

## Authors' response to referee comments

### Anonymous Referee #2

#### Specific comments, and authors' responses:

*Figure 2: Please add the Katmai EC marker in the DV99.1 age plot (even if uncertain).*  
Added as suggested.

*It was not possible to analyze ionic species: Why? During the melting no discrete samples were taken? The instruments were not available*

At the time the instruments and funding were not available to measure ionic species.

*The only EC measurement available is the one done with the hand held device?*

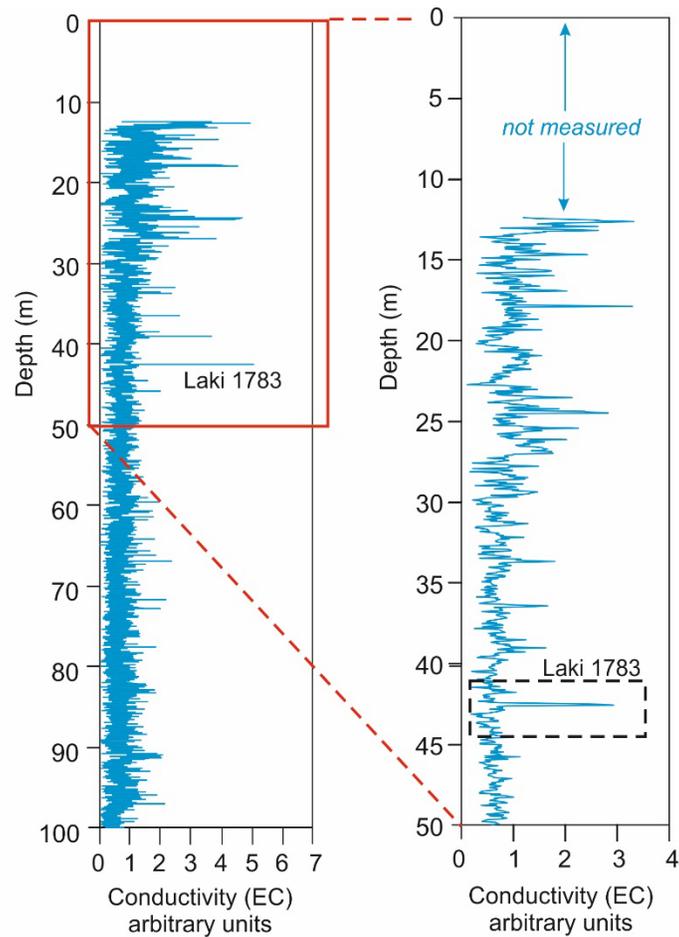
Yes.

*Was the core in good conditions below the 38 m?*

See our earlier response to the first round of revisions: There was an error in the original version of the manuscript. The part of the DV99.1 archive core that was shipped to Curtin University for rBC analyses reached 48 m depth (not 38 m as was wrongly stated). This depth range was chosen based on the age model for the core to ensure that the rBC record thus produced would extend back into the early 19th to mid-18th century. The uppermost 2.8 m of the DV99.1 core were made of very crumbly firm, and could not be preserved. Below this, the core was recovered in increments of length varying from 0.4 to 1.1 m (average 0.9 m for the part of the core considered in the present study). At depths greater than 48 m, some, but not all, of the core archive pieces were fractured in many pieces inside the layflat bags.

*How accurate are those measurements ?*

The hand-held EC measurement system that was used is an earlier version of the unit designed and sold by Icefield Instruments Inc. (see: <http://www.icefield.yk.ca/portable-ecm-unit.html>). When we used this system in the field, we started by manually scrapping off a few mm of ice from the core sections to be measured using a stainless steel knife, then we ran the electrodes along the length of each core section at a speed of approximately 2 cm per second, which, based on the 19 Hz digitizing rate of the instrument, gives approximately one measurement of EC per mm along the core surface. We did not attempt to calibrate the voltage readout because we were only interested in changes in relative EC along the core, so we can not quantify the accuracy in mV. There are several possible sources of uncertainty in such EC measurements. One is the heterogeneity of H<sup>+</sup> distribution in the ice, which may result in a variable EC on different faces of the same core section (this is true even if a different EC measurement system is used). If there are breaks on the core surface, or the surface is very uneven (as can be the case with crumbly firm), the contact of the electrodes with the firm or ice may be poor. This is why we only started the measurements at 12.5 m depth. The EC recordings from each segment were later spliced together to produce a continuous profile, registered against the core depths. To get an idea of how the EC profile of the top 50 m of the DV99.1 core compares to deeper sections, see figure on next page.



Above: Comparison of the EC profile in the DV99.1 core down to 100 m depth (left) with the top 50 m section enlarged and presented in the manuscript (Fig. 3c). The image at right is the raw EC data. At left (panel from Fig. 3), the ECM data were smoothed with a running mean equivalent to a 1-cm vertical resolution, in order to make the main features of the EC profile appear more clearly, which explains why the range of values on the  $x$ -axis of these two panels are different.

*Figure S10: there is a cross in the period 1840-1850, is it an outlier? If yes how was it defined?*

The whiskers on each box-plot span approximately 99 % of the probability distribution of rBC concentrations in each decade, and values that lie outside of the probability range are classified as outliers. There were rBC outliers in all the 10-year periods. When we prepared Fig. S10 we chose not to display them because they visually cluttered the plot, and what we mostly wanted to emphasize here was how the median and interquartile ranges vary from decade to decade. This particular outlier was accidentally left in the plot. This has now been fixed in the revised version of the figure, and more details added in the caption to specify how the whiskers are defined.

*Figure S13: rBC and elemental carbon concentrations needs correction factors in order to be directly compared. In the caption and in the y-axis you wrote «rBC or Elemental carbon», please report specifically for which Greenland ice core was measured rBC and/or elemental carbon (if some of them were analyzed not with an SP2 you shouldn't call the resulting concentration with «rBC»). Therefore, the same correction has to be done in Figure 5 of the main text.*

We modified the figure to display snow and rBC accumulations rates on Greenland and Devon ice cap as a function of latitude, instead of showing rBC concentrations vs. snow accumulation rates, as before. We excluded the data from Holtedahlfonna core (Ruppel *et al.*, 2014) from this plot, such that only data based on rBC measurements by the SP2 method are now shown. The data shown on Fig. 5 in the manuscript are also only rBC measurements by the SP2 method. We also re-wrote the last paragraph of section 4.4. in the manuscript (L491-L517), to reflect these changes.

*Line 46/47: please consider adding the utilization of the CETAC nebulizer as a possible source of losses on real BC particles during the analyses.*

The sentence is about factors that might explain the observed differences between the DV99.1 rBC record and Greenland records developed by the same method (SP2). Since the Greenland records were also developed using the CETAC system, what really matters is how the effects of melt would reduce the detection efficiency of rBC in the DV99.1 core, relative to Greenland cores with little or no melt. The sentence already makes that point and does not need further editing.

*Line 81: add the word «concentration» after «rBC»*

Added as suggested.

*Line 100: please add that the crumble firn part was not preserved at the time of the drilling.*

Added as suggested.

*Line 124: what does it mean was «essentially» the same? Did all of them use an SP2? Did they use different nebulizers?*

The word "essentially" was removed. The methods were the same.

*Line 186/187 and Figure S7: it is known that melting and refreezing cycles tend to reduce the Delta18O oscillations in snow/ice; so how can you confidently speculate that 40-45% of snow was annually removed considering that both wind and melting affects the DV99.1 site?*

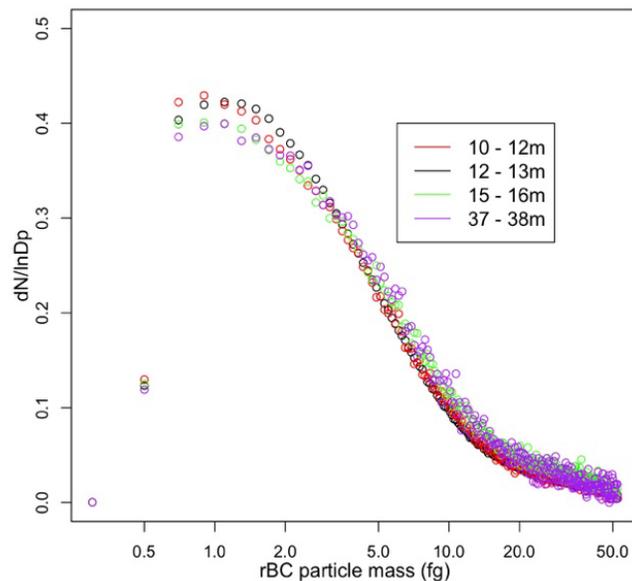
The estimate is based on the comparison of the amplitude of the  $\delta^{18}\text{O}$  signals between the D98.3 and the DV99.1 cores. The two coring sites are situated at elevations that only differ by 30 m (see Table 1) and it is almost certain that they experience the same range of seasonal temperatures, and therefore the same amount of summer surface melt (but not necessarily the same volume of refrozen meltwater in the firn). In that case the observed difference in the  $\delta^{18}\text{O}$  amplitude must be accounted for by other factors, such as the rate of net snow accumulation (which also affects the volumetric percentage of refrozen meltwater in firn). The two coring sites are also close to each other (see Fig. 1) and it is very unlikely that precipitation rates would be vastly different over such a short distance. Therefore the most likely explanation for the  $\delta^{18}\text{O}$  signal differences is wind scouring of winter snow, and this is coherent with the truncation of the most negative  $\delta^{18}\text{O}$  values in the DV99.1 core compared to the DV98.3 core, as seen before at other sites in the Canadian High Arctic (see references in manuscript).

Change the scale of the Figure S6b in order to make the D18O oscillations more evident (the same in Figure S7).

Changed as suggested.

In order to understand if the CETAC system contributed in hiding the increase of the rBC concentration in the last century due to the increase of the particles dimensions caused by coagulation during melting and refreezing cycles, it would be very important (and the results shown in this paper absolutely need this) to compare the mass size distribution of BC particles in the real sample in a period with very low melting features and in one with very high volumetric percentage of icy melt features.

Changes in the rBC particle mass distribution and aggregation is a concern. However, we found no evidence of this from the rBC mass probability distribution. In support of this conclusion, we have added a figure to the supplement (Fig. S3), reproduced below. This figure shows the normalized probability distributions of rBC mass in different ice-core sections, some of which date back to the interval ~1803-1814 during which the ice-core melt feature percentage was only 1 % (vol.), and the other spanning the interval ~1943-1963 during which melt feature percentages were as high as 53 % (min. 9 % vol.). As can be seen, the rBC mass have similar probability distributions in all these core sections, and lack any evidence for marked differences that could be attributed to rBC particle aggregation during periods of higher surface melt. The text in section 4.2, L376-L384 of the manuscript, was also amended to account for these results.



Above: Figure S3 from supplement, showing normalized probability distributions of rBC mass determined by SP2 in sections of the DV99.1 core spanning depths 10-12 m, 12-13m, 15-16 m, and 37-38m. The 10-16 m sections are from years ~1943-1963, while the 37-38 m section is from years ~1803-1814.

*Line 268: In the decade 1780-1990? Please correct these dates.*

Corrected: 1780-1790.

*Line 289: I would rather use more general terms saying «wet deposition of BC containing particles» (not only the hydrophilic part of them).*

Changed as suggested.

*Line 470: underestimation of 20-40% without considering the 25% of efficiency of the CETAC system?*

This was a mistake, now corrected in the text (L477-L478). The possible underestimation of the net rBC deposition rate was evaluated based on the assumption that the rBC concentrations in snow may be underestimated by 60-80 %, (not 20-40 % as we wrote) due to the combined effects of wind scouring and the CETAC system detection inefficiency. To be clear: What we did is to recalculate the net deposition rate of rBC in snow that would result if the true rBC concentrations in snow were 60 to 80 % greater than what was actually measured, and obtained corrected deposition rates of 0.19 to 0.23 mg m<sup>-2</sup> a<sup>-1</sup>, averaging 0.2 mg m<sup>-2</sup> a<sup>-1</sup> (the rounded figure cited in the text). The estimates bracket a possible range of conservative scenarios. For example, if wind scouring removes 45 % of the rBC, and the remainder is also underestimated by 25 % due to the CETAC system limitations, then the true rBC concentration would be underestimated by 65 %, i.e. between 60-80 %.

## **SP2 Calibration**

*How did you analyze the data? Did you write your own code for analyzing the SP2 raw data? Or did you use any prepared toolkit?*

The raw SP2 binary files (.sp2) were converted into ASCII files using the Performance Application Programming Interface toolkit (WaveMetrics IGOR) supplied by the SP2 manufacturer (Droplet Measurement Technologies). We used a custom code written in R and CRAN R open-source software to filter broadband incandescence peaks and convert incandescence peaks to mass using the calibration relationships (supplied by Droplet Measurement Technologies). Peak filter parameters recommended by DMT.

*You used the «Ebony MIS, EB-6K» material for SP2 calibration, what is that? Is there any reference paper about it? How the particles mass was measured? Cite the work that has characterized it, e.g. for its «effective density» (as Gysel Martin did for Aquadag and Fullerene, the most used calibration materials, in «Effective density of Aquadag and fullerene soot black carbon reference materials used for SP2 calibration»). Moreover, using the CETAC system with its typical cutoff in the nebulization efficiency it is important that the peak of the mass size distribution of the calibration material is in the window of the highest nebulization efficiency, otherwise you cannot trust the absolute concentration values.*

The EB-6K is a commercially available, 100% carbon black pigment. This material was used in preference to the standards used by McConnell et al. (2007) because of its larger particle size, which is closer to the geometric mean volume equivalent diameter (~200 nm) of BC found in the remote atmosphere. We have added a plot of the probability distribution of particle mass (Figure S3) to the supplement. The rBC particles were within the CETAC aerosol cutoff window. The actual size of the standard particles were also confirmed by transmission electron microscopy (TEM). TEM is really the only way to know the actual size and morphology of the particles.

*Please be more precise in explaining the calibration procedure of the SP2. What is the «Response»? Did you get the SP2 internally calibrated from DMT and well aligned before using it?*

We have changed the y axis label in Figure S4 from “response” to “rBC mass ( $10^{-15}$ g sec<sup>-1</sup>)”. The SP2 was calibrated and aligned by DMT.

*Did you perform the SP2 alignment and the laser’s beam shape check prior to the analyses? Was the laser beam into the TEMoo mode as reported by the instrument manual?*

The laser alignment / laser beam (TEMoo) shape was checked before use with a DMT-supplied beam scan camera and software, following the instruction manuals (DOC-0175, DOC-0229) provided by Droplet Measurement Technologies.

*You said that «the CETAC efficiency was typically 25%». What does it mean? The nebulization efficiency? Does it mean that only the 25% of the sample was nebulized and carried in the SP2? Therefore the measured rBC concentration could be 25% of the actual value?*

The CETAC efficiency is defined as the mass conversion of water to aerosol at the nebulizer transducer section of the nebulizer. The nebulizer efficiency is calculated as the mass flow rate of water entering the nebulizer to the mass flow rate of water exiting the nebulizer drain below the transducer. An efficiency of 25% means that only 25% of the standard or sample mass was carried into the remaining sections of the nebulizer desolvation system. External standards are used to construct a linear relationship between rBC entering the nebulizer and the SP2 determined rBC mass per cm of core melted, or corresponding time period. The external calibration is used to correct for mass transport losses in the nebulizer. This is a standard practice for many instrumental methods. For example ICP-MS, ICP-OES, GC-MS. Nearly all analytical instruments used with an introduction system rely on external or internal (or both) standards to correct for losses and bias in the introduction system.

*Could you provide the number concentration to mass concentration ratio (from the SP2) for the standards and for a part of the real sample? This is very important if you are not referring to a paper describing in details the new calibration material that you used (in terms of size distribution measured for instance with an SMPS).*

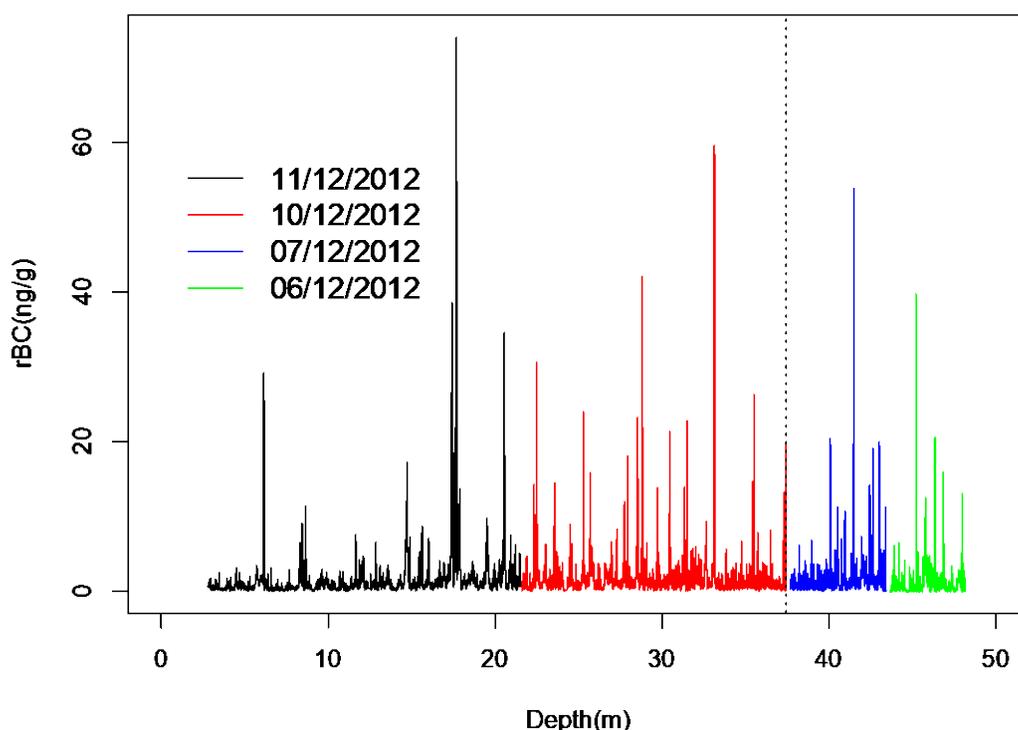
We have added a normalized probability distribution plot of particle masses in a standard and an ice core sample to the supplement (now Figure S3) and some additional text on page 3 of the document.

*Why do you call the calibration «External»?*

Good question. “External calibration” is a common quantitative chemistry term. An external calibration is constructed by relating instrumental responses to external standard concentrations etc. External standards are not mixed with the sample itself, hence the word “external” as opposed to “internal”. Internal standards are mixed with the sample itself.

*Do you sonicate the standard solutions before each calibration? Do you keep a standard solution with a very high concentration and then dilute it every day for making the low concentration ones? And how do you know that the CETAC system was not the responsible for the decrease in the calibration slope? Were the most recent sections of the core analyzed before or after the decrease in sensitivity?*

No, we sonicated the (high concentration) primary standard bottle before opening it. The other diluted standards were prepared from the primary bottle and well shaken. We are not sure of the cause in the calibration shift, only that it was systematic. However we found no shift in the rBC concentration, as described on page 5 of the supplement. To clarify the position of the shift we have added a high depth resolution figure of the rBC concentration and depths for the different dates and the position of the calibration shift (Fig. S5, also shown below)



Above: Figure S5 from supplement, showing rBC concentrations in the DV99.1 core versus depth. Different colors highlight the ice-core analysis date. The dashed vertical line at ~37 m marks the shift in calibration slope.

#### **Typing errors:**

*Please refer to «rBC» only when reporting the mass concentration measurements done with the SP2 (e.g. remove the «r» before «rBC particles» in line 300, before showing the TEM image in the supplementary material, in the caption of the Figure S2...).*

Corrected throughout the text, where necessary.

*Be more specific in the caption of the Figure S2: explain what the aggregates shown are, maybe graphite or soot.*

Corrected: "Transmission Electron Microscope image of colloidal carbon black pigment particles (MIS EB-6K) used as standards for calibration of the SP2."

*Figure S3: Insert a space before (ppb) in the caption of this figure.*  
Corrected.

*Write the dates in a coherent way in the figures «S3».*  
Corrected.

*Please add the «melting speed» in the supplementary material.*  
The melting speed (3 cm min<sup>-1</sup>) has been added to the supplementary document, page 2.

*Page 7, line 199: remove the comma.*  
Corrected.

*Line 142 spelling error: «potential»*  
Corrected.