

Answers to Reviewer1

We thank the reviewer for the in-depth discussion and helpful comments.

Please elaborate on the following topics:

- Snow property influences: Both water isotope diffusion during storage and percolation are influenced by snow properties such as density and grain size which should be discussed in both sections. Please also add a statement about the density of the snow cores analyzed in this study.

Answer to the reviewer - microstructure and density vs stable water isotopes:

In general the interplay of density and microstructure (grain size) in the snow originates from layering, i.e. the deposition of single layers. This structure is not seen / kept in the isotope signal, as diffusion smoothes very quickly. So we do not expect to see influences of layered variations of density and/or microstructure in the isotope signal. A in-depth study of high-resolution microstructure (including density) and its link to trace components and stable water isotopes at the Kohlen Station was given here: Moser et al., 2020, <https://doi.org/10.3389/feart.2020.00023>

The only potential effect is that strong changes in density may affect the melt speed - which is actually considered by the highly-resolved measurement of melt speed, and the amount of percolation, when for example changing from a lower-density (larger grains) layer to a higher-density layer (smaller grains). However, we consider this effect to be much smaller compared to the overall mixing. In fact we can show that changes in the melt speed (when comparing different CFA runs) do not affect the overall mixing.

Changes in the text:

- We add in the paragraph: Characterization of mixing length by comparison to discrete samples the following sentence: “High-resolution density measurements display the layered character of the snow, which induces mm-to-cm variations in density and microstructure. However, stable water isotopes do not capture these variations, as the diffusion on site smoothes the signal rather quickly (Moser et al. 2020).”
- We add the new paragraph 4.2 in the discussion, where the effect of variations in melt speed to the mixing length is discussed.
- We moved the paragraph on the storage effect to the discussion. We add the following sentence: “However the strength of the observed diffusion during storage is due to the low density of the snow cores and we do not expect such a strong change for firm and ice core samples from greater depth and with higher density.”

- Melt rate: How was the optimal melt rate chosen and how does this influence the results? Isotope CFA systems are often run in parallel with other instruments and thus the overall CFA melt rate is constrained by more than the water isotope line alone, but if high-resolution water isotope records from snow were the primary goal, which melt rate should be chosen, and what are the constraints? Please also add the statistics of the melt rates of your experiments to the text, both intra and inter snow core variability. Currently, only the mean melt rates are given in the figure captions and are thus hard to find.

Answer to the reviewer:

While the major focus of the CFA experiments lay on the stable water isotope measurements, other lines were operated (see figure 1). Thus, the amount of connected lines determines the required melt water to be generated and accordingly the required flow - here approx. 8ml/minute. The estimate of the necessary melt speed also considers the diameter of the inner channel, being 30mm, and the density of the snow cores (on average 340kg.m⁻³). Based on these assumptions our

constraint of the melt speed was ~33 mm/min. However, in order to assess any dependency of the observed mixing to melt speed, we applied different melt speeds between 2.87 and 4.95 cm/min.

Changes in the text (discussion):

We added a section 4.2 in the discussion:

- Further we explored the sensitivity of mixing length to melt speed. We melted the snow cores at different melt speeds, varying from 28.7 mm per minute to 49.5 mm per minute (Table 4). As the obtained mixing lengths do not show any trend (see Table 3), we are confident that the mixing length is not sensitive to melt speed variations. We however observed variability of melt speed within each core between 10 and 20 % of the mean speed (Table 5), which can be related to small-scale variations of snow density or friction within the sample holder.
- We added a table displaying the different melt speeds and the standard deviation:

	KF13	KF14	KF15	KF16	KF17	KF18
Average speed	x	28.7	31	33	46	49.5
Standard deviation	x	3.8 (13%)	4.4 (14%)	5.6 (17%)	9 (19%)	5.3 (11%)

New Table 4: Melt speed statistics for the different snow cores, expressed in mm.min⁻¹. The upper row shows the averaged melt speed of each run, while the lower row indicates the corresponding variability (standard deviation observed in mm.min⁻¹), and in parenthesis as a percentage of the mean value.

- In line 159 the authors declare that they will compare two different diffusion length calculations (normal CDF and two lognormal CDFS) but these results are not presented, although they would be of interest to the reader as the asymmetry in the impulse response is obvious from Figure 5b.

Answer to the reviewer:

As the results are similar we use the normal Gaussian distribution function in the rest of the manuscript. In order to clarify, we added a sentence at the end of section 2.2., but include both results in table 2

Changes in the text:

- We added a sentence at the end of section 2.2.: “Our results show very small differences in the resulting mixing lengths obtained by the different approaches (Table 2). We therefore focus this work on the straight forward Gaussian approach to determine the diffusion lengths and assessment of contributions to the overall mixing”

- We modified Table 2, such that it includes both results, from Gaussian distribution function and Skew distribution function.

	MH-filled	CRDS-line	MH-empty	MH	DB
Skew	<i>20.0 (1.9)</i>	<i>11.5 (2.2)</i>	<i>13.7 (1.1)</i>		
	12,7 (1.2)	7.3 (1.4)	8.7 (0.7)	9.2	4.7
Normal	<i>21.6 (2.4)</i>	<i>12.6 (1.8)</i>	<i>14.5 (1.2)</i>		
	13.6 (1.5)	8.0 (1.1)	9.2 (0.7)	10.0	4.5

Updated Table 2: δD means mixing length derived from the skew and normal PDFs, expressed in seconds (italic) and in mm (bold). Values in parenthesis represent 1SD. The conversion of seconds to mm is based on a melt-speed of 38 mm.min⁻¹. σ_{MH} and $\sigma_{MH\ to\ WI-SV}$ correspond to differences in quadrature between $\sigma_{MH-filled}$ and $\sigma_{MH-empty}$, and between $\sigma_{MH-empty}$ and $\sigma_{CRDS-line}$, respectively.

- It would be interesting to see a deconvoluted CFA record in comparison to the discrete samples of 2019 as this would be the final post-processing step for a snow CFA campaign when producing data for climate analysis. Arguably, the reverse was done to find the percolation mixing length contribution, but these data are not visualized and the statistics (RMS, l. 267) on the agreement with the convoluted discrete samples and the CFA data are not given. As such the reader has no sense for the agreement between discrete and post-processed CFA data. A visualization of such a final data product would help the reader understand the importance of the system characterization and demonstrate the utility of the Snow CFA line.

Answer to the reviewer:

While we agree that this is of great interest, we emphasize that it is not the goal of this study to correct for diffusion. We however did such tests on a shallow firn core in the past. For the full convolution assessment and deconvolution (which includes an additional work on frequency filtering during the deconvolution step) we refer to a Master thesis (not published). If the reviewer is interested: Hannah Meyer (2020, Uni Bremen), “Characterization of a continuous-flow analysis facility and development of data correction techniques: An analysis of the instrument-induced mixing of the water isotopic record in firn cores”.

In the study presented here we aim at assessing and quantifying the quality of the measurement.

Specific comments:

L. 21: The sentence “With our obtained mixing lengths...” is difficult to understand. Please rephrase.

The abstract has been rephrased in order to clarify the main focus of the study. It now reads: “We systematically determine the mixing length at different parts of the system. We measure and analyze six snow cores from Kohnen station, Antarctica, and find the largest contribution to mixing to originate in the percolation of melt water on top of the melt head.”

L. 46: “percolation” is often used in snow science to describe the vertical, gravity-driven water flow in a snowpack. To avoid confusion, please consider exchanging the term “percolation” with “wicking” (as done in (Jones et al., 2017)) or including a short terminology explanation.

Answer to the reviewer:

We here use the term describing the upflow of meltwater into the snowpack due to capillary effects, i.e. the melt water gets sucked into the snow above.

In the literature dealing with this phenomenon at the CFA melt head, both terms are used, i.e. “wicking” in for example Erich C. Osterberg, Michael J. Handley, Sharon B. Sneed, Paul A. Mayewski, and Karl J. Kreutz *Environmental Science & Technology* **2006** *40* (10), 3355-3361, DOI: 10.1021/es052536w

but also the term “percolation” is used, for example in: Kjær, H. A., Lolk Hauge, L., Simonsen, M., Yoldi, Z., Koldtoft, I., Hörhold, M., Freitag, J., Kipfstuhl, S., Svensson, A., and Vallelonga, P.: A portable lightweight in situ analysis (LISA) box for ice and snow analysis, *The Cryosphere*, 15, 3719–3730, <https://doi.org/10.5194/tc-15-3719-2021>, 2021.

We here stick to the term “percolation”, but add a sentence with a definition.

Changes in the text:

In the introduction, when the term “percolation” is used for the first time, we add/modify the sentences to:

“However, in the past, firn and ice cores were analyzed only starting in several meter depth. Due to the very high porosity and poor stability of surface snow, the upper meter of the polar snow pack has not been analyzed by CFA, but was occasionally sampled discreetly. One obstacle for measurements with CFA is the strong percolation taking place in the highly porous snow. We here refer to “percolation” as the upward movement of meltwater into the snow due to capillary effects. The percolation in the snow above the melt head leads to mixing of melt water of adjacent snow layers. This physical mixing inevitably leads to a smoothing of the derived snow record including the isotope signal (Gkinis et al., 2011).“

L. 46: The authors mention here that percolation is the reason why snow cores have not been measured routinely with CFA. The results presented in this paper support this statement. However, it is not made clear whether the authors conclude that their presented method has overcome this hurdle or which limitations remain with the system presented in this manuscript. I suggest the authors include a “best-practices” or “limitations” section in the discussion.

Answer to the reviewer:

In our study we quantify for the first time the effect of percolation on the overall mixing of the isotope signal, by separating this effect from the instrumental contribution.

We further suggest as a “best-practice”, the development of a new melt head that can better handle the melt water, thereby minimizing the percolation. This paragraph has been moved to the discussion.

Changes in the text:

We moved/added a paragraph into the discussion “Suggestion to address the percolation”

L. 54: In the introduction it would be helpful to include a short paragraph on the characteristic “mixing of the system” or “smoothing” that all water CFA systems suffer from and that is the drawback of CFA analysis of ice cores. In the current version the “mixing of the system” is first mentioned in L.54 but it is not explained until Section 2.2, (L. 136). Since the “diffusion length” is the focus of the analyses in this manuscript it would help to explain these terms already in the introduction.

Changes in the text:

We added/modified the sentences in the introduction to:

“However, in the past, firn and ice cores were only analyzed starting at several meter depth. Due to the very high porosity and poor stability of surface snow, the upper meter of the polar snow pack has not been analyzed by CFA, and was only occasionally sampled discretely. One challenge for CFA measurements is the strong percolation taking place in the highly porous snow. Here, we refer to “percolation” as the upward movement of meltwater into the snow due to capillary effects. Percolation in the snow above the melt head leads to mixing of melt water from adjacent snow layers. This physical mixing inevitably smooths the derived snow record including the isotope signal (Gkinis et al., 2011).“

L. 59: Is this set-up significantly different from other CFA systems that are being used in ice core analysis laboratories? Explain the differences or cite studies where this setup has been used previously.

Answer to the reviewer:

Indeed, the CFA system used here is similar to the system used for ice-cores. The specificity of our system refers to the adapted melting unit: the melt head for snow cores combined with the core guide, allowing to hold and melt snow cores of 10cm in diameter (where usual CFA applications use a melt head to melt a stick of 3.4 x3.4 cm size.

Changes in the text:

- In the introduction we rephrased the sentence to: “In order to enable stable water isotopes measurements in snow cores by CFA, we modified the melting unit of our CFA-system developed a (...)”
- In 2.1. we rephrased the sentence to: “The system for analyzing 1-meter snow-cores consists of a melting unit adapted to the geometry of the snow cores, a degassing unit, a (...)”
- We changed the title of the paragraph to: “Melting unit adapted for snow cores”

L. 126: What are typical lag times between the different lines?

Answer to the reviewer:

During the corresponding melting experiments, we observed averaged lags of 39.8s for the conductivity line, 40.6s for the Micro-particles line, 70s for the Fraction collection line, and 145s for the water isotopes line. These delays are significantly different as each of them is defined by each line length and by the flow applied from the manifold to each detection unit (Fig.1).

Changes in the text: None, as not relevant for the paper

L. 154: Were all mixing times (in s) converted to mixing lengths (in cm) using the same melt-rate? How stable was the melt-rate of the system during the experiments considering density variability in the snow cores?

Answer to the reviewer:

All mixing times (in seconds) were converted to mixing length using the same melt speed - using an average value of 38 mm/minute. This enabled us to derive consistency between the different contributors (percolation, instrument). We do not find an effect of variable melt speed to the derived mixing length. We now strengthen this finding by adding a paragraph in the discussion.

Changes in the text:

We add a paragraph 4.2 “The effect of variation of melt speed on the mixing length”.

L. 166: If available, please add age and density of the analyzed snow cores.

Changes in the text:

In the paragraph “Characterization of mixing by comparison to discrete samples” we add the sentence: “The 1 meter average density of these snow cores ranges between 340 - 345 kg m⁻³ (Münch et al., 2017).”

L. 178: Were the Allan variance tests performed by injecting MQ water at the Master IV valve? Would you expect the stability to be different for MQ water injected at the MH?

Answer to the reviewer:

The Allan Variance test was performed by injecting MQ at the WI selection valve. This is needed in order to get a stable stream. If the MQ was added as the Master IV (or further upstream, i.e. MH), the stream stability could potentially be affected, leading to a bias in our check of the analytical Picarro performances.

Changes in the text:

We modified the sentence to: “(...) where over a period of more than 12 hours MQ water is continuously injected at the selection valve for water isotopes (Fig.1).”

Fig. 3: I suggest removing the upper row of the figure since both plots don't add much information

Changes in the text/figure: The upper row of figure 3 has been removed.

Fig 4: Consider moving this figure to the Appendix.

Changes in the text: Previous Figure 4 was moved to Appendix B, now being Figure B1

L. 207: Is the diffusion length dependent on the step size, i.e. the standards used? Please add which standards were used to simulate the step.

Answer to the reviewer:

The isotopic steps were realized during each calibration procedure. Each of these procedures consists of a switch between MQ to standard NZE (~100 permille drop in dD), NZE to TD1 (~120 permille drop), and TD1 to JASE (~140 permille). Based on our 15 steps applied, we did not observe relationships between isotopic steps and diffusion times/lengths. Regarding the isotopic steps applied at the melt head (Filled or empty), the switch was realized between the standard TD1 and MQ water (>200 permille step).

Changes in the text:

We rephrase this section to:

“We estimate the mixing length using isotopic liquid standards across different experiments (details given in Table C1 in the supplement). First, during each calibration procedure, three abrupt isotopic changes are applied (dataset CRDS-line, Fig. 4) at the water isotopes selection valve (Fig.1) . These steps range between ~100 ‰ and ~140 ‰ (Appendix C), and show no dependency between isotopic step size and diffusion length. In a second experiment, we applied an isotopic step (~230 ‰) at the melt head with its concave volume filled (dataset MH-filled, Fig.5). Finally, the same step was then applied with the concave volume empty (dataset MH-empty, Fig.5).”

L. 208: I would appreciate a table listing the different experiments and the corresponding naming conventions of the different s to ease the reading

Changes in the text

In order to clarify all the experiments realized, we added a summarizing Table in supplement. As shown above we refer to this additional Table in the text.

Experiment	Abbreviation	Number of runs	Standards switch	Isotopic step size
Water Isotopes Calibration (step 1)	CRDS-line	5	MQ to NZE	~100 ‰
Water Isotopes Calibration (step 2)	CRDS-line	5	NZE to TD1	~120 ‰
Water Isotopes Calibration (step 3)	CRDS-line	5	TD1 to JASE	~140 ‰
Melt head filled	MH-filled	4	TD1 to MQ	~ 230 ‰
Melt head empty	MH_empty	4	TD1 to MQ	~ 230 ‰

Table C1: Details of the different experiments conducted to assess the overall instrumental mixing, and separating the different contributions along the setup.

L. 217: Please also give the results for d18O, even if you focus the discussion on dD

Answer to the reviewer:

We agree that presenting all results is informative. However, to avoid potential confusion from including all numbers in a single table, we modified Table 2 to include all results for dD and added an additional table in the appendix with the results for d18O.

Changes in the text:

We rephrase the sentence to: “The results for both isotopologues δD and $\delta^{18}O$ are very similar (Appendix C, Table C2), consistently showing a slightly longer diffusion length for δD . Therefore, we focus our study on the results for δD (Table 2).”

L. 249: Can this depth assignment mismatch be a result of the system lag between the core hitting the melt head and the time the CRDS is measuring the respective sample? Or is this lag time accounted for?

Answer to the reviewer:

This lag between the snow hitting the melt head and the melt water arriving at the CRDS is accounted for (as for every other analytical line in the system). We also discuss other factors such as density variations (not affecting the depth assignment) and the cutting of discrete samples.

Changes in the text:

- We add: “One reason for the mismatch could be the short-term fluctuation in the melt speed induced by density variations. However, the melt speed is measured with high resolution and variations are included in the depth assignment. We therefore assume that the depth assignment from the CFA is quite accurate. On the other hand the depth assignment of the discrete samples is less accurate, as the subsampling generates uncertainty in the exact size and position of each sample (i.e. loss of material due to the cutting). This uncertainty in the depth assignment and the corresponding matching to the CFA data may be one major reason for the observed mismatch of discrete and continuous data.”

L. 267: How well do the convoluted and continuous records agree? Please give RMS values.

Answer to the reviewer:

It's an automated routine finding the best match and providing the respective mixing length. So we do not have the specific numbers, but from previous experiments, assuming a comparable behavior, we believe RMS is in the range of 0.1‰ for d18O as shown in the Table below (from Hannah Meyer’s Master Thesis).

117

Appendix D

σ_{CFA} for the depth domain approach-Additional tables

TABLE D.1: σ_{CFA} for G_{normal} and G_{skew} retrieved from the depth domain approach over $\sim 4 m$ length and the mean RMS distances of CFA and discrete before and after the convolution for $\delta^{18}O$.

meters	σ_{normal} [cm]	CFA- discrete convolved with σ_{normal} [‰]	σ_{skew} [cm]	skewness factor α	CFA- discrete convolved with σ_{skew} [‰]	CFA- discrete [‰]
5-9	1.49	0.14	1.46	9.85	0.14	0.15
9-14	1.87	0.11	1.87	1.61	0.11	0.14
14-18.01	1.72	0.14	1.63	1.07	0.09	0.15
18.01-21.6	1.91	0.13	1.76	0.86	0.08	0.14
29-32.16	1.15	0.10	2.00	12.67	0.1	0.10
5-14	1.73	0.13	1.71	2.00	0.13	0.15
14-21.6	1.89	0.13	1.78	0.90	0.09	0.15
5-21.6	1.78	0.14	1.75	1.55	0.12	0.15

Table from the Master Thesis by Hanna Meyer

L. 280: Please give variability of this percolation diffusion length. Discuss the dependence on melt-rate or snow properties (e.g. (Calonne et al., 2012; Yamaguchi et al., 2010; Colbeck, 1974)?

Answer to the reviewer:

If you are referring to mixing length, we demonstrate that it is not dependent on melt speed (i.e. melt rate) or snow properties at this length-scale (1 m snow cores).

Changes in the text:

Please see our reply and related changes in the text above (first comment of the reviewer & the comment on melt rate)

L. 285: Please add short statement on how the snow cores were stored (temperature, sealing, ...)

Changes in the text:

We added: “The snow cores were stored in carbon tubes, sealed at each end with plastic bags (WhirlPack), and kept inside a Styrofoam box at -25°C.”

Table 4: Please add the differences between the two measurement campaigns to the table

Answer to the reviewer:

There have been no differences in the campaigns, just the timing

L. 337: The effect of density or other snow properties on the percolation strength is not discussed up to this point. Please include in discussion.

Answer to the reviewer:

Please see our answer and related changes above (in the first comment)

L. 339: As mentioned above, a clear conclusion and recommendation is missing whether the presented snow-CFA system is recommendable to use and, if not, what restrictions or limitations (accumulation threshold, density etc) apply.

Answer to the reviewer:

In our study, we quantify for the first time the effect of percolation on the overall mixing of the isotope signal, by separating this effect from the instrumental contribution.

We further suggest as “best-practice” to develop a new melt head that is better able to deal with the melt water, thereby minimizing the percolation. This paragraph has been moved to the discussion.

Changes in the text:

We moved/added a paragraph into the discussion “Suggestion to address the percolation”

Appendix B: Please add short introduction to the two presented figures and cite the model that is being used. I recommend highlighting AWI storage temperature and Kohonen annual mean temperature to Fig B2.

Changes in the text:

- We added to Figure D1: “Exemplary firn-diffusion length estimates for firn samples with a density of 370 kg.m⁻³ as function of storage time. The firn diffusion length is computed

based on the model by Gkinis et al. (2014), using a temperature of -20°C and an accumulation rate of $75\text{ mm}^{\text{yr}^{-1}}$

- We updated Figure D2:

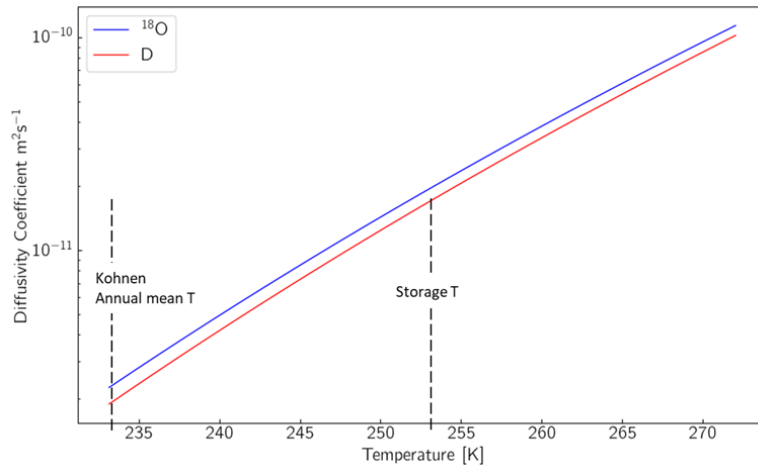


Figure D2: Diffusivity coefficients versus temperature, constraints as above, and displaying the annual mean temperature at Kohnen station (-43°C , Weinhart et al., 2020) and the storage temperature (-20°C).

Technical corrections:

L. 21: What does “continuous analyze” mean? → removed (Abstract rephrased)

L. 28: delete one “stable” → removed (Abstract rephrased)

L. 29: Capitalize “East Antarctic Ice Sheet” → DONE

L. 31: change “variabilities” to “variability” → DONE

L. 52: Delete “In order” → we kept this

L. 56: replace “signal, with...” with “signal, and show that...” → Rephrased to: “(...) isotope signal, and show that the percolation above the melt head is the major contributor.”

Fig. 1: What does “PP” stand for? → Peristaltic Pump, explanation has been added to the figure caption

L. 80: melting → renamed to “Melting unit adapted for snow cores”

L. 143: Refer here to Fig. 5 → DONE

L. 183: replace “optimal” with “minimal” → DONE

Fig. 3 and other Figures: Please add panel labels to all plots and refer to them in the captions

- Figure 1 - no panels
- Figure 2 - panels are labeled with a,b, c
- Figure 3 - only 2 subpanels left, referred to as “left” and “right” panel
- Figure 4 - (previous figure 5) - figure caption is changed to refer to the “upper” and “lower” panel

- Figure 5 (previous figure 6) - figure captions is modified such, that it refers to “upper” and “lower” panel
- Figure 6 (previous figure 7) - no panels

Table 1: Please add uncertainties of these in-house standards. → DONE, see table1

Table 2 caption: Change “means mixing length” to “mean mixing lengths”, add number of measurements → figure caption changed, number of measurements is given in table C1

L. 294: delete “the” from “the both” → DONE

L. 334: replace “Niels-Bohr Institute” with “PICE” to stay consistent → deleted “Niels-Bohr Institute

Fig A1: Please refer to this detailed schematic in the caption of Fig 1 in main text. → DONE