## Answers to Reviewer2

This manuscript focuses on the continuous measurements of water isotopes in firn using a continuous flow analytical (CFA) set-up and uses this set-up, combined with disctrete analyses, to address the effect of diffusion of water isotopes during storage. The study presents some new measurements from 1 m sections (2.4 to 3.4 m) on 6 firn cores. Because CFA is affected to some mixing due to percolation, analyses of discrete samples performed in 2015 and 2019 over the same sections are also used to infer the effect of diffusion over 4 years. The authors deduce a diffusion length of 45 mm for storage diffusion during 4 years.

The manuscript is short, useful and in general well written. I suggest to accept it but I would like to suggest a few points of the study which should be explained in more details before acceptation.

# We thank the reviewer for the helpful comments.

• It was not clear to me what was new in the set-up presented here compared to the previous one in addition to the change of the melting head. It could be better explained.

# 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 <u>melting unit of our</u> CFA-system developed a (...)"
- In 2.1. we rephrased the sentence to: "The system to analyze 1-meter snow-cores consists of a melting unit <u>adapted to the snow cores geometry</u>, a degassing unit, a (...)"
- We changed the title of the paragraph to: "Melting unit <u>adapted for snow cores</u>"
- Is there any comparison between the performances of the old and the new melt-head for firn analysis and how could the improvement be quantified?

<u>Answer to the reviewer</u>: Usually the melt heads for firn and ice are designed to follow the geometry of the ice sample, i.e. for most ice core projects a square of  $3.4 \times 3.4$  cm, which is cut from the ice core sample prior to the measurement campaign. The melt head used here (and in Kjaer et al...) has a different geometry - as the snow cannot be subsampled, the full core is melted. The melt head has the geometry of a 10cm diameter snow core. Therefore, a comparison of the performance of the two meld heads with respect to snow is difficult.

Suggested change in the text: None

• Why was only the section between 2.4 and 3.4 m studied ? Why not studying the effect of diffusion during storage at different densities (e.g. a section of very low density on the section covering 1 m at the very top of the firn, a section of 1 m at 3 m depth, a section of 1 m at 10 m depth and a section of 1 m near the close-off) ?

#### Answer to the reviewer:

Indeed, investigating the storage effect on samples with different density would be helpful. However, the storage effect was not the purpose of this study, but rather a side observation. We chose this depth interval for convenience.

### Changes in the text:

We moved the paragraph to the discussion and rephrase it to:

#### 4.4 Diffusion of the isotope signal during storage of snow cores

From comparing the CFA data with discrete measurements (Fig. 5), we observed a significant difference between the stable water isotopic profiles of the same snow cores sampled at different times.

This difference is not related to instrumental induced mixing, but instead indicates the effect of long-term storage of snow samples. We assume that diffusion, known to occur in snow and firn (Gkinis et al., 2014) also occurs in the cold storage environment. Using our results, we can now quantity this storage-induced diffusion. Assuming that the mixing of the discrete-15 dataset corresponds to the mixing of the discrete-19 dataset convolved with an independent smoothing filter induced by the storage, comes: [TL1] [RD2] (Equation 8)

Using the calculated mean mixing lengths  $\sigma_{CFA-discrete19} = 30$  mm and  $\sigma_{CFA-discrete15} = 54$  mm (Table 3), we estimate a diffusion length of approximately 45 mm. These findings indicate that during the 4 years of storage (from the first analysis in 2015 to the second analysis in 2019), the isotope signal in the snow cores was smoothed by this diffusion length.

Additionally, we computed for each 1-meter long snow core the mean and variability (standard deviation) of the both discrete datasets (Table 5). The decrease in amplitude indicates an average attenuation of 0.54 ‰ and 4.5 ‰ for  $\delta^{18}$ O and  $\delta$ D, respectively. The mean values show on average an enrichment of isotopic composition of +0.31 ‰ for  $\delta^{18}$ O and +1.6 ‰ for  $\delta$ D, likely due to the repeated contact with laboratory-air when bags are opened, and the loss of sample (frost) in the bag.

	$\delta^{_{18}}O$	$\delta^{_{18}}O$	δD	δD
	Discrete-15	Discrete-19	Discrete-15	Discrete-19
KF13	-45.29 (1.3)	-45.076 (0.85)	-356.31 (11.93)	-355.77 (8.05)
KF14	-45.14 (1.45)	-44.71 (0.85)	-354.85 (12.24)	-353.12 (7.69)
KF15	-46.38 (2.39)	-45.91 (2.05)	-364.36 (19.53)	-361.51 (16.75)
KF16	-44.95 (1.70)	-44.76 (1.16)	-353.87 (14.72)	-353.30 (10.23)

**Table 5:**  $\delta^{18}$ O,  $\delta$ D means (standard deviation) for each snow core discrete dataset, expressed in ‰.

We show the effect of storage on diffusion lengths for both isotopologues (Fig. D1 Appendix D) based on firn-diffusion model (Gkinis et al., 2014). The model run, assuming a "storage" temperature of -20°C, a density of 370 kg.m-3, an accumulation rate of 75 mm w.e. yr-1 (even though there is no accumulation during storage). For a time window of 4 years, we found a diffusion length for  $\delta D$  similar to our observations (Fig. D1). As the diffusivity coefficients are positively correlated to temperature, the diffusion during storage is likely of stronger magnitude than on the East-Antarctic plateau (Fig. D2, Appendix D). 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 firn and ice core samples from greater depths, where the density is higher.

• Is it possible to make some recommendations from this study on the storage conditions ? For example, depending on the accumulation rate at each site, the diffusion may affect the recording of the seasonal signal. Is it possible to say that below a certain accumulation rate, the seasonal signal is no more visible after « a certain number » (to be precised) of years of storage at -20°C ?

# Answer to the reviewer:

We expect the diffusion during storage to be strongest in snow cores, but likely not critical for high-density firn and ice cores. However, further investigation is needed. Note, that at low accumulation rates, a "seasonal" signal is generally not visible in stable water isotopes due to diffusion - see Laepple et al. 2018: Laepple, T., Münch, T., Casado, M., Hoerhold, M., Landais, A., and Kipfstuhl, S.: On the similarity and apparent cycles of isotopic variations in East Antarctic snow pits, The Cryosphere, 12, 169–187, https://doi.org/10.5194/tc-12-169-2018, 2018.

Then, I have some minor remarks :

- 1. 34-37 : can you precise at which timescales the ice cores of the East Antarctic plateau are dominated by noise ? As such, without any quantitative indication, these sentences are not very useful.

#### Answer to the reviewer:

There a different time scales involved, depending on the processes generating noise, We refer to the study by Casado et al. 2020: Casado, M., Münch, T., and Laepple, T.: Climatic information archived in ice cores: impact of intermittency and diffusion on the recorded isotopic signal in Antarctica, Clim. Past, 16, 1581–1598, https://doi.org/10.5194/cp-16-1581-2020, 2020.

As for this study only short time scales are relevant; we restrict the introduction to stratigraphic noise, as done in line 34ff.

- Figure 4 : to see the (small) deviations of each data point from the regression line, it could be nice to show on top of each figure the difference in d18O for each standards between the real value and the value calculated from the measured value and the regression line.

#### Answer to the reviewer:

The figure displays the calibration line, i.e. the x-axis shows the measured value, the y-axis the defined one. The off-set between the measured and defined value (prior to calibration) can be visually taken from the figure.

# Changes in the text:

- We now add the 1:1 line (which is similar to "calibrated" measured value), displaying the off-set BEFORE calibration.
- According to a comment by the other reviewer, we move this figure to the appendix.
- We apply the regression to each raw measurement and compare the calibrated value with the defined value. The results are displayed in table B1 in Appendix B:

	Value after calibration		Difference with defined value	
	$\delta^{_{18}}\mathrm{O}$	δD	$\delta^{_{18}}\mathrm{O}$	δD
NZE	-19.804	-152.422	-0.045	-0.278
TD1	-33.935	-266.732	0.084	0.532
JASE	-50.181	-392.247	-0.039	-0.252

Table B1: Deviations between calibrated and defined values. All values are expressed in ‰.

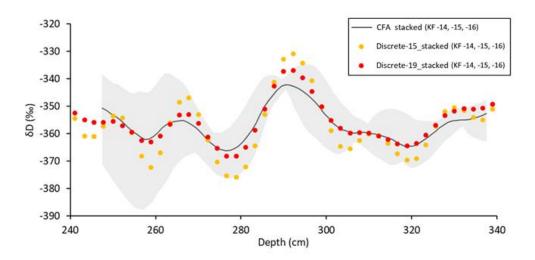
- Figure 6 : Is it possible to display an envelop showing the spread of the CFA profiles in addition to the stack ?

Answer to the reviewer:

Very good idea, It pictures the spread of the CFA profiles, which in fact displays the spatial variability.

Changes in the text:

We modified the figure accordingly



Lower panel: Mean datasets of the stacked CFA (black) and discrete (dotted) profiles of the snow cores KF-14, -15, -16. The gray shaded area displays the spread of the three CFA profiles.

- In general, I was wondering why you chose a value of 22 mm for the discrete sampling. It is probably not very convenient for the sampling of 1 m core section. Why not 20 mm ? What additionnal information (if any) could we learn with a higher resolution discrete sampling ?

### Answer to the reviewer:

In fact, the intention was 20mm samples but including the thickness of the blade, when cuttin the samples, the net sampling resolution is 22 mm = 20 mm sample thickness + 1mm material loss from the blade at each side of the sample = 22mm. This is usually not considered, but as we compare the discrete data to the CFA we refer to the "real" resolution.

We would not learn more /gain more information with respect to stable water isotopes using a higher resolution, as the isotope profile is smoothed. Infact, a higher resolution would increase the error due to depth assignment and the mass loss through cutting.

Changes in the text: None

- 1. 319 : « Vostok » and not « Vostock »  $\rightarrow$  removed

- I did not get exactly what should be improved on l. 324. Is it possible to further explain ?

#### Changes in the text (discussion, section 4.1: Suggestion to address the percolation):

We modified the statement to: "The significant contribution of the Picarro analyzer (CRDS-line, section 3.3) could be addressed as well, and requires likely a collaboration with the manufacturer to improve the analytical unit itself (e.g. reduction of the large volume at its inlet before a pressuredrop to the 40 Torr cavity)."