13}C$ values related to carbonates in the Arctic atmosphere. In this context, we have modified the sentence in the introduction as follows to make it more clear (red text is newly added): “In the Arctic region, observed higher aerosol $\delta^{13}C$ values in atmospheric aerosols are often attributed to dissolved particulate organic matter from marine aerosol sources while the influence of carbonates is ignored”

There is a conceptual point that the authors do not deal with which is important because this work is about carbonates. If EC is the same as BC but carbonate are colorless thus carbonate is

not part of BC then in which group, do we set the carbonates? If the answer is that carbonates are part of EC then this proves that EC is not the same as BC, right? Carbonates belong to what fraction of the carbonaceous matter?

In principle, EC and BC are not the same, as each is measured in a different way and defined differently – see, e.g., Petzold et al. (2013). In general, carbonates can be classified as inorganic carbon. However, this is different from both EC and OC, for which the EC/OC method of analysis is primarily designed.

Regarding the method, when carbonates are present in a sample, they are either interpreted as OC or EC (depending on the temperature protocol) based on simple thermogram from Sunset analyzer. However, carbonate concentrations are usually negligible (especially in fine aerosol), so they are usually not considered in studies. Nevertheless, when carbonates are present in a sample, they need to be distinguished from OC and EC in a particular method, for which different techniques are used (Jankowski et al., 2008; Karanasiou et al., 2011). We used one of these methods that uses HCl fuming. Here, it is also important to mention that one of the results of this study is a new approach for the estimation of carbonates in aerosol using d13C isotopic composition of TC - see subsection 2.5. The results (Fig. 8) suggest that the proportion of CC in TC determined in this approach is maybe more accurate than by HCl fuming method.

Results

Weak demonstration of quantitative analysis of carbonate with Sunset. I have problems believing that carbonates can be quantitatively analyzed by the proposed Sunset method due to the Sunset lower temperature comparing with elementar analyzer (1000 deg). I do believe that certain amount of carbonate evolves qualitatively during Sunset OC and EC fractions but it is hard to believe that 100% of carbonates becomes CO2 at EC2 temperature.

After seeing Chow et al 2007 and Hu et al 2023, I can not find a method developed and rigorously proved about the quantitatively analysis of carbonate with the Sunset temperature in any of the provided references. Of course, the claim is correct in line 141 “These are temperature steps during which we should expect the release of carbonate carbon”. But that does not prove that it is release quantitatively to accurately measure CC as TC-TC_{HCl}

Jankowski et al. shows qualitatively that CC evolves at 600-650 deg but the quantitatively part was done measuring TC that includes CC at 1000 deg.

We newly have added references to studies on carbonates analyses in aerosols (Jankowski et al., 2008; Karanasiou et al., 2011). In particular, Karanasiou et al. (2011) discusses the quantification of atmospheric carbonates using the Sunset analyzer and in this respect demonstrates its applicability.

Here we would mention that the EC2 step (740°C) is not the highest used temperatures. In the Improve_A used protocol, step EC3 followed with a temperature of 840°C, but very little mass usually was released during this step. For this reason, we consider the given temperature protocol to be sufficient for the release of commonly occurring carbonates. Another thing is that by using EA method, TC release proceeded at 1000 °C. This may account for the slightly higher TC concentrations from EA (+2%) compared to the EC/OC analyzer (Fig. S1). For this reason, we added the following new sentence at the end of subsection 2.2: “The slightly higher

TC concentrations using EA (2 %) may be due to the use of a higher maximum temperature (1000 °C vs 840 °C) for sample release."

The result in figure S1 (left) comparing TC Sunset before any HCl treatment look to me in average lower than the TC from EA-IRMS. The slope (1.014) looks high due to the outlier at approximately 1.1 ug/m3. By removing this outlier with the strongest magnitude, you will get a lower slope and the method from this work (Sunset carbonate) is underestimating, in average. The same applies to figure S4 where the outlier, strongest in magnitude, is lifting up the slope to 0.95.

In Figures S1 and S4, we added a second linear fit that does not include the mentioned outlier. The slope in Fig.S1 changed from 1.01 to 0.93, which is still a good agreement within aerosol analyses. In the case of comparison of CC results using TC analyses from EA and Sunset analyzer in Fig. S4, however, the discrepancy is higher (change of the slope from 0.95 to 0.73). Regarding this, we have made the following change in the text.

"…and the resulting CC values show good agreement (r = 0.87, y = 0.95 x, Fig. S4). Unless otherwise stated, CC values calculated from EC/OC analyses are discussed in this study."

Red is newly added/changed: "and the resulting CC values show acceptable agreement (**Fig. S4**). Fig. S4 shows that CC values based on analyses from the EC/OC analyzer may be slightly underestimated. However, unless otherwise stated, CC values calculated from EC/OC analyses are discussed in this study."

If you check the publication from Baudin et al. 2023 (doi 10.2516/stet/2023038), you can see that the temperature depends on the type of carbonate (Fig. 5, Fig. 6) where they increased all the way until 1200 degrees. Yes, it is a fact that the carbonate evolve temperature decreases with the amount (Fig. 1). Because your manuscript is dealing with very small amounts then you oxidize most of it but conceptually and empirically (Fig. S1 of the manuscript), I believe that your method is losing a small part and it is not quantitative. If true, you should mention this.

The only carbonate released above 900°C in work of Baudin et al. (2023) is strontianite, which is a rare carbonate mineral that we do not expect to be significantly abundant - see, for example, the negligible abundance of strontium in Arctic aerosols (Landsberger et al., 1990).

Anyway, we have taken this particular comment into account and we have added following new sentence to the subsection 2.3.: "This procedure is probably not able to analyze all carbonates (Baudin et al., 2023) but quantitatively, this method leads to the analysis of at least 90% of the carbonates in samples (Karanasiou et al., 2011)."

Source apportionment

It is hard to believe that the origin of CC is mainly from North America as claimed in the abstract and conclusions. In Fig. 7, it seems that the stronger changes of d13C are due to North America but with episodes coming from Greenland too. For example, in Fig. 7, at 01/03/2018 there is a very strong episode (peak of d13C before HCl) colored in green with yellow (Greenland, Europe). Or a mixture of both, for example at 01/09/2016 the peak of d13C before HCl is a mix of green and pink (Greenland, North America). Later in the text, the authors did explain that the influence is also coming from Greenland, Europe but why the conclusion of North America as main source in the abstract and conclusion?

We mention in both the abstract and the conclusions that, in addition to a main source of carbonates in dust from sites in northern Canada, we have identified other source, which is likely to be marine phytoplankton.

In the abstract, see: “Another potential minor source of CC is -marine aerosol -, including calcified marine phytoplankton shells (coccoliths) introduced into the atmosphere via sea-to-air emission.”

In the conclusions, see: ” The second source may be calcareous shells (coccoliths) produced by marine phytoplankton and transported from both the Arctic Ocean and the North Atlantic Ocean.”

As you correctly note, we discuss this phenomenon in more detail in subsection 3.2 and in Fig. 7. The conclusions that main source of carbonates is probably north Canadian resuspended dust is based on both the location of Alert station and on prevailing winds there (see supplementary data in repository). Both the conclusions and especially in the abstract are usually limited in length, and the findings there are presented briefly. In this respect, we therefore consider the current references to the marine carbonate source in these sections to be sufficient.

References:

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