This study provides a systematic investigation into the origin of "excess" methane measured in dusty [Greenland] ice core samples. The authors build on previous work of Lee et al., 2020, adding d13C-CH4 and dD-CH4 isotopic data as well as evidence of coproduction of ethane and propane. Overall, this work comprises an important contribution to the literature by advancing our understanding of the potential mechanism(s) responsible. Congratulations to the authors on an excellent set of measurements. I have a few suggestions, mostly minor or even grammatical. I would like to highlight the need to tighten up the discussion of uncertainties (marked * below), particularly in light of Reviewer 2's misgivings.

Comments listed in line order:

Title: Suggest removing first 'excess'.
Done/ deleted

L23: kyears should be kyr or ka
This is an editorial requirement

L26 and throughout: Why is 'in extractu' italicised and 'in situ' is not?
This is an editorial requirement

L26-29: Can the term 'excess' be defined here when first used? It may not be obvious to many readers. It is defined at L121 after being used several times.
The term is only used before in the abstract, however, no definitions/explanations should be used here. The first presence is in line 121, where it is then explained.
No changes in the text.

L31-32 and throughout: Can a threshold for 'dusty' ice be defined up-front in the abstract? If the excess alkanes scale with dust content then where to you draw the line? When is dust content low enough for this effect to not be a problem/not detectable?
Based on our current knowledge, the amount of excess alkanes scales linearly with the amount of mineral dust within the ice samples. Therefore, indicating a threshold would be misleading. But for a better understanding we re-structured the text accordingly.

Changes in the text:

Abstract. Air trapped in polar ice provides unique records of the past atmospheric composition ranging from key greenhouse gases such as methane (CH$_4$) to short-lived trace gases like ethane (C$_2$H$_6$) and propane (C$_3$H$_8$). Recently, the comparison of CH$_4$ records obtained using different extraction methods revealed disagreements in the CH$_4$ concentration for the last glacial in Greenland ice. Elevated methane levels were detected in dust-rich ice core sections measured discretely pointing to a process sensitive to the melt extraction technique. To shed light on the underlying mechanism, we performed targeted experiments and analyzed samples for methane and the short-chain alkanes ethane and propane covering the time interval from 12 to 42 kyears. Here, we report our findings of these elevated alkane concentrations, which scale linearly with the amount of mineral dust within the ice samples. The alkane production happens during the melt extraction step of the classic wet extraction technique and reaches 14 to 91 ppb of CH$_4$ excess in dusty ice samples. We document for the first time a co-production of excess methane, ethane, and propane with the observed concentrations for ethane and propane exceeding their past atmospheric background at least by a factor of 10. Independent of the produced amounts, excess alkanes were produced in a fixed molar ratio of approximately

14:2:1, indicating a shared origin. The carbon isotopic signature of excess methane is (-47.0 ± 2.9) ‰ and its deuterium isotopic signature is (-326 ± 57) ‰ in the samples analyzed. With the co-production ratios of excess alkanes and the isotopic composition of excess methane we established a fingerprint that allows us to constrain potential formation processes. This fingerprint is not in line with a microbial origin. Moreover, an adsorption-desorption process of thermogenic gas on dust particles transported to Greenland appears not very likely. Rather the alkane pattern appears to be indicative of abiotic decomposition of organic matter as found in soils and plant leaves.

L36: change 'confine' to 'refine'
Done/ changed

L67: "the good guy" – can a less gendered term be used here? Maybe methane is female…
Done/ changed

L74: should be "relative" contribution?
Done/ changed

L108: change 'as well' to 'also'
Done/ changed

L115-116: I couldn't see this thesis available online…could the magnitude of the Antarctic dD variations at least be quantified here please?
No, unfortunately this is not available online. We therefore changed it to "unpublished data", and we also give a value (3-4 ‰).

L159: 'evidences' should be 'evidence'. 'hypotheses PROPOSED by Lee'
Done/ changed

*L272 (then also L295, L339 etc.): All mention of precision or uncertainty needs to be clarified. Are you talking about a 2 sigma precision here? Are these values obtained from repeated/pooled measurements? L443 mentions a 2 sigma uncertainty.
Sorry for the confusion and thank you for this important notice! The uncertainties given in the numbers are 1 sigma here and throughout the manuscript. We changed it accordingly. This implies, that the results are not significantly different within the 2 sigma error, as stated in our manuscript.
Reading the comments from both reviews, we also realized that to prevent ambiguities we need to better explain how we dealt with the blank contribution throughout the manuscript. Throughout the paper, we showed the data without blank correction, i.e. we plotted the actual values of the measurements which is the ice core derived amount plus the amount derived from the system (blank). Except for the CH_4 amount measured in the 2nd extraction which has a considerable amount of "blank" contribution, the system blank values for ethane and propane for both the 1st and the 2nd extraction are sufficiently small compared to the sample-derived amount. The advantage of showing the non blank-corrected values is that we can plot both the blank and ice core measurements in a single figure which allows to see the size of the blank contribution and also the respective alkane ratio of the blank contribution.
With regard to $\delta^{13}C$-CH_4, indeed the $\delta^{13}C$-CH_4 signature of the blank (EDC) is similar and only a few ‰ heavier (-39.0 ‰) to the signature of our Greenland samples. Applying an isotope mass balance approach, we see that the leverage on our NGRIP values is small (0.31 ‰). Thus,

applying a blank correction has only little leverage but would shift the sample values a bit towards isotopically lighter values, and therefore more into the direction of the values obtained from the Keeling plot approach. For the sake of the length of the paper, we did not expand on these corrections for the δ^{13}C-CH$_4$-signature. We wish to stress that measuring the δ^{13}C-CH$_4$ signature of such small CH$_4$ samples as available from the 2nd extraction is at the edge of what is possible with our measurement device.

We clarified in the main text that we are not performing a blank correction (except for Fig. C1 where the blank correction is necessary).

We also clarified the section explaining the blank determination and precision of our method.

We added another Figure (Appendix B, Figure B1) with a description of the blank determination.

Figure 8 is revised.
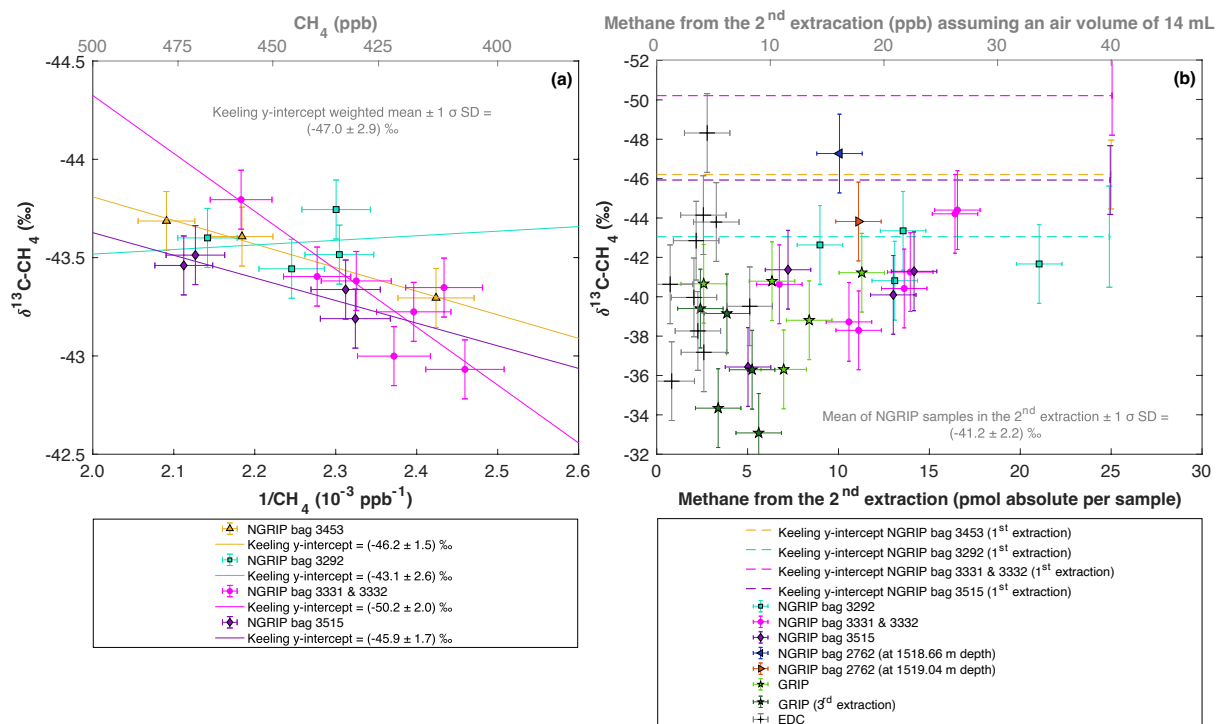
Changes in the text:

... Precision of this method for CH$_4$ is about 8 ppb and 0.1 ‰ for δ^{13}C-CH$_4$ based on the reproducibility of the 1st extraction ice core samples where isotopic data are expressed using the δ notation on the international Vienna Pee Dee Belemnite (VPDB) scale. For C$_2$H$_6$ the precision is 0.02 ppb or 1 %, for C$_3$H$_8$ 0.03 ppb or 5 % (whatever is higher) based on the reproducibility of standard air samples which are by definition not subject to excess production (Schmitt et al., 2014). Blank levels for these species based on melted artificial (gas-free) ice samples are 1-2 ppb for CH$_4$, 0.3 ppb for C$_2$H$_6$ and 0.2 ppb for C$_3$H$_8$ (Schmitt et al., 2014), which are below the values measured on Antarctic ice, where excess production is minimal compared to glacial Greenland samples (see Appendix B for details).

... The amount of gases that we obtain from the 1st extraction comprises the atmospheric amount, a possible contribution by in situ production, and a potential time-dependent production/release in the melt water (in extractu). The 2nd extraction, however, targets only the in extractu fraction. The system blank for the 2nd extraction was estimated using the 2nd extraction of Antarctic ice (Talos Dome, EDC) and were 2 ppb, 0.3 ppb and 0.3 ppb for CH_4, C_2H_6 and C_3H_8, respectively, assuming an ice core sample air volume of 14 mL at standard temperature and pressure, which is the typical ice sample size of 150 g with a total air content of 0.09 mL/g. For CH_4 this and is < 1% of the amount of extracted species in the 1st extraction of glacial Greenland ice. Due to the small amount of CH_4 analyzed in this 2nd extraction (about a factor of 20 to 50 less than for an ice core sample) the precision for the $\delta^{13}C$ analysis is much lower than for the 1st (ice sample) extraction and we estimate the precision of $\delta^{13}C$-CH_4 to 2 ‰ and for $[CH_4]$ to be 2 ppb or 10 % (based on the reproducibility of 2nd extractions of Antarctic EDC samples). For C_2H_6 and C_3H_8, the precision is comparable to the 1st extraction. Note that throughout the manuscript we do not perform blank corrections (neither for the measured alkane concentrations nor for the isotopic values). The only exception is for the calculation of the temporal dynamics of excess ethane production (Fig. C1) as the blank contribution would otherwise bias the samples with low Ca^{2+} content.

... Another caveat is the considerable blank contribution for CH_4 that we observe for the 2nd extraction. Since Antarctic ice cores do not show a sizable in extractu production (Fig. 7, grey crosses for EDC) we measured EDC samples with the same protocol of a 2nd extraction as for our Greenland samples to provide an upper boundary of this blank. Hence the 2nd extraction of the EDC samples are a conservative blank estimate while the true system blank is lower. As can be seen in Fig. 8 (right panel) the amount of CH_4 measured for these EDC samples (grey crosses) is on average about 2 pmol (equivalent to about 3 ppb). For comparison, our ice samples from Greenland show a range of about 5 to 20 pmol, indicating a considerable blank contribution in the 2nd extraction.

To estimate the influence of the blank on the isotopic signature that occurs during the 2nd extraction we used the values from our EDC measurements and applied an isotope mass balance approach. The $\delta^{13}C$-CH_4 blank signature obtained from these EDC samples is -39.0 ‰, hence a few ‰ heavier than the mean $\delta^{13}C$-CH_4 signature of the excess CH_4 from this 2nd extraction for the Greenland samples. On average, the correction would shift our NGRIP values towards lighter (more negative) values by 0.31 ‰. This systematic correction is thus small compared to the typical measurement precision obtained both from the Keeling-plot approach and the direct measurement of the $CH_{4(xs)}$ with the 2nd extraction. As the $\delta^{13}C$-CH_4 signature of the blank is close to the NGRIP values, performing a blank correction has only little leverage. Considering these analytical limitations of our 2nd extraction for $\delta^{13}C$-CH_4, these findings suggest that $CH_{4(xs)}$ produced during the 1st and 2nd extraction has the same $\delta^{13}C$-CH_4 isotopic signature within the 2 σ error limits and is likely produced/released by the same process in both extractions.
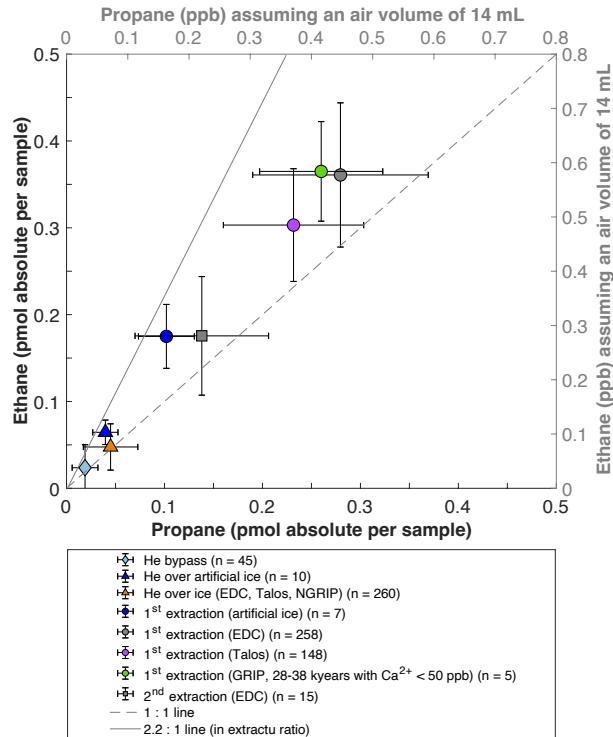
*Figure B1: **Collection of different measurement modes and ice core sample locations to estimate individual "blank" contributions.** The mode "He bypass" (diamond) refers to a measurement type where helium is injected into our system but without flowing through our extraction vessel. "He over ice" (triangles) refers to helium injections over the unmelted ice core sample. Results from the 1st extraction are shown for different ice cores (artificial ice, Talos Dome, EDC, GRIP; colored circles). The 2nd extraction of the Antarctic EDC ice core is marked as red square. Lines with ethane/propane ratios are for orientation only.*

In this section we provide background information of how we determined the blank contributions for our alkane measurements for the different measurement modes. Overall, our strategy is similar to the measurements which were published earlier in 2014 (Schmitt et al., 2014). Here we include more measurements performed since then with our $\delta^{13}C$-CH_4 device. Following the classic usage, blank contributions are related to the measurement device itself rather than to the sample, thus we report the measured values of the species as absolute amount in pmol with respect to a measurement procedure (sample run). To compare these absolute values with the classic units of species concentration in the air for an ice sample in ppb, Figure B1 has secondary axes (grey) for the species concentrations in ppb for an assumed sample size of air of 14 mL STP (our typical ice core).

Since our extraction device is at vacuum conditions, a blank contribution from leaks that allow ambient air with relatively high ethane and propane concentrations to be collected together with our sample seems the most straightforward risk. To quantify this leak contribution, we routinely perform so called "He over ice" runs where a helium flow is passed over the unmelted ice core sample and the species are trapped on the cold activated carbon trap (see details in Schmitt et al., 2014). The trapping duration is the same as for the 1st extraction, thus this "He over ice" run mimics the contribution for the 1st extraction. As can be seen in Fig. B1, for ethane this "leak contribution" is typically <0.1 ppb, thus small compared to concentrations we see for dust-rich Greenland ice samples with about 6 ppb (see Fig. 5a). However, this "He over ice" does not capture the actual melting process of the ice sample and represents the lowest blank boundary for our ice core samples. To mimic the full procedure an ice core samples experiences, we run a limited number of artificial gas free ice samples (blue circles in Fig. B1). The ethane values obtained for these artificial ice sample is around 0.3 ppb and thus

considerably higher than for the procedure without melting. This indicates that either the presence of liquid water leads to a desorption or production of alkanes from the inner walls of our extraction vessel. Alternatively, our artificial ice still contains traces of alkanes. So far, we could not solve this issue and more experiments are needed. A much larger data set on the upper boundary of the extraction blank comes from routine measurements of Antarctic ice core samples with the primary target of stable isotope analyses of CH_4 and N_2O. These Antarctic samples cover glacial and interglacial time intervals and the measured ethane values are typically around 0.55 ppb. Since the reconstructed atmospheric background for ethane in Antarctic ice is lower with values in the range of 0.1 – 0.15 ppb for the late Holocene (Nicewonger et al., 2018), a realistic blank contribution for our 1st extraction is on the order of 0.4 to 0.5 ppb. An additional constraint comes from five stadial GRIP samples from the time interval 28 – 38 kyears (green circle in Fig. B1) that have very low Ca^{2+} content (< 50 ppb) and thus have likely a negligible contribution from a dust-related in extractu component. The measured ethane concentration from these GRIP samples is very similar to the Antarctic ice core samples. One possible explanation would be that the atmospheric ethane concentration during the glacial was similar and low for both hemispheres. Regardless of the individual contributions, for our considerations of dust-related in extractu production in Greenland ice cores the upper estimate for the sum of atmospheric background and blank contribution is ca. 0.55 ppb (about 0.35 pmol) for ethane. Since the ethane to propane ratio for these non-dust contributions is ca. 1.5 the corresponding propane values are lower by that value. Importantly, since the ethane to propane ratio for our dust-related production is with 2.2 rather similar, its impact on the calculated ethane to propane ratio (e.g. Fig. 5) is very minor and small within the error estimate. For that reason, we did not correct our Greenland measurements for any "blank" contribution and showed the values as measured along with measurements of Antarctic ice cores samples which serve as first-order blank estimates.

Figure 4: grey hatched area doesn't show up.

The grey hatched area is very small, only 0-0.39 ppb of ethane. It is the background concentration and just given to illustrate the difference to the measured values. It should therefore not stick out, but of course it should be visible. I strengthened the shade of grey.

L491: Sorry I don't get the meaning here…how do you define the gas extraction as quantitative (or qualitative)?

Done/ deleted (as also desired by reviewer No.1)

*L581 onwards and Figure 8: Looking at the figure, the intercepts do not overlap within uncertainties given, yet the text suggests they do…please clarify.
*L601: as above

Sorry, it is again 1 sigma here.

L695-697: Suggest removing this last sentence – it is confusing and implies you actually know something concrete about the rate of desorption.

Done/ deleted

L727: Could 'deflation' be defined, for those not familiar?

Done

Figure 10: Great figure.

Thank you.

L743: Please check papers cited here. Bory et al., 2003 did not analyse glacial dust samples, Rhodes et al., 2013 did not analyse any dust.
Done

L747: Doesn't make sense as written.
Done/ clarified in the text

L935: phrase not sentence
Done/ clarified in the text

L937: Could you expand – what is abiotic conditioning?

Changes in the text:
… We stress that although we can exclude a direct UV effect during sample extraction, it is possible that UV irradiation during dust aerosol transport to Greenland and within the upper snow layer after deposition until the snow gets buried into deeper layers may precondition organic precursors attached to mineral dust to allow for alkane production to occur during extraction. In particular, the first step of the reaction (excitation of the homolytic bond of a precursor compound) may start already in the atmosphere or in the upper firn layer where energy from UV radiation is available. Within the ice sheet the reaction may be paused ("frozen reaction") and only becomes reactivated during the melting process when liquid water is present.

L1011: Seems difficult to reconcile the dust coming from desert regions and it being rich in organic material.
Dust from the Taklamakan (and Gobi) desert might not be "rich" in organic material, but it definitely contains organic material, and it can accumulate organic matter during transport and organic aerosol formation in the atmosphere.
Ventura, A.; Simões, E.F.C.; Almeida, A.S.; Martins, R.; Duarte, A.C.; Loureiro, S.; Duarte, R.M.B.O. Deposition of Aerosols onto Upper Ocean and Their Impacts on Marine Biota. *Atmosphere* 2021, *12*, 684. https://doi.org/10.3390/atmos12060684

Huo, W., He, Q., Yang, F. *et al.* Observed particle sizes and fluxes of Aeolian sediment in the near surface layer during sand-dust storms in the Taklamakan Desert. *Theor Appl Climatol* 130, 735–746 (2017). https://doi.org/10.1007/s00704-016-1917-4

The uptake of organic substances during transport is explained in the text:
… Organic precursors for this abiotic production during extraction could be any organic matter (either microbial or plant-derived). As the amount of excess alkanes is tightly coupled to the amount of dust, we assume that these organic compounds are attached to dust particles. This "docking" of the organic precursor onto the mineral dust could happen already in the dust source region involving organic material available at the surface. Or it could happen by adhering of volatile organic molecules or secondary organic aerosols from the atmosphere to the mineral dust aerosol either before deflation at the source region or during transport to Greenland.
No changes in the text.

L1036: Can you go further? Could this explain previously reported lab offsets?
Unfortunately not.
Previously reported lab offsets concern Antarctic ice samples, which do not show any signs of *in extractu* production. Explaining lab offsets for Greenland ice samples would be beyond the scope of this paper.
No changes in the text.

L1158: Should 'contradicting' be 'corroborating'? The meaning is not clear here.
No, "contradicting" is right. What we want to say here, is, unless we do not have anything specific speaking AGAINST the ROS hypothesis, we see this as the most likely process.
No changes in the text.

I am also in agreement with Reviewer 2 that this paper is unnecessarily lengthy, containing significant repetition (although generally well-written). This will cause many less-interested readers to give up before reaching the punchline! Some heavy-handed editing from co-authors would be beneficial. The conclusions section could be much more stream-lined with a more compelling punchline. Finally, could a summary figure or table be included which compares/evaluates the different potential production mechanisms? It is difficult to keep track through the bulk of text.
We have deleted repetitions and not ultimately necessary information.
We have also included a new table (Table 1) which displays the three hypotheses in relation to our experimental and analytical findings. This table should help to see (at a glance), which fingerprint characteristic is in line / is not in line with the respective hypotheses.

Table 1: **Overview of the different hypotheses explaining the possible sources for excess alkanes (as illustrated in Figure 10) in relation to our experimental and analytical observations.** A green checkmark indicates that the observation is in line with the respective mechanism, a purple cross indicates that the observation is in not line with the respective mechanism. A grey shaded area means that this observation does not apply or does not affect the respective mechanism.

	(1) Adsorption-desorption of thermogenic/ atmospheric gas		(2) Microbial production			(3) Abiotic/ chemical production	
	A1	A2	M0	M1	M2	C1	C2
Correlation to Ca^{2+}/ mineral dust	✓	✓	✓	✓	✓	✓	✓
Alkane pattern	✓	✗	✗	✗	✗	(✓)	(✓)
CFA evidence			✗				
$\delta^{13}C$-$CH_{4(xs)}$	✗	✓	✗	✗	✗	(✓)	(✓)
δD-$CH_{4(xs)}$	✓	✗	✓	✓	✓	(✓)	(✓)
δD-$CH_{4(xs)}$ estimated by Lee et al. (2020)	✓	✗	✓	✓	✓	(✓)	(✓)
Poisoning experiment by Lee et al. (2020)					✗		