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Climate of the Past
Discussions
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Interactive comment on "High-resolution glacial and deglacial record of atmospheric methane by continuous-flow and laser spectrometer analysis along the NEEM ice core" *by* J. Chappellaz et al.

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Dear Todd, dear anonymous referee, dear editor,

Thank you for your positive comments on this manuscript. Please find below our responses to your specific questions/remarks.

__Todd Sowers (referee 1)__

The manuscript submitted by Chappellaz et al., is extremely well written and completely suitable for publication in Climate of the Past. While the manuscript is long, it is important to have a reference publication that spells out the nuts and bolts associated with this new technique for measuring CH4 continuously along an ice core.

We thank Todd Sowers for his support about the need to get into details in such paper when using a new technique. This may help other research groups to setup their own system for continuous-flow measurements of trace gases in ice cores, as well as for data treatment.

I thus recommend that the manuscript be published in effectively its present form with some minor

changes for clarification.

Page 4, Line 23, Need to add a sentence or two on the Rhodes set up.

We agree. We propose to add the following sentences at the end of the corresponding section:

"The method has been successfully applied in the laboratory on a 400-m long core drilled during the 2011 field campaign of the North Greenland Eemian Ice Drilling (NEEM; 77.45° N, 51.06° W). It provided a detailed CH_4 record covering the last 2000 yr (Rhodes et al., 2013) as well as a CO profile (Faïn et al., this issue)."

To lighten the text, the following sentence is replaced by *"Here we present and discuss the methane results obtained during the spring-summer 2010 field campaign at NEEM, using a similar analytical setup. . . "*

Pg 6, Line 11, the following sentence is unclear. "A built-in vacuum pump of the WS

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CRDS instrument maintains a pressure gradient through the two laser spectrometer cavities until the bundle of hydrophobic, gas-permeable membrane tubes within the module, which is sufficient to extract non-dissolved air from the sample stream."

We propose to replace it by:

"A built-in vacuum pump of the WS-CRDS instrument maintains a pressure gradient between the WS-CRDS cavity (62 mbar), the OF-CEAS cavity (70 mbar) and the gas outlet of the hydrophobic, gas-permeable membrane in the module (364 to 450 mbar). The resulting pressure drop of ˜300-400 mbar across the membrane was sufficient to extract non-dissolved air from the sample stream."

Pg 17, L18. I'm a bit unclear about the following sentence:

The two raw laser spectroscopic CH4 datasets differ from each other on an absolute scale and are in general lower than discrete measurements on parallel ice sticks (upper left panel of Fig. 6), which mostly reflects a preferential dissolution of methane versus nitrogen during water/gas transfer from the CFA melthead to the MicroModule." The Henry's law solubility coefficient for CH4 is $>$2x that of nitrogen. From the melthead, the bubble stream will approach equilibrium between the gas in the bubbles and the dissolved gas in the water. At equilibrium, the [CH4] in the bubbles in the bubble stream will be lower than in the bubble from the ice core. But this is a solubility issue not a dissolution issue. Also, this is an equilibrium effect. The kinetics associated with gas diffusion between the bubble and the water in the bubble stream must impact the partioning and one should not forget O2.

We propose to clarify the sentence as follows:

"The two raw laser spectroscopic CH4 datasets differ from each other on an absolute scale and are in general lower than discrete measurements on parallel ice sticks (upper left panel of Fig. 6). It mostly reflects the larger solubility co-

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efficient of methane versus nitrogen and oxygen in water. Note that solubility equilibrium is not necessarily reached during water/gas transfer from the CFA melthead to the MicroModule."

Pg 18, L10, "During the 8-week of coupled CFA-gas measurements of the NEEM 2010 field campaign, several changes affecting the analytical setup were made (Table 1). Notably a small leak at the OF-CEAS gas outlet contaminated with a varying amount the WSCRDS (and GC) measurements. This can be seen e.g. for the WS-CRDS data that was measured without the OF-CEAS being connected upstream (light blue in Fig. 6)." The reader is left with a sense that the WS-CRDS data has been compromised throughout by this "small leak". I think it would be worthwhile quantifying the magnitude of the impact on the WS-CRDS data here as it is obviously not large.

It is correct that the WS-CRDS data have been biased by this small leak, but not compromised. We propose to slightly modify the sentences as follows:

"During the 8-week of coupled CFA-gas measurements of the NEEM 2010 field campaign, several changes affecting the analytical setup were made (Table 1). Notably a small leak at the OF-CEAS gas outlet contaminated with a varying but small amount (˜5 to 10% of the measured concentration) the WS-CRDS (and GC) measurements. This can be seen e.g. for the WS-CRDS data that was measured without the OF-CEAS being connected upstream (light blue in Fig.6)."

Pg 18, L26, It is useful to compare the current CFA CH4 data with previous discrete data. My concern is the fact that those data sets were all measured by different people in different labs using different standards and different techniques on different ice cores with different age models. Issues associated with the blanks, solubility, and standard

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reference and age scales offsets are paramount and difficult to quantify. I would like to suggest some verbage highlighting the uncertainties associated with the older data sets values if correcting all the data is not reasonable.

As stressed on Pg19 L2-4, all discrete data have been put on the same GISP2 CH_4 standard scale in order to reduce the biases pointed out by Todd Sowers here. We also pointed out on Pg19 L12-26 that one must be cautious when using our dataset on an absolute scale. To stress even more the point, we propose to extend the sentence on Pg19 L18-20 as follows:

"For other sections, the correction often relies on a limited number of discrete measurements with a worse experimental uncertainty than those from OSU. This amplifies possible biases on the absolute scale of our record due to different blanks, standard reference and/or age scales used in each discrete dataset."

Pg 23, L9, Probably need to specify northern hemisphere warming here as the SH warms throughout the GS events.

We agree. We will add *"in the Northern hemisphere"* at the end of the sentence.

Pg 23, L15, Another plausible explanation might be other climate related forcing factors (Heinrich events of differing extents, orbitally driven monsoon intensity, sea level or changes in AMOC).

We propose to add the following sentence at the end of L16:

"Aside from temperature, alternative sources of CH_4 emission buffering could also be considered, such as the strength of Heinrich events, the monsoon intensity, sea level or the AMOC structure and strength, all affecting continental

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hydrology".

Referee 2

This manuscript presents the methods and results of quasi-continuous CH4 measurements on the NEEM ice core performed during the 2010 field campaign. It is very detailed and well written, and the topic and results are of large importance for icecore and paleoclimatic communities. I praise the huge effort of the research teams that made this dataset.

We thank the referee for his very kind appreciation of the work needed to make this dataset.

The manuscript should be published after minor revision for clarification.

Minor comments:

p2520, l6-10. Replace "melting-refreezing" with just "melting". There are groups that do not use the refreezing step (e.g. Nakazawa et al., 1993, GRL). The references here should also (at least) include papers of Australian group and Japanese group.

We agree. We will add Nakazawa et al. 1993 as well as Etheridge et al. 1998 in the corresponding reference list.

p2522, l16. Could you give a typical value of the upstream pressure?

Yes. We will add *"(set in the range 364-450 mbar during the field campaign)"* between *"the upstream pressure"* and *"at the outlet of the gas extraction module"*.

p2539, l6-9. This suggestions is only valid if the rates of warming and cooling are the same. Do the authors suggest it is indeed the case? If so, please clarify it in the text with appropriate citations. If not, please change the text accordingly.

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Good point. Although the lower rates of cooling (at the very end of interstadials, we do not consider here the slow cooling trend characterizing most of the Greenland interstadials) compared to the rates of warming in the NEEM isotopic record is less evident than the respective methane trends, it is true that the final cooling of interstadials is usually slower than the initial warming. We therefore propose to change the text on L6-9 as follows:

"The same holds in general for the water isotopic record of Greenland interstadials. This indicates that the mechanisms responsible for changes to the CH4 budget at these time scales (e.g., wetland extent and/or CH4 fluxes, oxidative capacity of the atmosphere, biomass burning; see Baumgartner et al. (2012) for a recent review) remained closely tight to temperature changes as recorded in Greenland."