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Composition of firn air at the North Greenland Ice Core Project (NGRIP) site

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Abstract: Reconstructions of the past variations of atmospheric composition are important for better understanding of the changes in climate and atmospheric chemistry. The data from direct atmospheric observations of various trace gas mole fractions and isotope ratios have become available over the last few decades. The analyses of air bubbles in polar ice cores have provided those from the pre-industrial era to the mid-20th century. Old air is also found in porous snow layers (firn) on top of polar ice sheets, because the gas movements in firn occur mainly by molecular diffusion. Depth profiles of firn air components are therefore useful for bridging the records from direct observations and ice-core analyses (covering up to about a century). The firn air data are also helpful for constraining firn air transport models toward better understanding of snow densification and interpretation of ice core data. Here we present the depth profiles of air composition in the firn at the North Greenland Ice Core

Project (NGRIP) site. Various gas components, including atmospheric O_2/N_2 ratio, greenhouse gases, halocarbons and their isotope ratios, were measured from air samples collected from the NGRIP firn by using combination of high-precision measurement systems. The data are presented in a spreadsheet format (.xlsx).

1. Background & Summary

Atmospheric composition provides important information on climate and atmospheric chemistry, and thus extensive measurements of various air components have been made worldwide over the last decades. Air extracted from polar ice cores has been analyzed to reconstruct the past history of atmospheric composition. Firn is a compacted but porous snow layer above ice sheets, which also preserves atmospheric composition from the present to about a century back in time[1]. Measurements of firn air samples are therefore useful to fill the data gap between the direct atmospheric measurements and ice core analyses.

Studying firn air is also important for better interpretation of ice core records. Air found in ice core is younger than the enclosing ice matrix, since the air was trapped at the bottom of the firn. To estimate difference between the ice and gas ages, information on past properties of the firn layer is necessary. Furthermore, during the air movement in the firn, its composition is affected by diffusive transport and bubble close-off processes. These processes alter the original composition of the atmosphere. Therefore, firn air transport models, in which the aforementioned processes are taken into account, have been examined to reconstruct the past variations of trace gas mole fractions and isotope ratios[2].

Here we present depth profiles of composition of firn air at the Greenland site NGRIP (North Greenland Ice Core Project) collected in 2001: stable isotope ratios of the major atmospheric components δ^{15}N of N_2 and δ^{18}O of O_2, atmospheric O_2/N_2 ratio $\delta(O_2/N_2)$, carbon dioxide (CO_2) mole fraction and its stable carbon isotope ratio δ^{13}C of CO_2, methane (CH_4) mole fraction and its stable carbon and hydrogen isotope ratios δ^{13}C and δD of CH_4, nitrous oxide (N_2O) mole fraction and its stable nitrogen and oxygen isotope ratios δ^{15}N and δ^{18}O of N_2O, and mole fractions of various trace gases i.e. sulfur hexafluoride (SF_6), CFC-11 (trichlorofluoromethane, CCl_3F), CFC-12 (dichlorodifluoromethane, CCl_2F_2), CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane, $C_2Cl_3F_3$) and methyl chloroform (1,1,1-trichloroethane, CH_3CCl_3). Besides NGRIP, firn air samples were collected at the summit of the Greenland ice sheet in 1989, and the mean CO_2 age of air at the bottom of the firn was estimated to be 12 years[1]. Another set of firn air samples was collected at the NEEM (North Greenland Eemian Ice Drilling) site, Northern Greenland, in 2008, and the mean CO_2 age at bottom of the firn was estimated to be about 70 years[3]. Compared to these firn air sample datasets reported previously, the mean CO_2 age at the bottom of the NGRIP firn is estimated to be about 60 years. Therefore, the present dataset provides an opportunity for reconstructing various trace gas histories over the past period as old as or older than that covered by NEEM, when the dataset is appropriately combined with firn air transport modeling[4].

2. Location

Firn air was sampled at the Greenland site NGRIP (75°10′N, 42°32′W, 2959 m above sea level, Figure 1) in May–June 2001. Accumulation rate, surface density, mean temperature and pressure are 179 kg m^{-2} yr^{-1}, 300 kg m^{-3}, 241 K and 680 hPa, respectively. Other physical characteristics of the firn have been described previously[4,5]. At the NGRIP site, two shallow holes (EU and Japanese holes) were drilled in 2001[5,6], and the present dataset is from the firn air samples collected from the Japanese hole.

3. Methods

Details of our firn air sampling have been described previously[4,5]. Briefly, it is similar to that developed by Schawander *et al*. (1993)[1]; it consisted of a bladder, two plastic tubes, an air compressor system and a sample flask (metal or glass). The bladder was made of a natural rubber tube with stainless steel flanges at both ends, which was used to seal a borehole in the firn. The bladder was inflated by sending surface air by the compressor through one of the tubes, and firn air at the bottom of the borehole was withdrawn through the other tube that passed through the bladder. The metal sample flasks were made of stainless steel with metal bellows valves at both ends, and the volume was ~1500 mL. The glass flasks had the volume of ~500 mL with valves with Viton O-rings and aluminum shafts at both ends. The sampling procedures are as follows. After drilling to a sampling depth, the bladder was inserted into the bottom of the borehole and inflated. Then the firn air was withdrawn and pressurized into the metal sample flask to ~1.0 MPa above the ambient pressure or filled into the glass sample flask at the ambient pressure. The glass flask samples were analyzed for $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2 and $\delta(O_2/N_2)$. The total number of air-sampling depths was 24.

Stable isotope ratios of N_2 and O_2 ($\delta^{15}N$-N_2 and $\delta^{18}O$-O_2) were determined against our reference air (cylinder No. NSX41-11; commercially available purified air containing N_2, O_2 and Ar) using two isotope ratio mass spectrometers (IRMS) (Finnigan MAT DELTA S and Finnigan MAT 252)[5,7]. $\delta(O_2/N_2)$ was determined against our reference air (cylinder No. PLM37172; dried natural air) using an IRMS (Finnigan MAT 252)[7].

CO_2, CH_4, N_2O and SF_6 mole fractions were measured at Tohoku University (TU). CO_2 mole fractions were measured by using a nondispersive infrared gas analyzer (NDIR; VIA-500R, HORIBA Ltd.)[8,9,10], CH_4 by using a gas chromatograph (Agilent 6890, Agilent Technologies Inc.) equipped with a flame ionization detector (GC-FID)[11], N_2O and SF_6 by using a GC equipped with an electron capture detector (GC-ECD)[4,10].

Stable carbon isotope ratio of CO_2 ($\delta^{13}C$-CO_2) was analyzed at TU. CO_2 in the sample air was separated and collected cryogenically in a glass ampoule, and was measured on an IRMS (Finnigan MAT DELTA S)[8,9,12].

Stable carbon and hydrogen isotope ratios of CH_4 ($\delta^{13}C$-CH_4 and δD-CH_4) were also analyzed at TU. CH_4 in the sample air was preconcentrated, gas-chromatographically separated from the remaining interfering gases, combusted for $\delta^{13}C$-CH_4 or pyrolyzed for δD-CH_4, and measured on an IRMS (ThermoFinnigan DELTA plus XP)[13].

Stable nitrogen and oxygen isotope ratios of N_2O ($\delta^{15}N$-N_2O and $\delta^{18}O$-N_2O) were analyzed at National Institute of Advanced Industrial Science and Technology. A mixture of N_2O and CO_2 was cryogenically extracted from the sample air and encapsulated in a Pyrex glass tube. The mixture was further processed for CO_2/H_2O removal and gas-chromatographic separation from the remaining interfering gases and subsequently measured on an IRMS (Finnigan MAT 252)[4].

Mole fractions of selected halocarbons (CFC-11, CFC-12, CFC-113 and CH_3CCl_3) were analyzed by using the Vacuum Preconcentration and Refocusing-Gas Chromatography/Mass Spectrometry (VPR-GC/MS) system (Agilent 6890/5973, Agilent Technologies Inc.), which was developed based on the work by Saito *et al*. (2006)[14]. An aliquot of the sample was transferred into an evacuated canister of ~0.3 L at around ambient pressure (~100 kPa) and the inner pressure of the canister was recorded. The air in the canister was extracted by a vacuum pump through a preconcentration trap filled with HayeSep D cooled at –135° C by using a free piston Stirling cooler. The preconcentration trap was heated to –70°C to release major atmospheric constituents and then up to 100°C to transfer the trapped compounds to a cryofocusing trap containing Carboxene 1000/Tenax TA at –100°C. Then the trap was heated to 180°C to inject the trapped gases onto a PoraBOND Q separation column for subsequent analysis on MS.

4. Data Records

Depth profiles of atmospheric trace gas composition in the NGRIP firn are presented in Figure 2. Flask number, depth, atmospheric trace gas composition and standard deviations of multiple measurements (or difference when the duplicate measurements were made) are provided in a spreadsheet format (.xlsx).

5. Technical Validation

The analytical reproducibilities of $\delta^{15}N$-N_2 and $\delta^{18}O$-O_2 were estimated to be 0.015 and 0.035 ‰ (0.012 and 0.026 ‰), respectively, for the measurements on Finnigan MAT delta S (Finnigan MAT 252), and that of $\delta(O_2/N_2)$ was estimated to be 0.005 ‰. The above estimates are made based on replicated analyses of standard gases from high-pressure cylinders or atmospheric air samples.

The measurement reproducibilities were estimated to be 0.02 ppm for CO_2, 2 ppb for CH_4, 0.3 ppb for N_2O and 0.09 ppt for SF_6. The mole fractions were determined against the TU2010-CO_2 scale[12] for CO_2, TU1987-CH_4 scale[15] for CH_4, TU1991-N_2O scale[16] for N_2O and TU2002-SF_6 scale[10] for SF_6, all of which are based on primary standard gases that are prepared gravimetrically. The results of intercomparisons with other international scales have been described elsewhere[10,17,18].

The δ^{13}C-CO_2 values are reported on the VPDB (Vienna PeeDee Belemnite) scale and the analytical reproducibility was estimated to be 0.02 ‰. The CO_2 extraction for δ^{13}C-CO_2 was done in 2002, 2005 and 2007. Temporal drift of −0.07‰ was observed for δ^{13}C-CO_2 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 were therefore shifted by +0.07‰. The δ^{13}C-CO_2 values were corrected for interference of N_2O. The calibration and correction used here follow the established procedures[2,9].

The δ^{13}C-CH_4 and δD-CH_4 values are reported on the VPDB and VSMOW (Vienna Standard Mean Ocean Water) scales, respectively, and the analytical reproducibilities were estimated to be 0.08 ‰ for δ^{13}C-CH_4 and 2.2 ‰ for δD-CH_4. Intercomparisons with other laboratories have been described elsewhere[19].

The δ^{15}N-N_2O and δ^{18}O-N_2O values were determined against standard gases calibrated with respect to the standard gases of Toyoda and Yoshida (1999)[20]. The original paper[4] reported these values against those of atmospheric N_2 and O_2, respectively, but this study presents δ^{18}O-N_2O values on the VSMOW scale as it is currently more commonly used in the research community. Note that a conversion equation by Kim and Craig (1990)[21] allow direct comparisons of δ^{18}O-N_2O values to those by Ishijima *et al.* (2007)[4]. The analytical reproducibilities were estimated to be 0.1 ‰ for δ^{15}N-N_2O and 0.2 ‰ for δ^{18}O-N_2O.

Mole fractions of halocarbons were determined against a working standard gas (compressed natural dry air) that was calibrated against the NIES-08 scale which is based on gravimetrically prepared synthetic standards (Taiyo Nippon Sanso CO. Ltd.). Repetitive measurements of a standard gas indicated that the analytical reproducibilities (relative standard deviations) were below 1% for the CFCs and about 3% for CH_3CCl_3. The result of intercomparisons of CFC-11 with other international scales have been described elsewhere[22].

The mole fractions of the trace gases were compared to data available at World Data Centre for Greenhouse Gases (WDCGG, https://gaw.kishou.go.jp). The surface data at the NGRIP site showed reasonable agreements to the data reported at the Arctic ground station Alert, Canada (82°30′N, 62°22′W) for May–June 2001, the period of the NGRIP firn samplings.

6. Figures

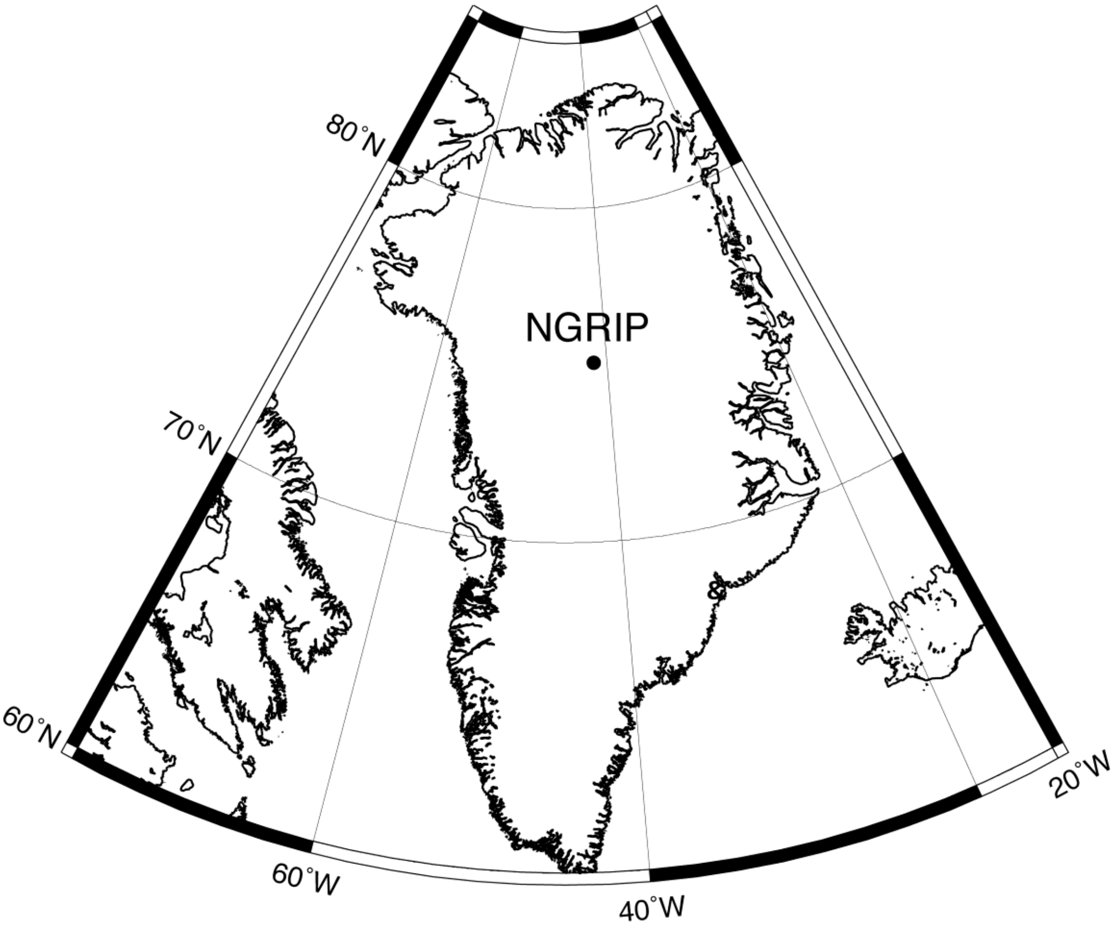

Fig. 1. Location of the NGRIP firn-air sampling in 2001.

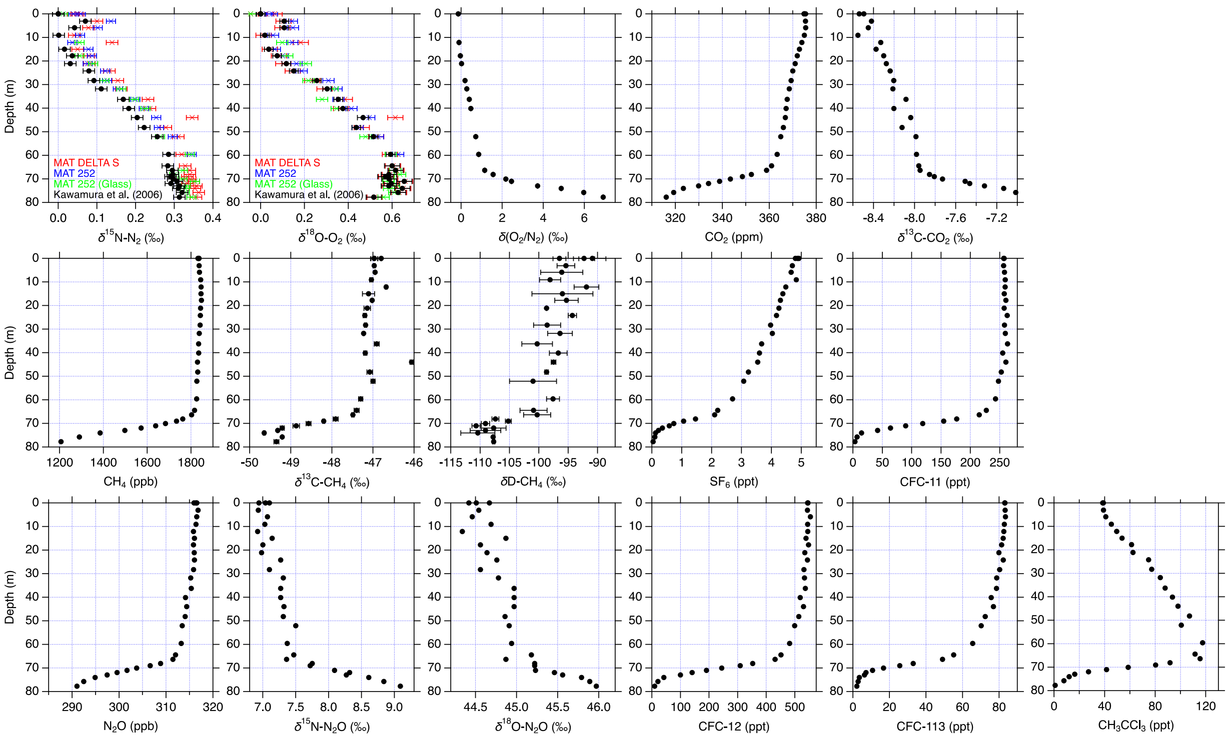

Fig. 2. Depth profiles of air composition and isotope ratios in the NGRIP firn.

Author contributions

K. Kawamura developed the sampling device with the support of S. Sugawara, and collected the firn air. T. Umezawa measured δ^{13}C-CH_4, δD-CH_4 and halocarbons, and wrote the draft. K. Ishijima and S. Sugawara measured CO_2, CH_4, N_2O, SF_6. S. Sugawara measured δ^{13}C-CO_2. S. Ishidoya measured δ^{15}N-N_2, δ^{18}O-O_2 and $\delta(O_2/N_2)$, and maintained the measurement system and calibration scales. K. Ishijima measured δ^{15}N-N_2O and δ^{18}O-N_2O. T. Saito established and maintained the measurement system and the calibration scales for halocarbons. I. Oyabu and K. Kawamura validated δ^{15}N-N_2 and δ^{18}O-O_2 data and their normalization. S. Murayama maintained the measurement system for δ^{15}N-N_2O and δ^{18}O-N_2O, and S. Morimoto improved their precisions. S. Morimoto, S. Aoki and T. Nakazawa established and maintained the measurement systems and the calibration scales at Tohoku University. All authors contributed to the manuscript.

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Data Citations

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