

Data Paper

Kenji Kawamura, Taku Umezawa, Satoshi Sugawara, Shigeyuki Ishidoya, Kentaro Ishijima, Takuya Saito, Ikumi Oyabu, Shohei Murayama, Shinji Morimoto, Shuji Aoki and Takakiyo Nakazawa. Composition of firn air at the North Greenland Ice Core Project (NGRIP) site. *Polar Data Journal*. 2021, 5, p.89–98. <http://doi.org/10.20575/00000030>.

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1st submission

Editor Start Date: 6/22/2021

Editor Stop Date: 7/23/2021

Reviewer #1 (6/23/2021–7/17/2021)

Reviewer #2 (6/23/2021–7/22/2021)

Editor comments to the Author:

Based on these reports, and my own assessment as Editor, I am pleased to inform you that it is potentially acceptable for publication in *Polar Data Journal*, once you have carried out minor revisions suggested by the reviewers.

Reviewer #1: Anonymous

The authors present well-organized data set with adequate explanations. I have only a few minor comments.

Section 1, third paragraph, L8-9.

To be consistent with other compounds' name, it would be better to write "1,1,1-trichloroethane" instead of "methyl chloroform".

Section 5, fifth paragraph and the data sheet "Nitrous oxide and its isotope ratios of firm air at the North Greenland Ice Core Project site".

Since only a few studies (including the one reported by Ishijima *et al.* 2007) reported d<sub>18</sub>O\_N<sub>2</sub>O with respect to atmospheric O<sub>2</sub>, I believe it would be more convenient for readers if the authors provide the data with respect to VSMOW. Also, the equation in the footnote of the spread sheet for converting airO<sub>2</sub>/VSMOW scale is not precise. It should be as follows if the authors refer to d<sub>18</sub>O(airO<sub>2</sub>/VSMOW) reported by Kroopnick and Craig (1972).  
$$\text{d}^{18}\text{O}(\text{Sample/VSMOW}) = 1.0235 * \text{d}^{18}\text{O}(\text{Sample/airO}_2) + 23.5 \text{ (not 23)}$$
 where d<sub>18</sub>O(A/B) means delta values of A with respect to B.

## Section 8 Figures.

The section number should be "6".

Data sheet "Composition of firn air at the North Greenland Ice Corfe Project site", footnote.

1. "Temporal drift was observed by -0.07 permil ..."   
Awkward and insufficient sentence. "Temporal drift of -0.07 permil was observed for d13C\_CO2 ... "?
2. Correct the typo of "N2O interfearence".
3. It would be better to explain more what the "temporal drift" means. I cannot fully understand this because d13C value is always determined by comparison measurements between sample and reference. Was the drift caused by change in d13C value of either sample or reference?

## Reviewer #2: Hideki Nara

This paper provides a valuable dataset from the analysis of firn gases collected at the North Greenland Ice Core Project site. The authors present depth profiles of dry mole fractions and stable isotope ratios for a number of trace gases measured using their measurement systems. These systems are well established as well as their calibration scales, which can be referenced to those from other laboratories such as inter-comparison campaigns. Overall, this paper is well written and presents analytical details enough to allow evaluation of the data quality. I recommend this paper for publication in Polar Data Journal. I have only a few minor comments, listed below.

## Section 3. Methods

1. Please describe the instrumental detail for NDIR (e.g., manufacturer, model)
2. No reference is given for the measurement of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub>. Please cite any reference describing their measurement methods in detail here.
3. I would suggest to add that the firn air samples collected in the stainless-steel canisters were analyzed for all gases reported in this study whereas the glass flask samples were analyzed only for d<sup>15</sup>N and d<sup>18</sup>O measurements.

## Section 5. Technical validation

1. What's these values in the parenthesis following the estimated reproducibilities for d<sup>15</sup>N and d<sup>18</sup>O?
2. In the sentence "dried atmospheric air collected at Tohoku University", please use "TU" instead of "Tohoku University".
3. For the halocarbons, dry mole fractions were determined on the NIES-08 scale. If there are any published results from inter-comparison campaigns, please refer here for data validation.

4. The analytical reproducibilities were given as less than 1% for the CFCs and about 3% for CH<sub>3</sub>CCl<sub>3</sub>. These values are expressed as relative standard deviation?
  5. For the analysis of the halocarbons, what was the sample stability in the stainless-steel canister especially for CH<sub>3</sub>CCl<sub>3</sub> during storage after sampling whereas I know the high stabilities for inert and long-lived gases.
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Authors Response:

Dear Editor,

Thank you very much for careful evaluation of our manuscript. We also thank the two reviewers for providing comments to improve our manuscript. Please find our revised manuscript attached. Our responses to comments from reviewers are detailed below. Please note that comments from reviewers and our responses are in different styles.

We also note that the present dataset, which is currently open on the Arctic Data archive System (ADS), should be corrected according to the revised manuscript. We will contact to ADS for the revision.

Response to Reviewer #1;

The authors present well-organized data set with adequate explanations. I have only a few minor comments.

We thank the reviewer for positive evaluation and helpful comments.

Section 1, third paragraph, L8-9.

To be consistent with other compounds' name, it would be better to write "1,1,1-trichloroethane" instead of "methyl chloroform".

According to the suggestion for consistency, IUPAC and common names as well as chemical formula have been given for the halocarbons.

Section 5, fifth paragraph and the data sheet "Nitrous oxide and its isotope ratios of firm air at the North Greenland Ice Core Project site".

Since only a few studies (including the one reported by Ishijima *et al.* 2007) reported d<sub>18</sub>O\_N<sub>2</sub>O with respect to atmospheric O<sub>2</sub>, I believe it would be more convenient for readers if the authors provide the data with respect to VSMOW. Also, the equation in the footnote of the spread sheet for converting airO<sub>2</sub>/VSMOW scale is not precise. It should be as follows if the authors refer to d<sub>18</sub>O(airO<sub>2</sub>/VSMOW) reported by Kroopnick and Craig (1972).  
$$\text{d}_{18}\text{O}(\text{Sample/VSMOW}) = 1.0235 * \text{d}_{18}\text{O}(\text{Sample/airO}_2) + 23.5 \text{ (not 23)}$$
 where d<sub>18</sub>O(A/B) means delta values of A with respect to B.

We thank the reviewer for this suggestion. Considering that the VSMOW scale is more commonly used for δ<sub>18</sub>O

measurements of N<sub>2</sub>O than in the past years, we have corrected the  $\delta$  18O-N<sub>2</sub>O values in the datasheet to the VSMOW scale. Corresponding descriptions in the text and data in the figure have been also modified. We note that the standard of  $\delta$ 18O-N<sub>2</sub>O used by Ishijima *et al.* (2007) was calibrated on the VSMOW scale by National Institute of Advanced Industrial Science and Technology, after which the measured values were converted to the AirO<sub>2</sub> scale. It is therefore more straightforward to report the  $\delta$ 18O-N<sub>2</sub>O data on the VSMOW scale.

For the scale conversion, Ishijima *et al.* (2007) employed the formula defined by Kim and Craig (1990), which had been commonly used in the research community of N<sub>2</sub>O isotopes at that time. We have added descriptions about a conversion equation from the VSMOW to AirO<sub>2</sub> scale and its reference (Kim and Craig 1990) in the data sheet so that readers can consistently compare the values in this study and Ishijima *et al.* (2007).

## Section 8 Figures.

The section number should be "6".

This has been corrected.

Data sheet "Composition of firn air at the North Greenland Ice Corfe Project site", footnote.

1. "Temporal drift was observed by -0.07 permil ..."

Awkward and insufficient sentence. "Temporal drift of -0.07 pemil was observed for d13C\_CO2 ... "?

According to the suggestion, the sentence has been corrected as follows:

"CO<sub>2</sub> extraction for  $\delta$ 13C was done in 2002, 2005 and 2007. Temporal drift of -0.07 per mil was observed for  $\delta$ 13C of CO<sub>2</sub> during the period 2002–2005, probably due to sample deterioration in the metal flasks. There was no appreciable difference between 2005 and 2007 values. All 2005 and 2007 values are therefore shifted by +0.07 per mil.  $\delta$ 13C data are corrected for N<sub>2</sub>O interference."

2. Correct the typo of "N<sub>2</sub>O interfearence".

This has been corrected.

3. It would be better to explain more what the "temporal drift" means. I cannot fully understand this because d13C value is always determined by comparison measurements between sample and reference. Was the drift caused by change in d13C value of either sample or reference?

We have added the following clause in the corresponding sentence:

"probably due to sample deterioration in the metal flasks"

Reponse to Reviewer #2;

This paper provides a valuable dataset from the analysis of firn gases collected at the North Greenland Ice Core Project

site. The authors present depth profiles of dry mole fractions and stable isotope ratios for a number of trace gases measured using their measurement systems. These systems are well established as well as their calibration scales, which can be referenced to those from other laboratories such as inter-comparison campaigns. Overall, this paper is well written and presents analytical details enough to allow evaluation of the data quality. I recommend this paper for publication in Polar Data Journal.

I have only a few minor comments, listed below.

We thank the reviewer for positive evaluation and helpful comments.

### Section 3. Methods

1. Please describe the instrumental detail for NDIR (e.g., manufacturer, model)

The model and manufacturer names (VIA-500R, HORIBA Ltd.) have been added.

2. No reference is given for the measurement of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub>. Please cite any reference describing their measurement methods in detail here.

Corresponding reference papers have been added in the revised manuscript.

3. I would suggest to add that the firn air samples collected in the stainless-steel canisters were analyzed for all gases reported in this study whereas the glass flask samples were analyzed only for δ<sup>15</sup>N and δ<sup>18</sup>O measurements.

The following sentence has been added in the first paragraph of section 3:

"The glass flask samples were analyzed only for δ<sup>15</sup>N of N<sub>2</sub>, δ<sup>18</sup>O of O<sub>2</sub> and δ(O<sub>2</sub>/N<sub>2</sub>)."

### Section 5. Technical validation

1. What's these values in the parenthesis following the estimated reproducibilities for δ<sup>15</sup>N and δ<sup>18</sup>O?

They are the analytical reproducibilities of δ<sup>15</sup>N-N<sub>2</sub> and δ<sup>18</sup>O-O<sub>2</sub> on Finnigan MAT 252. We hope to keep this sentence as is.

2. In the sentence "dried atmospheric air collected at Tohoku University", please use "TU" instead of "Tohoku University".

This has been corrected.

3. For the halocarbons, dry mole fractions were determined on the NIES-08 scale. If there are any published results from inter-comparison campaigns, please refer here for data validation.

The following sentence has been added:

"The result of intercomparisons of CFC-11 with the other international scales have been described elsewhere (Rigby *et al.* 2019)."

Rigby *et al.* Increase in CFC-11 emissions from eastern China based on atmospheric observations. 2019, Nature, 569, 546–550, <https://doi.org/10.1038/s41586-019-1193-4>.

4. The analytical reproducibilities were given as less than 1% for the CFCs and about 3% for CH<sub>3</sub>CCl<sub>3</sub>. These values are expressed as relative standard deviation?

Yes, they are. The term “relative standard deviations” has been added in the sentence.

5. For the analysis of the halocarbons, what was the sample stability in the stainless-steel canister especially for CH<sub>3</sub>CCl<sub>3</sub> during storage after sampling whereas I know the high stabilities for inert and long-lived gases.

There have been no experiments that can ensure stability of halocarbons in the sample canisters during storage. However, in a separate manuscript in preparation, we show that, using a firn air transport model, the depth profiles of the halocarbons shown in this study are consistent with past atmospheric histories of the individual compounds.

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2nd submission

Editor Start Date: 8/2/2021

Editor Stop Date: 8/4/2021

Reviewer #1 (8/3/2021–8/4/2021)

Editor Comments to the Author:

Based on reviewer's report, and my own assessment, I am pleased to inform you that it is acceptable for publication in PDJ. The title of chapter 2 is the same as shown in template ("location (or Observation)"), but I think it's better to revise it (e.g., "location" or "location and firn sample" etc.).

Reviewer #1: Anonymous

Now the manuscript has been improved well, and I think it should be published in its present form after the relevant revision of spread sheets.

Editorial Office's note

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