A High-Resolution Continuous Flow Analysis System for Polar Ice Cores

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Abstract

In recent decades, the development of continuous flow analysis (CFA) technology for ice core analysis has enabled greater sample throughput and greater depth resolution compared with the classic discrete sampling technique. We developed the first Japanese CFA system at the National Institute of Polar Research (NIPR) in Tokyo. The system allows the continuous analysis of stable water isotopes and electrical conductivity, as well as the collection of discrete samples from both inner and outer parts of the core. This CFA system was designed to have sufficiently high temporal resolution to detect signals of abrupt climate change in deep polar ice cores. To test its performance, we used the system to analyze different climate intervals in ice drilled at the NEEM (North Greenland Eemian Ice Drilling) site, Greenland. The quality of our continuous measurement of stable water isotopes has been confirmed through a comparison with different datasets. Moreover, our system presents a better measurement efficiency to resolve the signal of electrical conductivity in the ice core sample than that obtained with a similar system developed by the University of Bern, Switzerland, during a field campaign at NEEM camp.

Key words: Ice cores, continuous flow analysis, high resolution

1. Introduction

Understanding of global climate change has been revolutionized in recent decades by data obtained from ice cores (EPICA Community Members, 2004, 2006; Kawamura et al., 2007; NEEM Community Members, 2013; NGRIP Project Members, 2004). Deep polar drilling projects in Greenland and Antarctica provide valuable information about past climate conditions on timescales of up to 800 kyr (EPICA Community Members, 2004). During the last two decades, continuous flow analysis (CFA) techniques have improved the temporal resolution of ice core measurements and reduced the time required for analyses (Bigler et al., 2011; Kaufmann et al., 2008; McConnell et al., 2002; Osterberg et al., 2006; Röthlisberger et al., 2000). The 3035 m-long ice core drilled at Dome Fuji, East Antarctica (77°19′01″S, 39°42′12″E, 3810 m elevation) provides a climate archive dating back to ~720 kyr (Motoyama, 2007). However, until now the core has been analyzed using discrete samples that have to be cut, decontaminated, and melted manually, and the slow pace of this process means that only part of the core has been examined. Thus, there is a pressing need to develop a CFA system at the National Institute of Polar Research (NIPR) to provide the scientific community with the first high-resolution data from the Dome Fuji core.

Several types of CFA system have been developed that consist of a melting unit and an analytical unit (Bigler et al., 2011; Breton et al., 2012; Kaufmann et al., 2008; McConnell et al., 2002; Osterberg et al., 2006; Röthlisberger et al., 2000). In a typical melting unit, a longitudinalsubsection of the core remains frozen while the end is melted continuously on a chemically inert melt head. This approach provides uncontaminated samples from the core interior. Analytical units connected to this melting unit are located in a laboratory kept at room temperature. Therefore, although an inherent mixing of
the sample stream along the system limits its depth resolution, the CFA technique allows for fast, accurate, and reliable analyses of the entire ice core (Bigler et al., 2011; Kaufmann et al., 2008; Osterberg et al., 2006).

Here, we describe the structure of the new NIPR CFA system, which allows continuous measurements of stable water isotopes (Gkinis et al., 2010; 2011) and electrical conductivity, as well as collection of discrete samples (Osterberg et al., 2006) from both the inner and outer core at variable depth resolutions. Using a novel approach to regulate the degassing unit in order to minimize the mixing volume, we optimize the smoothing of the continuous sample stream. We evaluate the system using standard solutions and then apply the system to samples cut from a deep ice core drilled at the NEEM (North Greenland Eemian Ice Drilling) site, Greenland.

2. Material and method

Figure 1 shows the setup of the NIPR CFA system, which consists of a melting unit, a degassing unit, a water isotope measurement unit, an electrical conductivity ($\sigma$) data synchronization system, and fraction collector modules. The control, data acquisition, and processing components are not included in the schematic diagram. Upstream of the degassing unit, the stream is driven by a peristaltic pump (Minipuls3, Gilson, France) through a short length of perfluoroalkoxy (PFA) tubing with 1/16” outer diameter (OD) and 0.02” inner diameter (ID). Beyond the degassing unit, part of the bubble-free water stream is discarded, while the remainder is split in a polyether ether ketone (PEEK) manifold (P-150, Upchurch scientific, USA) and sent to the different analytical units. We employ a second peristaltic pump (Minipuls3, Gilson, France) through a PFA tube (OD 1/8” and ID 1/16”) to drain the outer-core stream from the melt head. This channel is not analyzed online but connected to a fraction collector for further analyses of species less prone to contamination.

2.1 Melting unit

A photographic illustration of the melting unit is presented in Fig. 2a. A sample holder 600 mm long and $34 \times 34$ mm in cross-sectional area is positioned centrally above the melt head to guide the ice sample during melting. An 850 g copper–zinc alloy weight is positioned atop the ice and applies a constant force to stabilize the melt speed. To avoid metal contamination, the weight is separated from the ice core by polypropylene end pieces. The melt head we use is a modified version of the University of Maine design (Osterberg et al., 2006) and was manufactured at the Nagaoka University of
Technology (Fig. 2b). Melt head temperature is regulated by a Proportional-Integral-Derivative (PID) temperature controller (MTCD, Misumi Corp, Japan) attached to two 250 W heating cartridges (Firerod, Watlow, USA) and a platinum resistance thermometer (Pt100). To avoid mixing samples of clean inner-core ice with potentially contaminated ice from the outer core, the melt head includes two collection areas that separate the sample into their respective drainage channels. The square-shaped inner channel has sides of 20 mm, while the circular outer channel has a radius of 33 mm. Effective separation of the two melt streams is guaranteed by a 0.5 mm-high triangle-shaped ridge located between the two collection areas. Furthermore, we apply a higher pumping rate (15.5 ml min$^{-1}$) to the outer channel to ensure that water cannot pass to the inner channel (pumping rate 6.5 ml min$^{-1}$). To generate these flow rates, we use a typical melting rate of ~1.6 cm min$^{-1}$, the speed of which is calculated by monitoring the position of the weight.

In contrast to other CFA systems, which use a wire encoder positioning sensor (e.g., Bigler et al., 2011; Breton et al., 2012; Kaufmann et al., 2008), we utilize a high-accuracy laser positioning sensor to assign the corresponding depth of our core samples. Specifically, this high-accuracy laser displacement sensor (LKG-G505, Keyence, Japan) determines the distance from the sensor to the top of the weight with a precision of 0.05 mm.

When the melting unit is not generating melt water from the inner channel of the melt head, we feed the analytical system with ultrapure water (Millipore Advantage, Milli-Q ≥ 18.2 MΩ cm$^{-1}$, hereafter MilliQ). The use of an automated six-port injection valve allows us to switch between the core sample and MilliQ at the beginning and end of each ice core analysis (V2500, Upchurch scientific, USA; 'IV' in Fig. 1).

2.2 Degassing unit

Most detection systems require a degassing unit (hereafter debubbler) to avoid the potentially severe effects of air in the sample stream. The debubbler consists of a simple polypropylene micropipette tip that is open to the atmosphere; water dripping through the pipette releases any gas to the air. However, because the exact distribution of air in the water can fluctuate, the volume of water in the debubbler is variable. Therefore, to keep the mixing in the debubbler stable we vary the amount of water that is removed from the bottom of the debubbler by inserting a variable overflow sent to the waste. This overflow is set in such a way that the mixing volume is minimized, while also maintaining a minimum safe volume to avoid air bubbles significantly interfering with detectors located downstream. The overflow line is regulated by a pump controlled by the weight of the debubbler, which is fixed to a balance (NewClassic MF MS603S, Mettler Toledo, Switzerland) connected to a

Fig 2. Melting Unit. a) The NEEM core sample melting process. b) Schematic diagram of the melt plate, which represents the top part of the melt head. The melted sample passes through the slits and central hole of the inner channel (shaded) and through the slits of the outer channel. Dimensions are given in mm.
2.3 Water isotope measurement unit

As shown in Fig. 1, the stream for water isotope analysis is driven by a peristaltic pump (Reglo Digital MS-2/12, Ismatec, Germany) through a PFA tube (0.02" ID) at a rate of 0.2 ml min\(^{-1}\), after which it passes through a 10 µm stainless steel filter and a conductivity cell (C3 in Fig. 1). The stream then enters a spectrometer for the detection of water isotopes. Specifically, δ\(D\) and δ\(^{18}\)O are measured continuously using a wavelength-scanned cavity ring down spectrometer (CRDS L2130-i, Picarro Inc., USA). To obtain the continuity and stability of vapor flow rate required for the Picarro instrument, a stream vaporization module was made based on the method of Gkinis et al. (2010) and implementing the upgrades of Maselli et al. (2013). A detailed diagram and corresponding photograph of the system are presented in Figs. 4a and 4b, respectively. We utilize a stainless steel micro-volume tee (U-428, Upchurch Scientific, USA; 'T1' in Fig. 4a) to split a micro-flow from the incoming stream for analysis. To obtain the micro-flow, we use a fused-silica capillary tube with 40 µm ID. The smaller ID (0.01") of the waste line creates a back-pressure, pushing the micro-flow through the capillary towards the oven. To control this back-pressure precisely and efficiently, we divided the waste line using a PEEK tee (T3) and added to one of the two sub-waste lines a 10-turn micrometering needle valve (P-445, Upchurch Scientific, USA). The sample micro-flow is injected into the stainless steel tee (T2, Valco ZT1M) mounted in the 180°C oven, where it vaporizes instantly and mixes with air to form a gas sample with the desired water vapor concentration. The air is dried by passing through a Drierite CaSO\(_4\) canister at a rate of 30 ml min\(^{-1}\), drawn by the CRDS pump, resulting in typical water vapor concentrations of <100 ppmv. During its transfer to the CRDS via a 6 cm-long OD 1/16" stainless steel tube, the sample flow is kept at 90°C to avoid any condensation, which could induce fractionation of the stable water isotopes.

2.4 Electrical conductivity and data synchronization system

We measure electrical conductivity (σ) using conductivity cells (conductivity meter model 1056, Amber Sciences, USA). As shown in Fig. 1, the first cell (C1) is located at the melting unit outlet, where it measures the conductivity of the air–water mixture arriving from the ice and gives a high-resolution reference conductivity...
signal. Each of our analytical systems features a conductivity cell (Ci) located as close as possible to the inlet of that particular system to obtain a conductivity signal representing that instrument. These signals allow for straightforward and efficient synchronization of the different analytical systems, as at the Desert Research Institute in Reno, USA (Maselli et al., 2013). Downstream, and closest to the debubbler, we chose C2 to give the electrical conductivity for our system.

2.5 Fraction collector modules

Both the inner and outer streams are collected for off-line discrete sample analyses using fraction collectors (FC204, Gilson, France). Samples are collected in 30 mL polypropylene vials, after which they are frozen and stored for analysis such as ion chromatography (IC). The inner-channel fraction collector is maintained in a clean air cabinet with HEPA (High Efficiency Particle Arresting) filtered air to avoid contamination from the laboratory, while the outer-channel fraction collector is kept in ambient air. As shown in Fig. 1, a peristaltic pump (Reglo Digital MS-2/12, Ismatec, Germany) maintains a flow rate in the inner-channel fraction collector of 2 ml min⁻¹. In addition to these systems, one sample line was used for the determination of dissolved reactive phosphorus. The details of this line are described in Kjær et al (2013; 2015).

2.6 Control, data acquisition, and processing system

We used LabVIEW 2010 to develop software to control the CFA system. All devices (melting unit, pumps, valves, degassing unit, and analytical systems) are connected to the controlling computer by Ethernet connections (Picarro L2130-i), serial connections (NI USB-232/4, National Instruments, USA), or analog/digital connections via multifunction data-acquisition devices (USB-6211, USB-6212, National Instruments, USA). The drivers are either provided by manufacturers (e.g., Ismatec Reglo pump) or developed to suit the purpose (e.g., Keyence laser, Gilson pumps, Mettler-Toledo balance, actuated valves, conductivity meters, CRDS, and fraction collectors). The data were acquired every 1 s by the software. To better understand the data generated, we record all technical signals and melting events such
as flooding at the melt head, cracks in the ice, and opening of the freezer door.

To process and analyze the data, we developed a second piece of software also using LabVIEW 2010. This data-processing software uses high-accuracy positioning, either by reporting all positions or applying a linear fit, to convert acquisition time to local depth. It also allows for rapid and efficient data synchronization using signals from the different conductivity cells (Maselli et al., 2013). Melting events are displayed for the reader to easily identify and remove potentially contaminated data.

### 2.7 Ice core sample

To evaluate the performance of the NIPR CFA system, we measured subsections of the NEEM ice core (NEEM Community Members, 2013) in November 2013. The sample corresponds to the last glacial period, including Greenland stadials and interstadials. Samples from the inner stream were collected continuously with a fraction collector at a 5 cm-resolution and analyzed for discrete phosphate by IC. The outer stream, meanwhile, was collected continuously with a fraction collector at 3 cm-resolution. We also cut and prepared discrete samples from leftover side pieces of the ice core using the same 3 cm-depth resolution. Here, we focus on the results from Greenland Stadial 8, which corresponds to the period 35.520–35.636 kyr before present (Rasmussen et al., 2013) and occurs in our core between the depths of 1723.7 and 1724.8 m. To validate the NIPR CFA system, we also present data for the same depths obtained by the CFA system of University of Bern (Kaufmann et al., 2008) and used during the 2010 NEEM field campaign.

### 3. Results and Discussion

#### 3.1 Sample positioning accuracy

Figure 5 shows the distance between two adjacent points acquired by the NIPR CFA system compared with those collected by the Bern system. The low melting speed, 1 s data acquisition rate, and high-accuracy laser positioning system enable us to position ice cores with a high degree of accuracy.

#### 3.2 Electrical conductivity

**3.2.1 Performance**

Prior to analyzing the samples, we evaluated the response time (i.e., duration required to transition from 10% above the baseline to 90% of the peak height) of the conductivity cell C2 by switching between MilliQ and three different conductivity standards at the injection valve (IV in Fig. 1). The three standards have dilutions of 5, 10, and 20 times the Amber Sciences conductivity calibration solution (74.7 µS cm\(^{-1}\)). We found the response times to be independent of both concentration and the duration of the switch. After normalizing the signals, our results from the 7.47 µS cm\(^{-1}\) standard show that the response time, going up, is 28 seconds, with a longer return (36 s) (Fig. 6). As there is a potential dispersion effect between the melt head and the valve, we assessed the total response time by injecting the same switch of streams on the melt head. We observed that the melt head adds a dispersion effect of only 2 s to the temporal resolutions (30 s and 38 s). When the ice sample is melting at 1.6 cm min\(^{-1}\), the temporal resolution for conductivity converts to a depth resolution of 0.8 cm for an increase, and 1.01 cm for a decrease. This difference reflects the asymmetric shape of the flow (Breton et al., 2012).

**3.2.2 NEEM sample measurements**

Figure 7 shows two synchronized conductivity records from the NIPR CFA system and the conductivity record determined at NEEM in 2010. For the NIPR CFA, conductivity cells C1 and C2 are located upstream and downstream of the debubbler, respectively. The comparison of these two signals reflects the efficiency and the smoothing effects of the degassing unit. The C1 signal shows the segmentation of the water stream by air bubbles, while the C2 signal demonstrates the efficiency...
of removing all air bubbles, with a slight smoothing of the conductivity signal. The NIPR CFA conductivity record is similar to that determined by the Bern CFA system at NEEM in 2010, but with more detailed variability due to the lower melt rate and the optimization of all mixing volumes. Also, our conductivity peaks exhibit higher intensities, resulting in a less smoothed signal. However, the depth resolution we calculated previously does not allow us to discern the expected 0.94 cm annual layer thickness at this depth (Rasmussen et al., 2013).

3.3 Stable isotopes of water

3.3.1 Performance

To demonstrate the stability and precision of our method, we injected MilliQ over a 24-hour period at a water level of ~21,000 ppm. This experiment yielded a standard deviation of 213 ppm for the water vapor level, and 0.105‰ and 0.310‰ for δ18O and δD, respectively. Fig. 8a depicts the dependency of δ18O and δD values on the water vapor concentration. MilliQ was injected into the cavity at 10-minute intervals at levels ranging from 3,000 to 30,000 ppm, after which we calculated the average and standard deviation for the final two minutes of each level. Our results appear to show that in a range of water vapor level between 13,000 and 24,000 ppm, δD increases linearly with water level, while the δ18O value stays within the standard deviation of the measurements. Therefore, the following water-vapor level calibration must be applied for δD at 20,000 ppm:

\[
\delta_{\text{calibrated}} = \delta_{\text{raw}} - a_{\text{slope}} \times ([H_2O]_{\text{raw}} - 20,000)
\]  

where \(\delta_{\text{calibrated}}\) is the corrected value at 20,000 ppm, \(\delta_{\text{raw}}\) the raw isotope data, \(a_{\text{slope}}\) the slope of the \(\delta_{\text{raw}}\) function of water level, and \([H_2O]_{\text{raw}}\) the water level.

To calibrate our data to the VSMOW/SLAP scale recommended by the International Atomic Energy Agency, we analyzed a set of three internal laboratory isotopic standards at the start and end of each measurement day. The isotopic ratios of these standards with respect to the VSMOW/SLAP scale were determined previously using the two reference materials VSMOW2 and SLAP2 through an inter-laboratory comparison with the Laboratoire des Sciences du Climat de l’Environnement, Saclay, France. A typical calibration dataset is shown in Fig. 8b. The three standards are injected for 10 minutes each, while the last 2 minutes of each isotopic step are averaged to determine the coefficients for linear regression, defined as follows:

\[
\delta_{\text{VSMOW}} = a_{\text{VSMOW}} \times \delta_{\text{measured}} + b_{\text{VSMOW}}
\]
3.3.2 NEEM sample measurements

We excluded from analysis the first and last 2 cm of the continuous dataset influenced by the MilliQ. In addition to the continuous measurements, we analyzed the discrete side-piece ice samples and the water samples collected on the outer line fraction collector (FC O’ in Fig. 1). The discrete outer samples were analyzed for $\delta^{18}O$ and $\delta D$ with a different CRDS (L2120-i, Picarro Inc., USA), using a similar method to that of Pol et al. (2010). The mean value of the last 4 of 20 injections per sample was used. The standard deviations of discrete water isotope measurements were 0.25‰ and 0.15‰ for $\delta D$ and $\delta^{18}O$, respectively (Fig. 9). With the exception of significant differences between discrete side-piece samples and the CFA data at the beginning of each core subsection (at depths of 1723.7, 1724.25, and 1724.4 m), the

Fig. 8. Calibration of the water isotopes measurements. a) $\delta^{18}O$ and $\delta D$ values for different water vapor concentrations, with error bars representing the standard deviation on the 2 minute averaged measurements. b) Calibration datasets.

Fig. 9. Comparison of three different isotopic datasets for Greenland Stadial 8. Top, middle, and bottom panels show the $\delta^{18}O$, $\delta D$, and deuterium excess (Excess) results, respectively. For all plots, the dashed black line, blue line, and red line represent CFA continuous data, CFA outer-channel fraction collector samples (FC O), and discrete side-piece samples, respectively.
records exhibit similar evolutions and reflect the efficiency of our measurements.

We calculated the deuterium excess (d = δ D − 8 × δ 18 O, Dansgaard, 1964), which is a parameter dependent on both δ 18 O and δ D. Due to this parameter’s sensitivity to both isotopes, the differences between datasets are of key interest. With the exception of a clear disparity at depths between 1724.43 and 1724.48 m the similarity of their evolution confirms the coherence of our isotopic datasets.

4. Conclusions and perspectives

The new CFA system enables high-resolution depth sampling because of a laser to monitor the sample position and a novel approach to measuring and regulating the mixing volume of the debubbler. Our comparison with previous data demonstrates both the excellent quality of the data and the high sample resolution of the new system. Additionally, a comparison between continuous and discrete measurements using a fraction collector and side pieces of the ice core confirms the accuracy of our measurements.

To analyze the Dome Fuji deep ice core, we now plan to add new detection units such as a micro-particle analyzer (Bigler et al., 2011), an inductively coupled plasma-mass spectrometer (McConnell et al., 2002), and a black carbon analyzer to detect impurities in the ice (McConnell et al., 2007). Furthermore, modification of the degassing unit is required to continuously measure the methane mixing ratio of gas trapped in the ice samples (Rhodes et al., 2013; Stowasser et al., 2012).

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