

Continuous Ice Core Melter System with Discrete Sampling for Major Ion, Trace Element, and Stable Isotope Analyses

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We present a novel ice/firn core melter system that uses fraction collectors to collect discrete, high-resolution (<1 cm/sample possible), continuous, coregistered meltwater samples for analysis of eight major ions by ion chromatography (IC), >32 trace elements by inductively coupled plasma sector field mass spectrometry (ICP-SMS), and stable oxygen and hydrogen isotopes by isotope ratio mass spectrometry (IRMS). The new continuous melting with discrete sampling (CMDS) system preserves an archive of each sample, reduces the problem of incomplete particle dissolution in ICP-SMS samples, and provides more precise trace element data than previous ice melter models by using longer ICP-SMS scan times and washing the instrument between samples. CMDS detection limits are similar to or lower than those published for ice melter systems coupled directly to analytical instruments and are suitable for analyses of polar and mid–low-latitude ice cores. Analysis of total calcium and sulfur by ICP-SMS and calcium ion, sulfate, and methanesulfonate by IC from the Mt. Logan Prospector-Russell Col ice core confirms data accuracy and coregistration of the split fractions from each sample. The reproducibility of all data acquired by the CMDS system is confirmed by replicate analyses of parallel sections of the GISP2 D ice core.

Introduction

Glaciochemical data from ice cores provide valuable information about past climate variability and atmospheric chemistry and their controlling forces. For example, time series of major ion (including Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, CH₃SO₃⁻, NO₃⁻, and SO₄²⁻) concentrations have revealed dramatic and abrupt changes in atmospheric circulation during glacial and interglacial conditions and provided insight into their forcing mechanisms (see ref 1 for a review). Stable oxygen and hydrogen isotopes in snow and ice ($\delta^{18}\text{O}$ and δD) contribute information about past temperature, moisture source regions, and hydrology (e.g., refs 2–5). Trace elements have received more attention in recent years because of their usefulness in determining aerosol sources (e.g., refs 6–8),

understanding biogeochemical cycles (9), and assessing the impact of anthropogenic (e.g., refs 10–12) and volcanic (e.g., refs 13 and 14) emissions on the past and present atmosphere.

The conventional technique for sampling ice cores for major ion and trace element analyses includes progressively chiseling away the potentially contaminated outer portion of the core under extremely clean conditions (15). Pioneering studies utilizing this technique provided the first accurate chemical time series from snow and ice samples and established their value as paleoenvironmental proxies, but they necessarily provided low-resolution (10–20 cm/sample) and often discontinuous data sets because the method is both time-consuming and labor-intensive. The development of continuous ice core melting systems (16–24) over the past decade has reduced sample preparation time and increased sample resolution while providing continuous and coregistered data for a large suite of elements. Previous ice core melter systems have utilized in-line continuous flow analysis (CFA) techniques (16, 17) or coupled the melter to ion chromatographs (IC; 18, 19) to measure a large suite of organic and inorganic ions at ~1 cm resolution. Recently, ice core melter technology has advanced to include continuous, on-line measurements of oxygen and hydrogen stable isotopes in ice core meltwater, as well as oxygen, nitrogen, and argon isotopes in air trapped within the ice core bubbles (20–22).

McConnell et al. (23) coupled an ice core melter directly to an inductively coupled plasma mass spectrometer (ICP-MS) and CFA system to provide continuous measurements of an extensive suite of major and trace elements. Knüsel et al. (24) expanded the number of elements measured by the McConnell-type CFA-TE (continuous flow analysis with trace elements) system by incorporating an ICP-sector field mass spectrometer (ICP-SMS) but found that 18 trace elements commonly associated with silicates (including Al, Fe, Pb, U, and lanthanides) were underestimated when compared to identical samples prepared by the conventional chiseling technique. They attribute this discrepancy to incomplete dissolution of the silicates due to limited exposure to acid (<5 min) and/or adsorption of dissolved trace elements and mineral dust to the ice melting device (24). CFA-TE ice melter systems currently lack the capability to collect a sample archive, and they require relatively short ICP-SMS scan times to achieve high-resolution data, reducing the precision of trace element measurements. In addition, continuous flow ICP-SMS measurements suffer from sample cross-contamination (smoothing effect) since it is not possible to wash the sample introduction system between samples as is standard procedure for low-concentration measurements (25).

Here, we present a novel ice core melter system that addresses these concerns by combining the cleanliness and high-resolution sampling of continuous melting with the flexibility and precision of conventional discrete sampling. This new method, referred to as continuous melting with discrete sampling (CMDS), uses fraction collectors to collect discrete, high-resolution (<1 cm core/sample possible), continuous, and coregistered meltwater samples from an ice/firn melter device for analysis of eight major ions by ion chromatography (IC), >32 trace elements by ICP-SMS, and oxygen and hydrogen isotopes in water by isotope ratio mass spectrometry (IRMS). “Discrete” in this context refers to separation of the continuous meltwater stream into separate, homogenized samples. There are no gaps in the time series produced by CMDS analysis. We describe this method in detail below, including the determination of procedural blanks, method detection limits, sample decontamination, and data reproducibility.

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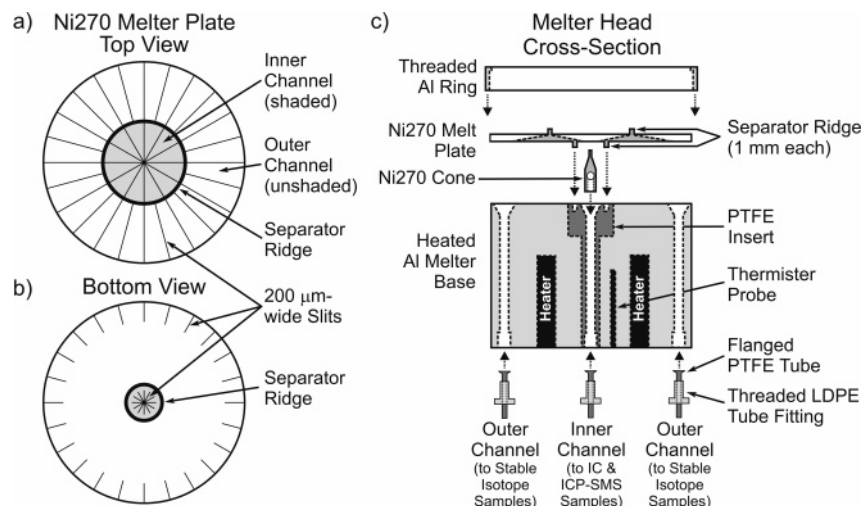


FIGURE 1. Diagram of the top (a) and bottom (b) of the modified Wagenbach-style (17) Ni270 firn and ice melter plate and cross-section (c) of the melter head assembly, which can be easily separated for cleaning between melting sessions.

Methods

Modified Wagenbach-Style Firn and Ice Melthead. We have constructed a modified Wagenbach-style (17) firn and ice melter head with a nickel 270 (>99.99% Ni) melter plate mounted on a heated aluminum base. The Ni melter plate is 3 mm thick with a series of radiating 200 μm wide slits through which meltwater flows (Figure 1). The slits produce a downward capillary force that prevents wicking of the meltwater into unmelted core, thereby allowing both firn and ice to be melted (17). The melter head splits the meltwater into two channels physically separated by a ridge (1 mm high) on the surface of the Ni plate. Meltwater from the potentially contaminated outer portion of the ice core is directed to the “outer channel” for stable isotope analysis, and meltwater from the uncontaminated, innermost portion of the ice core is directed to the circular “inner channel” for major ion and trace element analyses (Figure 1).

A 1 mm high circular separator ridge on the bottom of the Ni plate nests tightly into a poly(tetrafluoroethylene) (PTFE) insert, and the PTFE insert nests tightly within the heated Al base (Figure 1). A Ni270 “cone” is sandwiched between the PTFE insert and the center of the inner channel on the Ni plate to draw the meltwater down into the PTFE insert. The Ni melter plate, Ni cone, and PTFE insert provide a clean conduit through which meltwater flows from the inner channel such that it is never in contact with the Al base. A threaded Al ring screws onto the Al base and holds the complete melter head assembly together. Thus, the Ni melter plate, Ni cone, Al base, and PTFE insert can be separated for easy cleaning between melting sessions (Figure 1c). We have constructed several different melter head assemblies to accommodate slabs as small as 2.7 cm \times 2.7 cm up to whole cores as large as 10.2 cm (4 in.) in diameter. The diameter of the inner channel currently ranges from 15 mm (for 2.7 \times 2.7 cm slabs) to 30 mm (for >4.2 \times 4.2 cm slabs or whole core) on our various Ni plates.

The melter plate is machined from Ni270 because of its favorable thermal properties, availability in pure form, reasonable cost, and because Ni sample and skimmer cones are used in the UMaine ICP-SMS, already compromising measurements of low-level Ni. Testing indicates that a melter plate coated with metal, ceramic, or fluoropolymers is problematic because the coating degrades over time, exposing the base metal underneath and potentially contaminating the sample. A solid, pure Ni melter plate can degrade without ever contaminating the sample. In addition, applying any coating within the narrow slits of the Wagenbach-style melter head (17) is technologically difficult and expensive.

Ice Core Melting with Discrete Sampling. The entire UMaine CMDS system is housed in a dedicated clean room with high-efficiency particulate air (HEPA) filtered air. Non-particulating suits and booties, facemasks and wrist-length polypropylene (PP) gloves are worn during melting and all ice preparation. Deionized water from a MilliQ-Element system (Millipore, Milford, MA; >18.2 M Ω ; hereafter “DI water”) is pumped through the entire melter system between melting sessions to keep the system clean, and DI water blanks are collected prior to every melting session to confirm the cleanliness of the system. The melter head is heated to a constant temperature of 15–25 $^{\circ}\text{C}$ (depending on ice/firn density) by two 250-W cartridge heaters (Figure 1c), resulting in a 1.5–3 cm/min melt rate. The temperature of the melter head is measured by a thermocouple (Figure 1c) and maintained by an Omega Engineering (Stamford, CT) time-proportioning temperature controller. The ice/firn core or slab (hereafter referred to simply as “ice core”) is mounted upright in a 1 m long, precleaned Plexiglas container open only toward the bottom where the ice is in contact with the Ni melter plate. A PTFE-coated 250 g weight is often placed on top of the slab/core when melting firn to ensure a consistent melt rate. A high-density polyethylene (HDPE) stand holds the Plexiglas container in position over the melter head assembly. The melter head and core are housed within a dedicated upright freezer maintained at -20°C within the clean room, while the pumps and fraction collectors described below are all located outside the freezer within the clean room (Figure 2).

Meltwater from the uncontaminated inner channel is pumped from the melter head through PTFE tubing (1.6 mm i.d., 3.2 mm o.d.) and platinum-cured silicone/PTFE pump tubing (STA-PURE, Gore and Associates, Elkton, MD; 2.8 mm i.d.) by two Gilson (Middleton, WI) peristaltic pumps. A third peristaltic pump controls the flow of meltwater from the outer channel. Pump rates are dictated by the ice melt rate and ice core dimensions and are adjusted so that there is always net flow from the inner toward the outer part of the core to prevent contamination of the inner sample. PTFE tubes are flanged and connected to the Al melter base (for the outer channel) and PTFE insert (for the inner channel) with a threaded LDPE fitting (Figure 1c). DI water blank sample volumes are checked prior to each melting session to monitor any pump tube degradation, although the STA-PURE pump tubes have exceptional longevity (several months) compared to silicone or Tygon peristaltic pump tubes (days).

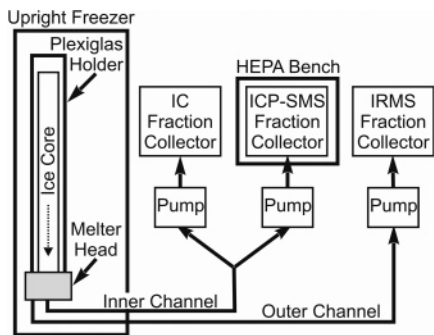


FIGURE 2. Schematic diagram of the continuous melter with discrete sampling (CMDS) system. Three fraction collectors collect discrete samples from a continuous meltwater stream for IC, ICP-SMS, and IRMS analyses. The entire CMDS system is housed in a dedicated clean room with HEPA-filtered air.

Meltwater from the inner channel is split between two Gilson fraction collectors: one that collects ICP-SMS samples in acid-precleaned, PP vials under a class-100 HEPA clean bench, and a second fraction collector that collects IC samples in PP vials pre-cleaned with DI water. Meltwater from the potentially contaminated outer channel is collected by a third Gilson fraction collector in 20–50 mL PP or high-density polyethylene (HDPE) vials for stable isotope analysis. The “master” fraction collector measures the IC sample volume by counting drops, and triggers the ICP-SMS and stable isotope fraction collectors to simultaneously advance to the next sample when the predetermined volume is collected.

The volume collected for each fraction depends on the melter head and ice core dimensions, number of analytes, and the desired sample resolution. A minimum of 4 mL is generally required for IC analyses, and 2 mL is desirable for ICP-SMS analysis. These requirements result in a maximum depth resolution of ~1 cm ice/sample (~2 cm/firn sample) when the Ni melter plate with a 30 mm inner channel diameter is used, assuming that both IC and ICP-SMS data are desired. Typically we collect larger sample volumes to preserve an archive for subsequent analyses. Higher sample resolution is possible with different melter head dimensions (i.e., larger inner channel diameter) and/or restricting inner samples to either IC or ICP-SMS analyses (see Efficiency of Ice Decontamination below); however, natural inhomogeneity in the ice may limit the usefulness of <1 cm resolution. IC and ICP-SMS samples can be collected in the vials in which they are analyzed, reducing sample manipulation (i.e., no aliquoting) and therefore reducing potential contamination. The fraction collectors can also be programmed to collect samples in vials of varying dimensions if desired, providing further analytical freedom.

Sample Vial Cleaning. All PP ICP-SMS vials are soaked in 15% trace metal-grade HNO₃ for 1 week, triple-rinsed in DI water, soaked in DI water for an additional week, triple-rinsed in DI water again, dried under a class-100 HEPA clean bench, capped, and stored dry until use. PP IC sample vials are triple-rinsed in DI water, soaked in DI water overnight, triple-rinsed in DI water again, dried, and capped under a class-100 HEPA clean bench. Extensive testing of both IC and ICP-SMS vials confirms their cleanliness. Stable isotope PP or HDPE vials are not cleaned prior to sampling but are ensured to be dry prior to sample collection.

Ice and Sample Preparation. Although the use of a melter system precludes the need to physically decontaminate the sides of the core, the ends of each piece of firn or ice must be decontaminated. Immediately before melting, the outermost 3–6 mm of ice or firn are removed from the ends of each piece with a pre-cleaned (with DI water) ceramic (ZrO) knife under a class-100 HEPA clean bench, and loaded into a pre-cleaned Plexiglas container for melting.

Immediately after melting, all ICP-SMS samples are acidified to 1% with double-distilled HNO₃ under a class-100 HEPA clean bench and allowed to react with the acid for approximately 24 h before being frozen at –20 °C. Samples are defrosted at room temperature approximately 24–48 h prior to analysis. Repeat measurements on samples that were left unfrozen and acidified for varying lengths of time over a 5-day period showed no change in trace element concentrations. Stable isotope and IC samples are frozen immediately after melting without acidification.

ICP-SMS Analyses. All trace element analyses were performed with the UMaine Thermo Electron Element2 ICP-SMS, with the isotopes measured in low and medium resolution listed in Table 2 (see Table S1, Supporting Information, for ICP-SMS analysis settings and components). The use of an ESI Apex high-sensitivity inlet system increases instrument sensitivity and reduces oxide formation in the plasma, lowering detection limits and allowing less abundant isotopes to be measured. The Cetac (Omaha, NE) Model ASX-260 autosampler is located within a class-100 HEPA clean bench adjacent to the instrument to further reduce contamination. The ICP-SMS is calibrated daily with five standards that bracket the expected sample concentration range. Certified water reference material, SLRS-4 (Environment Canada), is used to verify the calibration (Table 1). Similar to the method used by Krachler et al. (25), check standards are analyzed throughout the run to monitor long-term drift, and we use Thermo Electron’s auto lock mass software routine to compensate for mass drift. In an effort to minimize sample handling and possible contamination, no internal standard is used. Results from check standards, certified reference material, and duplicate analyses on the IC (see “sample coregistration” and Figure 4 below) confirm the validity of this technique for low-level meltwater samples.

IC Analyses. Major ions are analyzed on Dionex ion chromatographs with chemical suppression and conductivity detectors. Anions (CH₃SO₃⁻, Cl⁻, NO₃⁻, SO₄²⁻) are measured by use of an AS-11 column, 400 μL sample loop, and a Dionex reagent free controller producing a KOH eluent gradient of 1–8 mM. Cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) are measured by use of a CS-12A column, 500 μL loop, with 25 mM methanesulfonic acid eluent. We do not currently measure ammonium due to ambient contamination from cleaning products used in the building; however, we are progressing toward a solution for this problem. The two ion chromatographs are paired to a Gilson liquid handler autosampler for simultaneous anion and cation analysis. Calibration curves bracket the expected concentration range with correlation coefficients of >0.99.

IRMS Analyses. Stable isotope analyses (δ¹⁸O and δD) of meltwater samples are performed via gas source mass spectrometry. Oxygen isotope ratios are measured via standard CO₂ equilibration techniques with a Micromass Multiprep device coupled to a stable isotope ratio analysis (SIRA) mass spectrometer (±0.05‰ precision based on long-term standard analysis statistics). Hydrogen isotope ratios are measured via Cr reduction with a Eurovector elemental analyzer coupled to a Micromass Isoprime mass spectrometer (±0.5‰ precision based on long-term standard analysis statistics; 26). Data are reported in delta (δ) notation relative to standard mean ocean water (SMOW).

Results and Discussion

Accuracy, Precision, Blanks, and Detection Limits. Although no standard reference material currently exists for trace elements in polar ice, analyses of the reference materials (Environment Canada) SLRS-4 by ICP-SMS and ION-92 by IC produce concentrations within the certified range (Table 1), confirming accuracy. Instrument detection limits for the IC and ICP-SMS, equivalent to 3 times the standard deviation (3σ) of 10 DI water samples, are listed in Table 2 along with

TABLE 1. Comparison of Standard Reference Material (SLRS-4, ION-92) Certified Values (Environment Canada) with Values Determined from the UMaine ICP-SMS and IC

element	UMaine analyzed ^a (μg/L)	certified (μg/L)
Na ⁺ ^b	20.2 ± 0.4	19.3 ± 2.4
Ca ²⁺ ^b	44.4 ± 1.8	42.8 ± 4.0
Mg ²⁺ ^b	10.7 ± 0.5	9.6 ± 1.1
K ⁺ ^b	1.1 ± 0.2	0.9 ± 0.2
Cl ⁻ ^b	106.0 ± 3.4	105.5 ± 12.3
SO ₄ ²⁻ ^b	37.8 ± 2.5	37.0 ± 4.9
Al	53 ± 2	54 ± 4
As	0.70 ± 0.02	0.68 ± 0.06
Ba	12.0 ± 0.5	12.2 ± 0.6
Ca	6.4 ± 0.2	6.2 ± 0.2
Cd	0.012 ± 0.001	0.012 ± 0.002
Co	0.030 ± 0.003	0.033 ± 0.006
Cr	0.35 ± 0.01	0.33 ± 0.02
Cu	1.68 ± 0.07	1.81 ± 0.08
Fe	106 ± 4	103 ± 5
Mn	3.41 ± 0.10	3.37 ± 0.18
Pb	0.081 ± 0.001	0.086 ± 0.007
Sr	27.6 ± 0.9	26.3 ± 3.2
U	0.050 ± 0.004	0.050 ± 0.003
V	0.30 ± 0.01	0.32 ± 0.03

^a Values represent mean of 10 analyses. Errors correspond to 1σ.
^b IC data (ION-92).

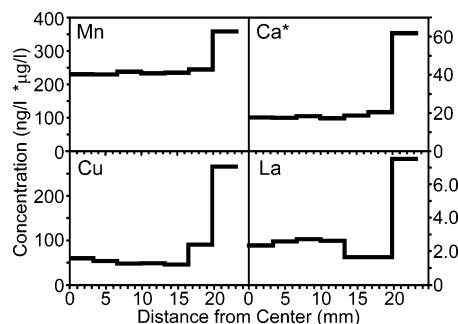
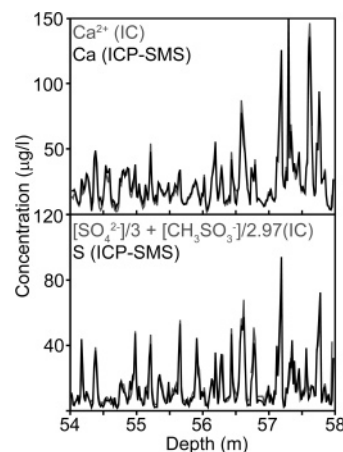
average DI blank concentrations. These detection limits and DI blank values are similar to or lower than published values on identical or comparable instruments (e.g., refs 24, 25, and 27; Table S2, Supporting Information).

Continuous melter method blanks and detection limits, calculated from 10 DI water blanks passed through the entire CMDS system, are listed in Table 2 and compared to Greenland ice concentrations (10, 28–31; unpublished UMaine data) from samples spanning the Holocene and glacial periods. CMDS detection limits are similar to or lower than published CFA-TE detection limits (24; see Table S2, Supporting Information), and are almost always lower than minimum Greenland ice values and an order of magnitude below average Greenland ice values (Table 2).

The δD ratio of a stable water isotope reference material (homogenized Antarctic surface snow) that was frozen and melted through the CMDS system (−202.4 ± 1.2‰, mean and 1σ of 10 samples) matches its δD ratio before melting (−201.8 ± 0.5‰), confirming the accuracy of stable isotope measurements.

We have discovered that Ni from the melter plate elutes close to Ca²⁺ on the CS-12A IC column. The two peaks are easily distinguishable when both are present (in core meltwater samples), but the Ni peak can be mistakenly interpreted as Ca²⁺ in method blanks when the true Ca²⁺ concentration is below the detection limit. This can lead to erroneously high concentrations of Ca²⁺ in melter blank tests when analyzed solely by IC.

Efficiency of Ice Decontamination. Figure 3 displays examples of concentration cross-sections generated by melting small pieces of firm sideways through the CMDS system at high resolution, analogous to cross-sections generated by physically removing successive veneers of ice and analyzing each veneer (15, 24). The firm is from the 2001 Prospector-Russell (PR) Col core collected on the summit plateau (5300 m elevation) of Mt. Logan, Yukon, Canada. Each data point in the cross-sections represents 3 mm of firm, which was achieved by sampling only for ICP-SMS analyses. In all cases, contamination is limited to the outermost 3–6 mm of the slab, and stable low-concentration plateaus are observed. Consequently, a 6 mm or larger buffer between the slab/core edge and the inner meltwater channel is always maintained when melting.

**FIGURE 3. Concentration cross-sections of Mt. Logan PR Col firm created by melting the firm sideways through the CMDS system at 3 mm/sample resolution. Only the outer 3–6 mm is contaminated.****FIGURE 4. CMDS calcium and sulfur profiles from the Mt. Logan PR Col ice core (~1893–1906 AD) showing exact coregistration of IC and ICP-SMS samples. Sample resolution is ~1.9 cm/sample (14–22 samples/year), and the data have not been smoothed.**

McConnell et al. (23) and Knüsel et al. (24) cite meltwater dispersion within the melter head, tubing, and debubblers as limiting sample resolution of the CFA-TE system to ~1 cm/sample. The ice decontamination data presented here, however, suggest that mixing does not significantly distort data at a resolution of 3 mm/sample. The PTFE tubing contains ~1 sample worth of meltwater (with the standard sample sizes of 4 and 2 mL for IC and ICP-SMS, respectively) during melting, minimizing any effects of mixing in the system.

Sample Coregistration. We currently measure Ca²⁺, SO₄²⁻, and CH₃SO₃⁻ on the IC and elemental Ca and S on the ICP-SMS, providing two time series with which to confirm sample coregistration. Elemental sulfur concentrations from the ICP-SMS can be directly compared to IC data by dividing SO₄²⁻ by 3 and CH₃SO₃⁻ by 2.97 and summing their concentrations. Figure 4 shows that Ca and S concentrations from the Mt. Logan PR Col core measured on the two instruments are very highly correlated ($R^2 = 0.88$ for Ca, $R^2 = 0.97$ for S) confirming sample coregistration. This comparison also validates the concentration values produced by the two different instruments.

Reproducibility of CMDS Data. Parallel 2 m long slabs of ice from the GISP2 D core (meters 2023–2025; ~25 800 BP; 31, 32) were melted to demonstrate the reproducibility of chemical measurements made with the CMDS system. IC, ICP-SMS, and stable isotope data are displayed in Figure 5 and compared to lower resolution (20 cm/sample) IC data processed with traditional scraping methods and/or an early version of a continuous ice melter (31). Outliers due to noise spikes in the mass spectra caused by small particles (24) have been removed from the ICP-SMS data, but the data

TABLE 2. Average Instrument and Procedural (CMDS) Blanks, and Instrument and Procedural Detection Limits (DL) Compared to Greenland Ice Concentrations (ng/L)

analyte ^a	DI water blank ^b	inst.DL ^c	CMDS blank ^d	CMDS DL ^e	Greenland concn min-max, (mean) ^f
Na ⁺ (IC)	<IDL	310	1070 ± 190	600	1000–144 000 (21 400)
Ca ²⁺ (IC)	<IDL	320	<CMDS DL	1970	1300–1 465 000 (81 400)
Mg ²⁺ (IC)	<IDL	60	<IDL	100	430–323 000 (9300)
K ⁺ (IC)	<IDL	120	<IDL	1350	30–31 100 (2800)
CH ₃ SO ₃ ⁻	<IDL	70	<IDL	70	1700–7600 (4100)
Cl ⁻ (IC)	<IDL	260	890 ± 220	710	1040–252 000 (39 700)
NO ₃ ⁻ (IC)	<IDL	240	<IDL	900	33 200–211 000 (77 200)
SO ₄ ²⁻ (IC)	<IDL	1160	3150 ± 740	1940	12 100–985 000 (97 400)
²⁷ Al (MR)	70 ± 10	40	580 ± 160	470	200–156 000 (11 980)
¹³⁸ Ba (LR)	<IDL	0.33	0.95 ± 0.17	0.51	93.1–8245.2 (471.9)
²⁰⁹ Bi (LR)	0.01 ± 0.01	0.03	0.13 ± 0.03	0.08	0.1–5.1 (0.5)
⁴⁴ Ca (MR)	<IDL	110	<CMDS DL	1230	1300–1 465 000 (81 400)
¹¹¹ Cd (LR)	<IDL	0.03	0.16 ± 0.04	0.13	0.2–25.3 (2.3)
⁵⁹ Co (MR)	<IDL	0.41	3.34 ± 0.28	0.83	0.65–144.21 (15.22)
⁵² Cr (MR)	0.18 ± 0.05	0.14	1.70 ± 0.25	0.76	3.4–240.6 (37.8)
¹³³ Cs (LR)	<IDL	0.007	<CMDS DL	0.040	2.4–58.3 (8.0)
⁶³ Cu (MR)	<IDL	3.3	68.6 ± 6.4	19.3	2.0–625.7 (95.5)
⁵⁶ Fe (MR)	<IDL	10	40 ± 10	20	1250–185 478 (14 555)
⁵⁵ Mn (MR)	<IDL	1	62 ± 7	21	211–7246 (905)
²⁰⁸ Pb (LR)	<IDL	0.2	1.6 ± 0.3	0.9	0.5–2700.0 (35.7)
³² S (MR)	<IDL	290	1820 ± 430	1280	4033–328 333 (32 467)
⁸⁸ Sr (LR)	0.2 ± 0.1	0.3	0.8 ± 0.2	0.7	120.0–3911.6 (421.5)
⁴⁷ Ti (MR)	<IDL	0.7	1.8 ± 0.5	1.4	125.8–6001.8 (875.1)
²⁰⁵ Tl (LR)	0.09 ± 0.01	0.03	0.19 ± 0.06	0.18	0.1–3.3 (0.4)
²³⁸ U (LR)	0.006 ± 0.002	0.006	0.030 ± 0.006	0.019	0.2–35.2 (4.2)
⁵¹ V (MR)	<IDL	0.1	0.2 ± 0.1	0.3	9.9–419.7 (60.6)
¹³⁹ La (LR)	<IDL	0.01	<CMDS DL	0.05	6.5–424.2 (33.4)
¹⁴⁰ Ce (LR)	<IDL	0.01	0.07 ± 0.01	0.04	13.9–915.4 (72.6)
¹⁴¹ Pr (LR)	<IDL	0.002	0.055 ± 0.004	0.012	1.7–112.8 (9.0)
¹⁴⁶ Nd (LR)	<IDL	0.012	0.045 ± 0.0134	0.040	7.0–448.4 (34.5)
¹⁴⁷ Sm (LR)	<IDL	0.006	<CMDS DL	0.016	1.5–90.7 (6.9)
¹⁵³ Eu (LR)	<IDL	0.003	<CMDS DL	0.004	0.3–19.3 (1.6)
¹⁵⁷ Gd (LR)	<IDL	0.003	<CMDS DL	0.008	1.1–66.0 (4.9)
¹⁵⁹ Tb (LR)	<IDL	0.001	<CMDS DL	0.003	0.2–12.9 (1.0)
¹⁶³ Dy (LR)	<IDL	0.011	<CMDS DL	0.011	0.9–68.7 (4.9)
¹⁶⁵ Ho (LR)	<IDL	0.001	<CMDS DL	0.005	0.2–11.7 (0.9)
¹⁶⁶ Er (LR)	<IDL	0.005	<IDL	0.007	0.5–31.5 (2.5)
¹⁶⁹ Tm (LR)	<IDL	0.002	<IDL	0.002	0.1–4.0 (0.4)
¹⁷² Yb (LR)	<IDL	0.01	<IDL	0.01	0.4–22.5 (1.9)
¹⁷⁵ Lu (LR)	<IDL	0.005	<IDL	0.005	0.1–2.9 (0.3)

^a IC denotes ion chromatographic data, LR denotes low-resolution ICP-SMS mode ($m/\Delta m = 300$), and MR denotes medium-resolution mode ($m/\Delta m = 4000$). ^b Mean of 10 DI water samples. ^c Instrument detection limits (IDL) calculated by 3σ of 10 DI water samples. ^d Mean of 10 DI water samples passed through the CMDS system. ^e CMDS detection limits calculated by 3σ of 10 DI water samples passed through the CMDS system. ^f From refs 10 and 28–31 and unpublished UMaine data. Errors correspond to 1σ .

have not been smoothed. Sample resolution is ~2.5 years/sample (~3.7 cm of ice/sample) for this experiment to avoid potential seasonal biasing.

All chemical series from the parallel slabs closely match, with minor differences between the time series, most likely due to natural chemical variability within the ice itself (24). CMDS major ion data fluctuate around the lower-resolution data (31), revealing multiannual to decadal-scale oscillations that are not apparent in the original data. Note that different elements with the same likely source (i.e., dust, sea salt, etc.) strongly covary. For example, sea salt proxies Na⁺ and Cl⁻ are highly correlated, as are dust proxies such as Fe and Mn (Figure 5). The detailed analysis of these data will follow in future publications.

Knüsel et al. (24) suggest that incomplete dissolution of silicate dust particles due to short acidification times (<5 min) and/or adsorption in their CFA-TE melter apparatus results in erroneously low concentrations of silicate-based elements when dust concentrations are elevated, whereas background values are correctly quantified. This suggests that incomplete dissolution, rather than adsorption, is to blame for the lower silicate concentrations in CFA-TE systems compared to chiseling techniques. The CMDS system reduces the incomplete particle dissolution problem because melt-

water samples are exposed to 1% HNO₃ for over 48 h before being analyzed, equivalent to the acidification of samples collected by conventional chiseling techniques (e.g., 7, 8, 10–12, 14), including the comparative study by Knüsel et al. (24). All of the tubing used on the inner channel of the CMDS system is composed of PTFE, which is strongly resistant to adsorption, especially over short exposure times (<2 min) (33, 34). Although adsorption to the Ni melter plate remains a possibility, the short exposure time (<5 s) suggests that any such adsorption would be minimal. Thus, we believe that the CMDS system provides data comparable to those determined by conventional chiseling techniques and similar instrumentation.

Ice cores from regions with coarse, locally sourced dust (e.g., Himalaya, Dry Valleys of Antarctica), however, present a complication to studies that use either continuous melting or chiseling techniques because nitric acid is incapable of completely dissolving large silicate particles. Such cores are presently melted by the CMDS system with larger PTFE tubing to prevent clogging and can be subsequently filtered to separate various particle-size fractions depending on the purpose of the study. Because ICP-SMS samples are collected discretely by the CMDS system, they can be acidified with HF, HCl, or digested to fully dissolve all particles if desired.

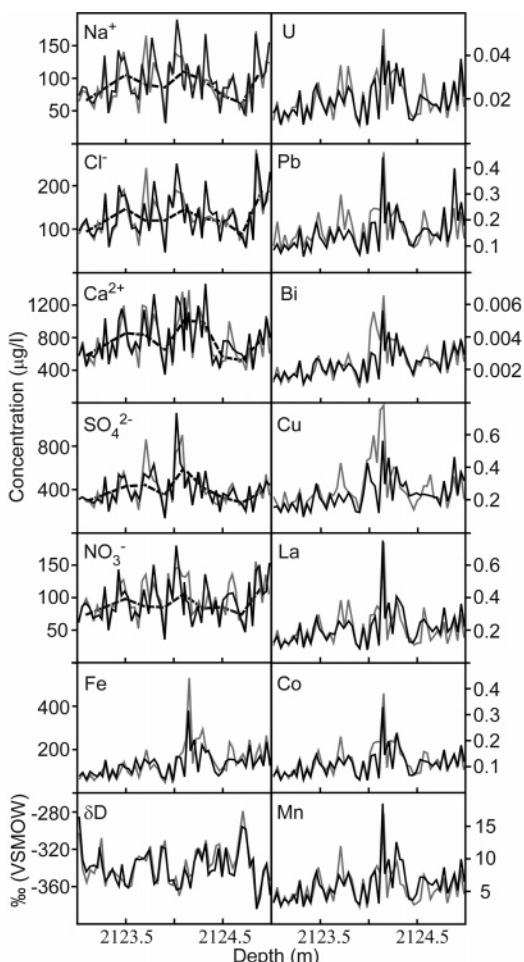


FIGURE 5. Parallel 2-m long sections of GISP2 D core (black and gray solid lines; dated ~25 800 BP; 32) demonstrating reproducibility of CMDS data compared to lower resolution (20 cm/sample) major ion data from Mayewski et al. (31).

Future modifications to the CMDS system include the development of an in-line filtering system and the use of an ice monitoring device to control fraction collectors as opposed to drop counting. We are also assessing the potential to collect tephra particles (from explosive volcanic eruptions) from the outer channel and determine their mineralogical composition using microprobe analysis. Such analyses can help identify the source volcano, providing a useful tool for validating ice core time series and extending volcanic records beyond the observational period.

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Supporting Information Available

Details of the UMaine ICP-SMS instrument and operational settings (Table S1) and instrument blanks, instrument

detection limits, procedural blanks, and procedural detection limits of the CMDS system compared to those of CFA-TE systems and comparable instruments (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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