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Climate of the Past
Discussions

Interactive comment on "Burning-derived vanillic acid in an Arctic ice core from Tunu, Northeastern Greenland" *by* Mackenzie M. Grieman

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The referee made several comments that are much appreciated. The manuscript has been updated as follows to take them into account.

1. "only briefly discuss any possible climatic influences (Section 3.6)."

The following has been added to paragraph 1 in Section 3.6: "Climate proxies from the North Sea, the Qinghai–Tibet Plateau, southwest Greenland, Spain, Iceland, and other Northern Hemisphere locations have shown increased climatic variability around the period of the Roman Warm Period (Wang et al., 2012; Bianchi et al., 1999). Temperature records using tree ring chronologies from the Russian Altai and European Alps show the cooling episode defined as the Late Antique Little Ice Age. This pe-

riod of cooling followed large volcanic eruptions (Buntgen et al., 2016). This period overlaps the Dark Ages Cold period, a period of colder climates spanning the Northern Hemisphere. The contributing factors for this period are under debate, but may involve ice-rafting events, North Atlantic Oscillation, and/or El Nino-Southern Oscillation (Helama et al., 2017). The characteristics of these climate periods depend on the location. For instance, proxy records of the Roman Warm Period indicate that the Mediterranean experienced a wet and humid climate episode (Wang et al., 2012)."

The following has been added to paragraph 2 in section 3.6: "Visual inspection of hemispheric mean temperature data suggests that elevated VA levels from 1080-1240 CE followed elevated Northern Hemisphere temperatures from about 970-1090 CE. Pages 2k Arctic and North American temperature reconstructions show a similar relationship with VA levels (Fig. S11). Elevated VA levels during the Roman Warm Period overlap elevated Arctic temperatures. Elevated VA levels from 1080-1250 CE follow elevated temperatures in the Arctic from about 930-1230 CE and North America from about 750-1150 CE."

Figure S11, showing the Pages 2k Arctic, North American, and European temperature reconstructions, has been added to the supplement.

References added:

Bianchi, G. G. and McCave, 5 I. N.: Holocene periodicity in North Atlantic climate and deep-ocean flow south of Iceland, Nature, 397, 515, doi:10.1038/17362, 1999.

Pages2k: Continental-scale temperature variability during the past two millennia, Nature geoscience, 6, 339, doi:10.1038/NGEO1797, 2013.}

2. "The authors do not compare the Tunu VA record to any other proxy information derived from the Tunu core, other than accumulation, which is surprising as the ice core data would help to better link the fire activity recorded at Tunu to climate variables influencing the site."

Figure S12, showing the Tunu δ18O record, has been added to the supplementary material. An increase in the record during the MCA is referenced in section 3.6. Other Tunu ice core climate proxies are outside the scope of this paper.

3. "Are these blanks the 58 MilliQ water blanks that were previously mentioned? Does the interference also occur in the procedural blanks? (It is unclear if you have both lab and procedural blanks. Please specify exactly how you created your blanks). This peak also occurs in your standards, suggesting that the source of contamination is local, yet you are able to quantify detection limits for pHBA. Please explain."

The blanks referred to are the 58 MilliQ water lab blanks previously mentioned. The source of contamination does appear to be local and likely occurred during sample handling prior to analysis. The source of the contamination has still not been determined. The detection limit for p-HBA was defined using MilliQ water blanks that did not show the contamination.

Section 2.2 has been edited as follows: "This peak was present in most of the ice core samples, several of the 58 MilliQ water blanks, and standards. The detection limit for p-HBA was determined using blanks that did not show this contamination. The presence of this peak in blanks and standards suggests that it is a contaminant that was introduced locally during sample handling. This peak was not observed in previous analyses of p-HBA in other Arctic ice cores (Grieman et al., 2017, 2018)."

4. "Section 2.2: However, more information from the Grieman et al., 2015 method paper is necessary within Section 2.2 of this paper. (Please also change your citations from Grieman et al., 2017, 2018, in review, to Grieman et al., 2015 and 2017 to correctly cite to work to which you refer). For example, what QA/QC measures do you use? Do you apply an internal standard? Readers cannot analyze your interpretations of the data without having a clear indication of the quality of the data."

The method is described in Grieman et al. (2017) and Grieman et al. (2018). Grieman et al. (2015) describes a different method.

The first paragraph of section 2.2 now reads as follows: "Vanillic acid (VA) and para-hydroxybenzoic acid (p-HBA) were analyzed by anion exchange chromatographic separation and tandem mass spectrometric detection with electrospray ionization in negative ion mode (IC-ESI-MS/MS) (Grieman et al., 2017, 2018). The experimental method is described in detail in Grieman et al. (2017). The experimental system is a Dionex AS-AP autosampler, ICS-2100 integrated reagent-free ion chromatograph, and ThermoFinnigan TSQ Quantum triple quadrupole mass spectrometer. VA and p-HBA were detected at mass transitions of m/z 167→108 and m/z 137→93, respectively. Synthetic external standards, ranging in concentration from 0.1-2 ppb, were prepared using reagent grade VA and p-HBA in MilliQ water. These standards were analysed in sequence with ice core samples. The retention times of VA and p-HBA were 11.1 minutes and 11.8 minutes, respectively, with peak width half heights of 0.4 minutes. Detection limits for VA and p-HBA were 0.005 ppb and 0.034 ppb, defined as 3x the standard deviation of MilliQ water blanks (n = 58). 575 ice core samples from the Tunu ice core were analyzed in this study."

5. "Section 3.3: If 17% of the back-trajectories are from North America in the summer, and if 3% are from European ecofloristic zones, and 2% from Siberian ecofloristic zones, where is the source of the rest of the summer back-trajectories?"

The rest of the back trajectories do not transect North American, European, or Siberian ecoflorisitic zones. They primarily originate from the ocean.

The following was added to section 3.3: "The remainder of the trajectories originate over the oceans and did not transect North American, European, or Siberian ecofloristic zones."

6. "Section 3.4 and Figure 8: However, while the relationships between these proxies after 1200 CE certainly are variable, and do not demonstrate any patterns either between themselves or with each other. The only relationship that does seem to exist – and this is really quite stretching the interpretation – is that the correlation coeffi-

cients for Tunu VA, NEEM NH4 versus Tunu VA, NEEM BC are out of phase with one another after 1300 CE. It is better to state that after 1300 CE no major relationships exist between these data. Panel 2 is difficult to read. Either separating each proxy or elongating the y-axis will help the reader."

Sentence in section 3.4 changed to: "The results show a strong positive correlation for all of the records from 650-1200 CE but not subsequently."

7. Section 3.5 and Figure S9: You mention "the qualitative similarities between the Tunu VA and western Canadian charcoal record suggest that this may be a source region of the Greenland burning signals, but the correlation is not significant at the 95% confidence interval." However, in examining Figure S9 closely, the only correlation occurs at 1400 CE, while all other peaks and low points are offset from one another. These records do not correlate, and ascribing western Canada as a source region based on this data is overreaching what the data actually demonstrate.

Sentence changed to: "Only the records from western Canada (40°-80°N, 110°-180°W) show any similarity to the Tunu VA record, with a slight increase around 1400."

Removed sentence: "The qualitative similarities between the Tunu VA and western Canadian charcoal record suggest that this may be a source region of the Greenland burning signals, but the correlation is not significant at the 95% confidence interval."

8. Section 3.6 and Figure 9: "The data suggest a positive correlation between North American fire and hemispheric mean temperature." This statement assumes that Tunu VA represents North American fire rather than boreal fire and/or regional fire. The comparison between Tunu VA and temperature for the entire northern hemisphere differs from your plots showing that the back-trajectories are primarily for high latitude regions. Using a temperature record that reflects your source region is a better comparison. (Using a representative temperature record is especially important as the MCA and LIA vary regionally, and therefore influence your time periods of interest). Did you calculate this correlation? Or do the data only "suggest" this correlation? The

peak in Tunu VA and the peak in the NHT anomaly are offset by at least a century. The decreased temperature and lower concentrations of Tunu VA do occur during similar time periods.

The following has been added to paragraph 2 in section 3.6: "Visual inspection of hemispheric mean temperature data suggests that elevated VA levels from 1080-1240 CE followed elevated Northern Hemisphere temperatures from about 970-1090 CE. Pages 2k Arctic and North American temperature reconstructions show a similar relationship with VA levels (Fig. S11). Elevated VA levels during the Roman Warm Period overlap elevated Arctic temperatures. Elevated VA levels from 1080-1250 CE follow elevated temperatures in the Arctic from about 930-1230 CE and North America from about 750-1150 CE."

Figure S11, showing the Pages 2k Arctic, North American, and European temperature reconstructions, has been added to the supplement.

Added Reference:

Pages2k: Continental-scale temperature variability during the past two millennia, Nature geoscience, 6, 339, doi:10.1038/NGEO1797, 2013.

9. Conclusions and abstract: The correlation between Tunu VA, and Neem ammonium and black carbon in the NEEM ice core only exists between 600 to 1200 CE, and so following statement is misleading: "The correlation between Tunu VA, and NEEM ammonium and black carbon in the NEEM ice core is encouraging evidence that a consistent pattern of centennial-scale variability in North American high latitude fire is recorded in Greenland ice, but further measurements on multiple ice cores will be needed to validate this conclusion". A similar sentence is also present in the abstract. This correlation is only true for one part of the record, but absolutely does not apply to the rest of the record.

Sentences in abstract changed as follows: "Analysis using a peak detection method revealed a positive correlation between vanillic acid in the Tunu ice core and both ammonium and black carbon in the north Greenland NEEM ice core from 600 to 1200 CE. The data provide multiproxy evidence of centennial-scale variability in North American high latitude fire during this time period."

Sentence in conclusion changed as follows: "The correlation between Tunu VA and ammonium and black carbon in the NEEM ice core from 600 to 1200 CE is evidence of centennial-scale variability in North American high latitude fire during this time period. Further measurements on multiple ice cores will be needed to validate this conclusion."

10. Conclusions: The statement "A clear link between the VA variability in Greenland ice and North American sedimentary charcoal is not evident, although a tentative connection to the Quebec region was noted". This statement contradicts your text in Section 3.5 in which you highlight possible similarities (with which the data do not actually demonstrate, as mentioned in the above comment addressing Section 3.5) between the Tunu NA and western Canadian charcoal syntheses. It is essential to omit the conclusion regarding Quebec.

Removed from conclusion: "…although a tentative connection to the Quebec region was noted."

11. Figure 5: The information given by the fraction of ice core samples exceeding the 70th percentile actually detracts from highlighting the difference between the fraction of ice core samples exceeding the set peak threshold in the 65th and 75th percentiles. However, as you use the 70th percentile in section 3.4 and as the basis for the second and third panels of Figure 8, it may be better to only show the 70th percentile. These colors (as in Figure 8) are unfortunately the most difficult to differentiate for people who are color blind, resulting in a figure that is unreadable for many people. Please choose other colors.

Now only use 75th percentile is shown in figures 5 and 8. Text reflects this choice. Color used for ammonium in panel 2 of figure 8 changed. Black line used in panel 3 of

figure 5.

12. Page 3 Lines 32 and 33 (and continuing throughout the paper): PC's and RC's should be changed to PCs and RCs.

Edit complete

13. Page 4, Line 11: Place "of" between "frequency large".

Edit complete

14. Page 4, Line 12: Change "fiers" to "fires".

Edit Complete

15. Page 4, Line 15: Omit the comma after "fluxes".

Edit Complete

16. Page 6, Line 25: "The Canada charcoal record exhibits no linear trend and century scale variability that is not significant at the 95% confidence interval". This is double negative. Do you mean "The Canada charcoal record exhibits neither a linear trend nor century-scale variability that is significant at the 95% confidence interval"?

The sentence has been changed as suggested.

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