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Complete List of Authors:	Motizuki, Yuko; RIKEN, Nishina Center Nakai, Yoichi; RIKEN, Nishina Center for Accelerator-Based Science Takahashi, Kazuya; RIKEN, Nishina Center for Accelerator-Based Science Hirose, Junya; RIKEN, Nishina Center for Accelerator-Based Science Sahoo, Yu Vin; RIKEN, Nishina Center for Accelerator-Based Science Yumoto, Masaki; RIKEN, Center for Advanced Photonics Maruyama, Masayuki; RIKEN, Center for Advanced Photonics Sakashita, Michio; RIKEN, Center for Advanced Photonics Kase, Kiwamu; RIKEN, Center for Advanced Photonics Wada, Satoshi; RIKEN, Center for Advanced Photonics Motoyama, Hideaki; National Institute of Polar Research, Yano, Yasushige; RIKEN, Nishina Center for Accelerator-Based Science
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A novel ice-core laser melting sampler for discrete, sub-centimeter depth-resolved analyses of stable water isotopes

Yuko Motizuki,[1] Yoichi Nakai,[1] Kazuya Takahashi,[1] Junya Hirose,[1] Yu Vin Sahoo,[1] Masaki Yumoto,[2] Masayuki Maruyama,[2] Michio Sakashita,[2] Kiwamu Kase,[2] Satoshi Wada,[2] Hideaki Motoyama,[3] and Yasushige Yano[1]

[1] RIKEN Nishina Center for Accelerator-Based Science, Wako, Japan; [2] RIKEN Center for Advanced Photonics Wako, Japan; [3] National Institute of Polar Research, Tachikawa, Japan

Abstract

We developed a novel ice-core laser melting sampler (LMS) to measure the stable water isotope ratios ($\delta^{18}O$ and δD) as temperature proxies at ultra-high depth resolutions. In this LMS system, a 2-mm diameter movable evacuation nozzle holds an optical fiber through which a laser beam irradiates the ice core. The movable nozzle intrudes into the ice core, the laser radiation meanwhile melting the ice cylindrically, and the meltwater is pumped away simultaneously through the same nozzle and transferred to a vial for analysis. To avoid isotopic fractionation of the ice-core components by vaporization, the laser power is adjusted to ensure that the temperature of the meltwater is always kept well below its boiling point. Internal contamination and cross-contamination were both found to be negligible using this LMS. A segment of a Dome Fuji shallow ice core (Antarctica), using the LMS, was then demonstrated to have been discretely sampled with a depth-resolution as small as 3 mm: subsequent measurements of $\delta^{18}O$ and δD were reasonably consistent with results obtained by hand segmentation. The LMS will thus enable us to seek the past temperature variations that may appear even in sub-centimeter resolutions in ice cores.

Introduction

Ice-core studies with annually resolved chemical and isotopic analyses are essential to ascertain information important in various aspects of glaciology. The annual layer thickness in ice cores collected at low accumulation sites from Antarctica, however, can be as small as ~1 cm or smaller at deeper depths, so we are facing a boundary of sampling technique. For example, at a depth of about 2,000 m in the DF2 ice core (Motoyama 2007; Kawamura and others, 2017; Motoyama and others, 2021) drilled at Dome Fuji Station (77° 19' 01" S, 39°42' 12" E) in East Antarctica, the estimated age is about 200,000 years and the annual layer thickness is estimated to be about 0.5 cm. When we try to reconstruct temperature variations in such deep ice cores to elucidate continuous, long-term, annually resolved profiles, we apparently need a new sampling method, specially designed for measuring the stable water isotope ratios, $\delta^{18}O$ and δD, to enable us to attain the necessary high depth-resolution.

So far, to sample and analyze ice cores, the heater-melting continuous flow analysis (CFA) method is widely used (Röthlisberger and others, 2000; McConnell and others, 2002; Traversi and others, 2002; Kaufmann PR and others, 2008; Bigler and others, 2011; Severi and others, 2015; Emanuelsson and others, 2015; Dallmayr and others, 2016; Jones and others, 2017; Grieman and others, 2022). The depth resolution of systems overall is usually ~10

mm or more, although a resolution of a few millimeters has been achieved for measurements of Na^+, NH_4^+, dust particles, and electrolytic conductivity (Bigler and others, 2011).

Laser ablation inductively coupled with plasma mass spectrometry (LA-ICP-MS) is another widely used method to sample and analyze ice cores (Reinhardt and others, 2001; Müller and others, 2011; Sneed and others, 2015; Della and others, 2017; Bohleber and others, 2020). Sneed and others (2015) reported an achievement of a sub-millimeter depth-resolution. The LA-ICP-MS method, however, is in principle ill-suited to water isotope analyses, because laser ablation causes isotopic fractionation by vaporization due to the very high temperature rise within the laser irradiation volume. We therefore developed a new device, a novel ice-core laser melting sampler (LMS), as to attain high depth-resolution without isotopic fractionation.

The LMS system is outlined as follows: In a low-temperature room, a sectional portion of an ice core segment of ~0.5 m in length and ~94 mm in diameter is laid on a horizontally sliding stage. A 2-mm diameter movable evacuation nozzle, that holds an optical fiber inside, intrudes into the ice, melting it cylindrically by laser irradiation and transferring the meltwater simultaneously into a collection buffer by means of a peristaltic tube pump. To avoid isotopic fractionation of the compositions by vaporization, the laser power is adjusted to keep the temperature of the meltwater well below its boiling point. The meltwater is collected repeatedly until the amount necessary for the planned analysis has been accumulated, and the collected water is then pumped into a vial for the offline analyzer. By a combination of vertical and horizontal movements the ice core segment is sampled discretely. The depth-resolution normally attained is as small as 3 mm, which has been difficult to achieve with conventional systems.

In the following section we will describe the details of the LMS. It will be shown through the performance tests that there are neither internal contamination nor cross-contamination in the system. A 3-mm depth-resolution sampling by the LMS and the subsequent measurement of the water isotope ratios, $\delta^{18}O$ and δD, will then be demonstrated on a portion of a Dome Fuji shallow ice core recovered from Antarctica.

The laser melting sampler (LMS)

Overview of the LMS system

The LMS (Fig. 1) consists of four major components: 1) Sampling Unit, 2) Sliding Stage, 3) SUS vials in two sets of Vial Trays, and 4) Conveyor System. The LMS is placed in a low-temperature room kept at –20 °C. The computer control system of the LMS and a continuous-wave operated Er-doped fiber laser (CEFL-TERA, Keopsys Inc.) for melting ice are placed in an ambient temperature room outside the low-temperature room.

The Sampling Unit of the LMS, the details of which are described in the following sub-section, is equipped with a specially designed nozzle made of silver, into which the optical fiber is inserted, and the meltwater produced by laser irradiation is removed by a peristaltic tube pump. Once collected in a sampling buffer tube inside the Sampling Unit, the meltwater is finally pumped to an SUS vial waiting outside. The position of the Sampling Unit is fixed in the z-direction in Fig. 1 (the depth direction of the ice core), and the Sampling Unit is moved in the x- and y-directions (Fig. 1) by a cross-ladder elevation mechanism and a ball screw linear actuator driven by a

stepping motor, respectively. The positioning reproducibility is better than ± 0.05 mm with rotary encoders. We can add another identical Sampling Unit for high throughput sampling, e.g., as illustrated in Figure 1a.

A 50 cm-long portion of ice core segment is laid horizontally, an orientation favorable for sampling even brittle firn cores, on the Sliding Stage. The position of the ice core is shifted horizontally (in the z-direction) by a ball-screw linear actuator equipped with a rotary encoder. By combining these Sampling Unit and Sliding Stage movements, we can sample the ice core selectively at whatever positions may be required.

The Vial Tray stores 54 (6 × 9) vials and the Conveyor System transports the vials one by one to the meltwater drain position underneath the outlet of the Sampling Unit, returning them to the tray after the vial has been filled with meltwater. The target volume of the meltwater stored in a vial is adjustable as mentioned in the next subsection and is typically 1.5 mL. At present, the Vial Trays are collected and set in position for the analyzers by hand.

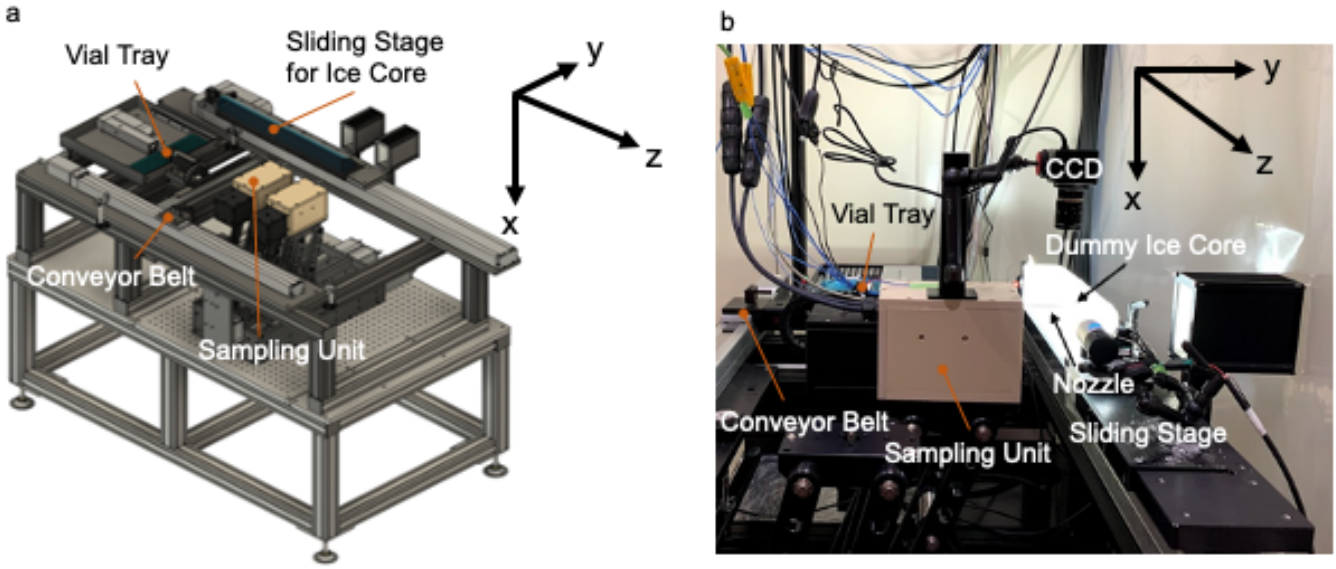

Fig. 1. (a) Schematic drawing of the LMS. (b) Photograph inside the low-temperature room. A CCD camera is mounted on the Sampling Unit to monitor the melted state of the ice core under laser irradiation.

Sampling Unit and operation

The components of the Sampling Unit (10 cm wide × 25 cm long × 13 cm high) are shown schematically in Fig. 2, and in the photograph of the interior viewed from above in Fig. 3. The interior of the Sampling Unit is kept warm, at above 0 °C, by resistive sheet heaters.

The laser beam is transferred through a silica core multimode optical fiber (core/clad diameter = 200/220 μm) to the Sampling Unit. The laser wavelength is 1.55 μm (near infrared), which does not cause photolysis in the samples, and the maximum output power is 10 W. The 1.55 μm wavelength takes advantage of the strong absorption bands of ice and water from 1.4–1.6 μm (Warren and Brandt, 2008; Kedenburg and others, 2012). A further merit of employing this wavelength is that suitable optical fibers are available commercially.

The 60 mm-long nozzle (Figs. 2 and 3) is made of commercially available pure Ag999 tubing (2 mm outer diameter and 1 mm inner diameter) and is kept warm, at well over 0 °C, in the –20 °C environment by the conduction of heat generated by the resistive heater block at the rear end of the nozzle (Figs. 2 and 3). The tip of the nozzle (Fig. 4) is plugged by a cylinder of polyether ether ketone (PEEK) resin 5-mm long, at the center of which a 0.5–0.35 mm diameter SUS capillary is inserted to hold the optical fiber in place with an acrylate coating (Coating diameter = 0.32 mm). The meltwater is siphoned through a small opening at the bottom of the PEEK plug (~0.2 mm^2).

At the beginning of sample collection, the tip of the nozzle is located at a point a few mm away from the side of the ice core. As the nozzle advances in the y-direction (see Fig. 1), the laser beam delivered through the optical fiber irradiates the ice core to melt it; the meltwater is simultaneously vacuumed through the nozzle and transferred through a perfluoroalkoxy alkane (PFA) polymer tube into a PFA sampling buffer (Figs. 2 and 3) which is depressurized by a peristaltic tube pump operated with a pressure drop of nearly 1 atm.

When the nozzle reaches the pre-specified intrusion depth, the nozzle is withdrawn to the start position. If more meltwater is needed, e.g., in a high-resolution sampling mode, the nozzle is shifted vertically and the sample collection is repeated. A non-contact water level sensor attached to the sampling buffer interrupts sampling when the target volume of sample water (adjustable: ~0.65 to ~2.5 mL) has been collected in the sampling buffer. Then, the Sampling Unit is pulled back from the ice and both the laser beam and the tube pump are deactivated. Immediately, the 3-way solenoid valve connected to the sampling buffer is switched and, by reversing the tube pump, the meltwater stored in the sampling buffer is pumped into a vial waiting underneath the drain outlet of the Sampling Unit.

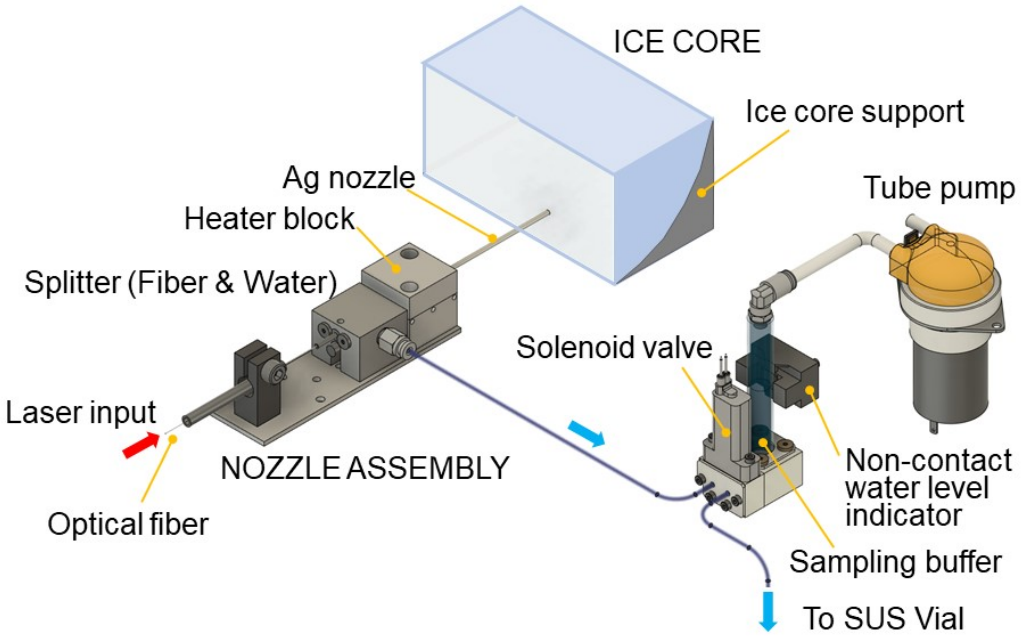

Fig. 2. Schematic development diagram detailing the components of the Sampling Unit.

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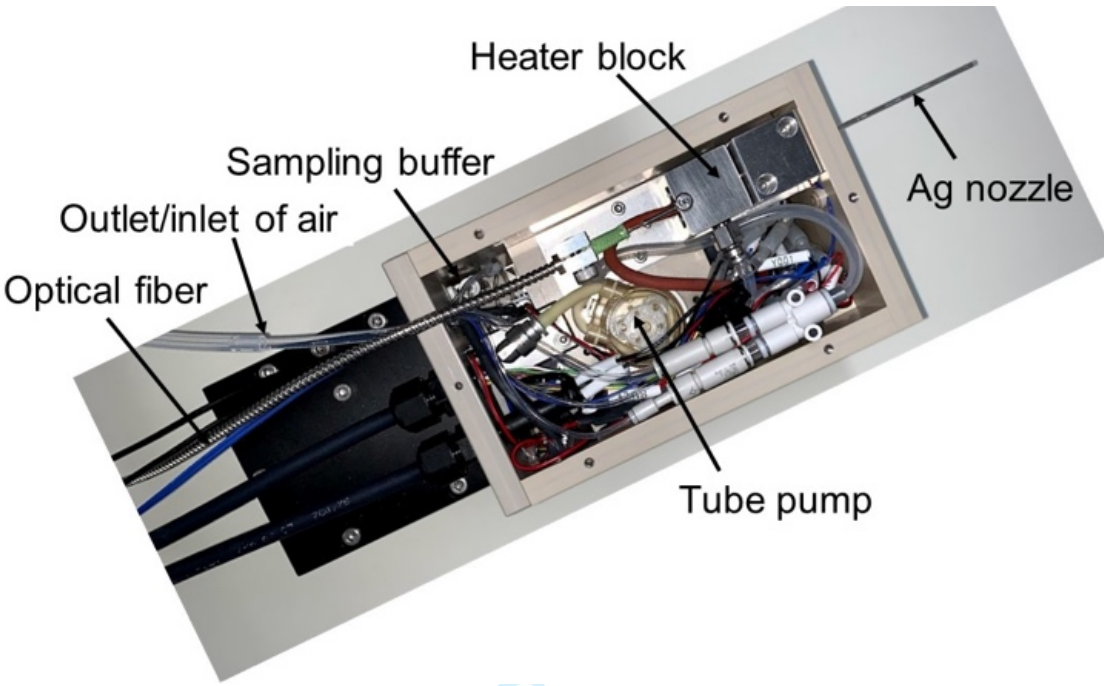

Fig. 3. A photograph of the top view of the interior of the Sampling Unit.

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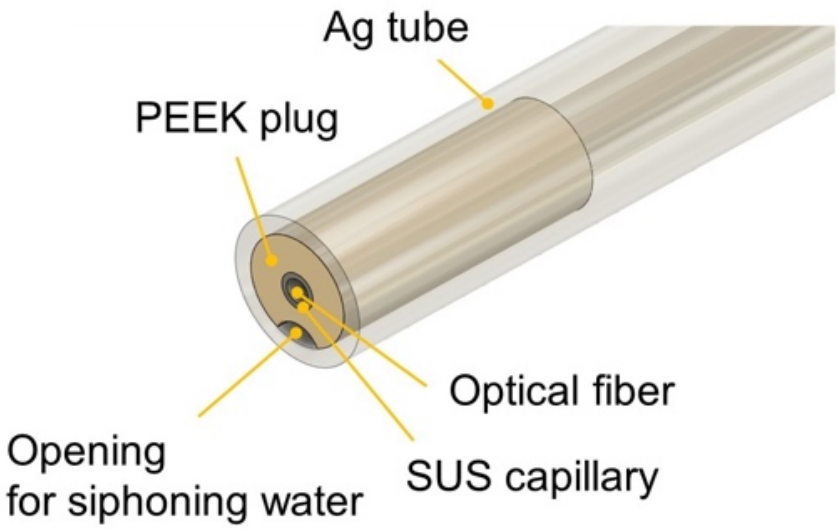

Fig. 4. Schematic diagram of the Ag999 nozzle tip for laser melting/sampling.

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Performance tests of the LMS

Sampling parameters and discreteness

First, the switch-on timing of the laser beam had to be determined and set to prevent the nozzle tip from colliding with the frozen ice-core surface. Then, to achieve smooth and efficient sampling, we needed to optimize 1) the laser power, 2) the intrusion speed of the nozzle into the melting ice core, and 3) the rate at which the meltwater is vacuumed up.

The higher the laser power, the faster the melting rate, but the meltwater must not boil. We determined an adequate laser power to be ~2.0 W in a –20 °C environment, under which conditions the meltwater never boils near the optical fiber tip. The meltwater had to be vacuumed up as quickly as possible to avoid overheating by the laser but, on the other hand, the meltwater would not have been vacuumed up efficiently had the pumping speed been too fast. As a result of trials using blocks (density ~0.93 g cm^{-3}) of frozen ultrapure water (Milli-Q water) at –20 °C and a laser power of ~2.0 W, we determined that a tube pump speed of ~5.5 mL min^{-1} was appropriate. Finally, the optimal nozzle intrusion speed to maintain a cylindrical melting region of ~3 mm in diameter was determined to be ~0.52 mm s^{-1}.

Considering the amount of meltwater collected, the time required for collection, and the pumping speed, we found that the meltwater was vacuumed up intermittently although the tube pump was operated continuously: for ~97 % of the pumping time, only air was vacuumed up.

Under the above conditions, by observing the irradiation point with the CCD camera (Fig. 1b) we ascertained that there were no signs of boiling during sampling. This result was consistent with the following rough estimation of the meltwater temperature ΔT on the assumption that the laser power of 2 W was balanced with the heat ΔH needed to melt the ice and warm up the meltwater. ΔH was estimated as:

$$\Delta H = [C_i \times 20 + H_m + C_w \times \Delta T] \times M_w \qquad (1)$$

where C_i (2.1 J $g^{-1}K^{-1}$) and C_w (4.2 J $g^{-1}K^{-1}$) are the specific heats of ice and water, respectively, and H_m (336 J g^{-1}) is the fusion heat of ice. The quantity M_w in Eq. (1), the meltwater weight per unit time, is estimated to be 0.0034 g s^{-1} using our values of melting diameter and intrusion speed. From the balance of input power with the heat used to warm and melt the ice, the meltwater temperature ΔT is estimated to be 49 °C. Given that we are neglecting heat dissipation from the melting region, the actual value of ΔT should be less. We therefore conclude that at such a mild temperature as 49 °C, negligible isotopic fractionation of stable water isotopes occurs.

Figure 5a shows a series of sampling holes in a block of Milli-Q ice, illustrating the discreteness of sampling that is possible with the LMS. The holes represent 10 meltwater samples of ~0.7 mL each, separated horizontally by 3 mm. In this demonstration, the laser power was set at ~1.8 W, the intrusion speed was 0.52 mm s^{-1}, and the pumping speed was 5.5 mL min^{-1}. In Fig. 5a, each track of the sampling holes is seen to be well separated. This shows that samplings can be very close together without any intermixing with neighboring samples, thus successfully attaining a depth-resolution of ~3 mm. In Fig. 5b a photograph taken at the beginning of the sampling

when the nozzle had intruded ~1 mm into the side of the ice is shown. The ice within the dashed line is melted by the laser irradiation.

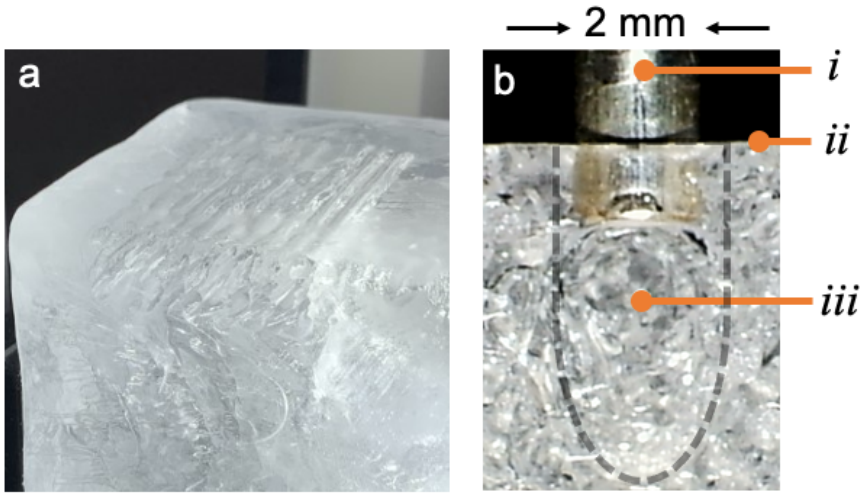

Fig. 5. (a) A photograph showing multiple cylindrical holes 3 mm apart made by the LMS in a Milli-Q ice block. (b) A photograph taken at the beginning of the sampling by CCD camera mounted on the Sampling Unit: (*i*) 2 mm ϕ Ag nozzle, (*ii*) Side of the ice, (*iii*) Meltwater zone.

Stability test for long series of samplings

To check the operational stability of the LMS in the –20 °C environment, we performed a long series of sampling tests in which 100 vials were filled with a minimal volume (~0.65 mL) of meltwater. In this test, the laser power was set at ~1.9 W, the nozzle intrusion speed was 0.52 mm s^{-1}, the pumping speed 5.5 mL min^{-1}, and the horizontal and vertical pitch 2.5 mm. This test took 8 hours 47 minutes to complete in the –20 °C environment, and yielded, without issues, an average sampling time per vial of 5.3 minutes: 4.0 minutes to collect the water sample and 1.3 minutes to cycle the laser power, evacuate the meltwater sample, and move the Sampling Unit from and to the starting position for sampling.

In this stability test with a series of 100 vials, the amount of meltwater collected was 0.65 ± 0.02 mL per vial. Thus, the time required to sample the preferred volume of 1.5 mL would be ~11 minutes. This time is considerably shorter than the measurement time per vial that is required for analysis of stable water isotopic compositions, using an isotopic analyzer; in our case, a liquid water isotope analyzer (LWIA, Los Gatos Research, Inc.) takes 41 minutes per sample analysis in our operating protocol. It is therefore concluded that the sampling rate will not be a bottleneck during offline isotopic analyses.

Contamination tests for the Sampling Unit

In the Sampling Unit, meltwater contacts the inner surfaces of various components, such as the nozzle, the transfer tubes, and the tube buffer. We therefore conducted two experiments to check for any leaching of ions from these components and to check the extent to which samples intermixed during a series of sample collections. In this first experiment, five samples of 1 mL of Milli-Q water were passed through the meltwater pathway. Then, the four

cation concentrations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in these samples were analyzed at high sensitivity by ICP-MS (Agilent 7700x). This experiment was conducted at ambient temperature.

Table 1 shows the result of the first experiment. The ion concentrations in the Milli-Q water that had been passed through the sample collection line repeatedly were too low to be a problem for ice core sample collection, since they were only slightly higher than in the original Milli-Q water, and the concentrations of ions, such as Na^+, in ice core samples are more than an order of magnitude greater than these variations. We thus confirmed that no internal contamination was admitted through the meltwater pathway inside the Sampling Unit.

In the second experiment, to check for cross-contamination, 1 mL of Milli-Q water with 100 μg L^{-1} Na^+ (~the highest observed in Dome Fuji ice core) was passed through the water sampling line in the Sampling Unit and its Na^+ concentration measured again; next, five 1 mL samples of Milli-Q water were passed through the sampling line consecutively and their Na^+ concentrations measured again by the ICP-MS. This second experiment was also conducted at ambient temperature.

Figure 6 shows the results of the second experiment. The initial Na^+ concentration of 100.3 μg L^{-1} fell to 2.4 μg L^{-1} in the sample of Milli-Q water that followed it. This indicates that a previous sample affects the subsequent sample by only ~2.4%. This ~2.4% "memory effect" is comparable with or usually significantly less than the analytical accuracy (a few μg L^{-1}) of ion analyses by ion chromatography. Furthermore, even the Na^+ concentration of 2.4 μg L^{-1} in the second sample, which was affected only by an initial sample containing the very high concentration of 100 μg L^{-1} Na^+, would be negligible compared with the variance in most ice core samples. As an example, in Fig. 6, the mean value (30.2 μg L^{-1}) after deleting peak values larger than 70 μg L^{-1} and those with the standard deviation ± 1σ (13.1 μg L^{-1}), representing the base-line variations in Na^+ concentrations in samples of a Dome Fuji shallow ice core (DF01) from 7.7 to 65.0 m (Motizuki and others, 2017; Data available at: https://ads.nipr.ac.jp/data/meta/A20181211-001), are shown, respectively, by the dashed line and by the two dotted lines. Thus, cross-contamination should not be an issue for the LMS.

It is concluded from these experiments that internal contamination and cross-contamination are both negligible with this LMS.

	Cation concentration (μg L^{-1})			
Sample run:	Na^+	Mg^{2+}	K^+	Ca^{2+}
Milli-Q water	0.022	0.057	0.010	0.018
1	0.378	0.421	0.011	0.041
2	0.254	0.300	0.064	0.028
3	0.222	0.270	0.044	0.025
4	0.218	0.277	0.022	0.025
5	0.288	0.277	0.056	0.041

Table 1. Results of the experiment passing Milli-Q water five times through the sampler. These cation analyses were performed by ICP-MS.

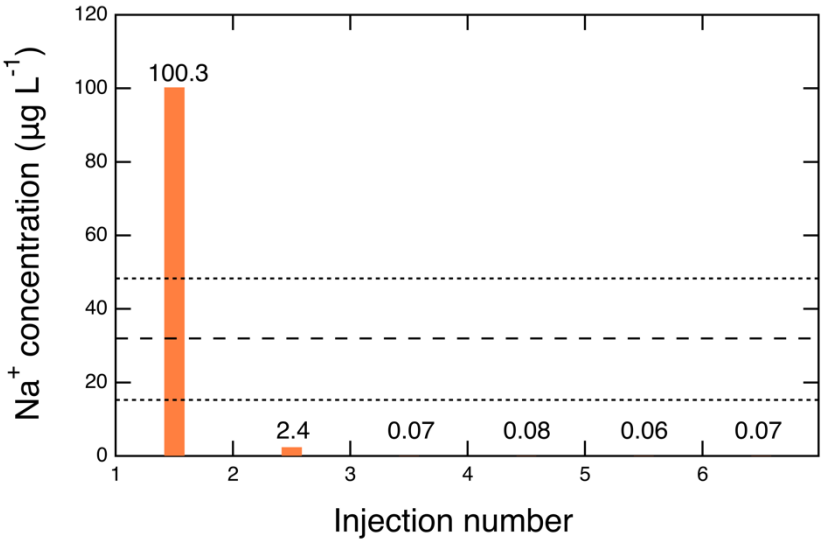

Fig. 6. Results from the cross-contamination experiment, in which successive samples of Milli-Q water were run following an initial sample containing 100.3 μg L^{-1} of Na^+. The dashed line indicates the reference mean value in baseline variations in Na^+ concentrations of DF01 core samples and the two dotted lines show the mean ± 1σ values, respectively (see text). The measurements of Na^+ were performed by ICP-MS.

Application of LMS to a Dome Fuji shallow ice core

We applied the LMS to sampling a 50 cm-long segment of a Dome Fuji shallow ice core (DFS10) drilled in East Antarctica by the 51st Japanese Antarctic Research Expedition in 2010. The segment corresponds to ~ 91.6 m in depth and is rectangular with a density of ~0.76 g cm^{-3}. In this first automatic sampling by the LMS of an Antarctic ice core, the sampling was undertaken over a depth span of 15 cm with a sampling pitch of 3 mm: 51 vials of meltwater at 3 mm depth-resolution were successfully sampled as shown in Fig. 7. The intrusion length of the sampling nozzle was set at 19.5 mm and meltwaters of 1.84 mL per vial were collected on average. This implies that almost 100% of meltwater was collected in the vials for the successive water isotope analyses.

The water isotope compositions ($\delta^{18}O$ and δD) with sampling at 3 mm pitch are shown in Fig. 8 for the deeper half of the 7.5 cm span from the depth of 91.575 m of the DFS10 core. The measurements were undertaken using a liquid water isotope analyzer (LWIA, Los Gatos Research, Inc.). The typical analytical uncertainties of the analyzer (LWIA) are given as ± 0.16‰ for $\delta^{18}O$ and ± 0.88‰ for δD. As the reference of the 3 mm pitch data, we also show in Fig. 8 our results for the segments divided by hand with 2.5 cm depth-resolution. Considering that both the 3 mm-pitch and the 2.5 cm depth-resolution measurements were subject to the above-mentioned typical measurement uncertainties, the 3 mm resolution data are generally close to the reference data although there are small systematic deviations for each 2.5 cm segment. We calculated the averages of the 3 mm resolution data within the depth span corresponding to each 2.5 cm-segment. The discrepancies between the averages of 3 mm-pitch data and the 2.5 cm data are within the ranges of ±0.4‰ and ±0.7‰ for $\delta^{18}O$ and δD, respectively, except for δD in one 2.5 cm-segment (-2.03‰). However, it is unlikely that the deviations are caused by isotopic fractionation in the LMS since the orientations of the discrepancies are not always the same. Thus, it is not

considered that our LMS causes significant isotopic fractionation, as indicated by the estimated meltwater temperature according to Eq. (1). The samples of the shallower half of the 7.5cm sampling span were lost, unfortunately, due to unexpected experimental contamination. We emphasize, however, that this does not diminish the importance of the success of the first 3-mm pitch sampling by the LMS as applied to the section of the Antarctic ice core shown in Fig. 7: This has opened up new possibilities for undertaking analyses of stable water isotopes at sub-centimeter depth-resolution which we were hitherto incapable of doing.

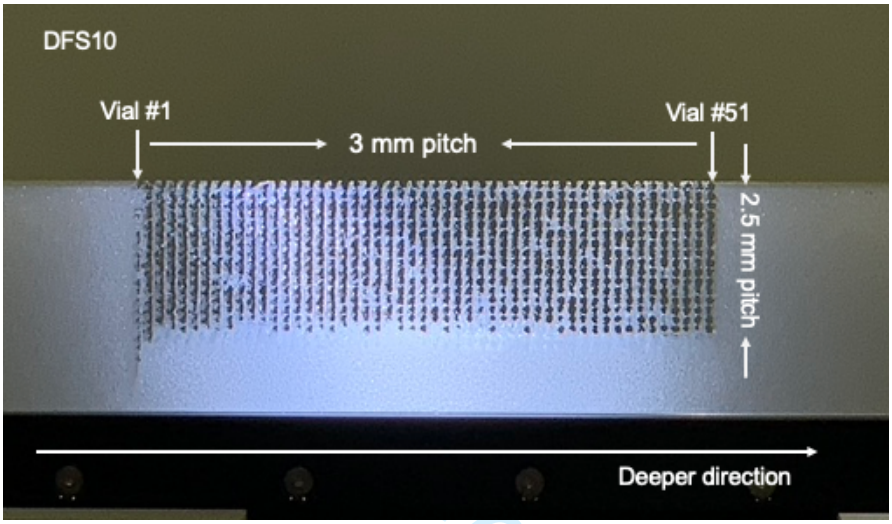

Fig. 7. A photograph showing discrete cylindrical holes after sampling (51 vials) a 15 cm-long section of a Dome Fuji shallow ice core (DFS10) drilled in East Antarctica. The sampling pitch in the depth direction of the ice core (the z-direction in Fig. 1) was set at 3 mm; the sampling pitch in the sectional direction (vertical direction in the photograph) was set at 2.5 mm. This photograph was taken from the direction of the Sampling Unit (see Fig. 1b).

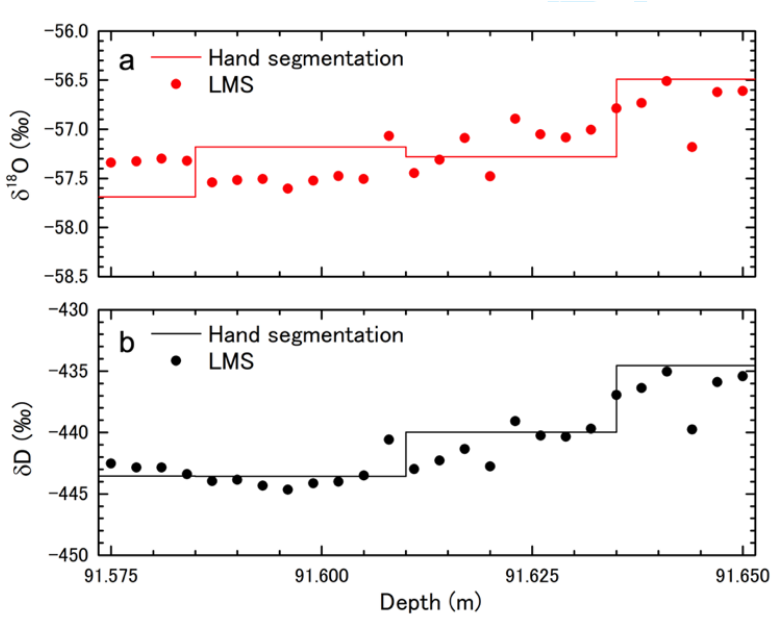

Fig. 8. (a) The depth profile of the water isotope ratios of $\delta^{18}O$ in the DFS10 shallow ice core obtained using the LMS at 3 mm pitch depth-resolution (filled circles), and hand segmentation at a 2.5 cm depth-resolution (solid line) for comparison. (b) The same as (a) but for the water isotope ratios of δD. The selected depth range, from 91.575 to 91.650 m, corresponds to the deeper half of the sampling span of the DFS10 ice core shown in Fig. 7.

Conclusion and perspective

We have successfully developed a novel laser melting sampler (LMS) for ice cores of a wide range of density. The LMS has the following advantages: 1) It can discretely sample ice cores, attaining depth-resolution as small as 3 mm with negligible cross contamination; 2) The temperature at which ice cores are melted by laser irradiation is well below the boiling point and so the compositions of stable water isotopes in the meltwater are unquestionably the same as those of the ice core; 3) Even a brittle low-density firn core could be sampled because it would be mounted on the Sliding Stage in a horizontal orientation; 4) The sampling speed of the LMS is higher than the measurement speed of a water isotope analyzer, so the sampling can proceed in parallel with the analysis without any lost time.

Since the sampling depth-resolution of the LMS is controlled by the installed software, the resolution can be set at even longer lengths or longer temporal resolutions, and so the LMS can be adapted to specific purposes of analyses. Using this flexibility, it is possible in principle to perform, for example, a combined analysis of a long-term survey of an annually resolved profile and, when an intriguing transient event is observed with annual resolution, fine-structure inspections within those single annual layers. The LMS will thus enable us to measure stable water isotope ratios at sub-centimeter depth-resolutions and reconstruct continuous, annually resolved temperature variations at deeper depths in ice cores recovered from low-accumulation sites. Seasonal variation studies of ice cores collected even at low-accumulation sites may also become possible using the LMS.

Finally, our newly-developed ice-core laser melting sampler, the LMS, may also be applicable to molecular ion analyses, especially those of molecular anions. This will require further development of the LMS, and is beyond the scope of this paper. This topic should be treated in future with an updated LMS device.

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