Supplementary Information

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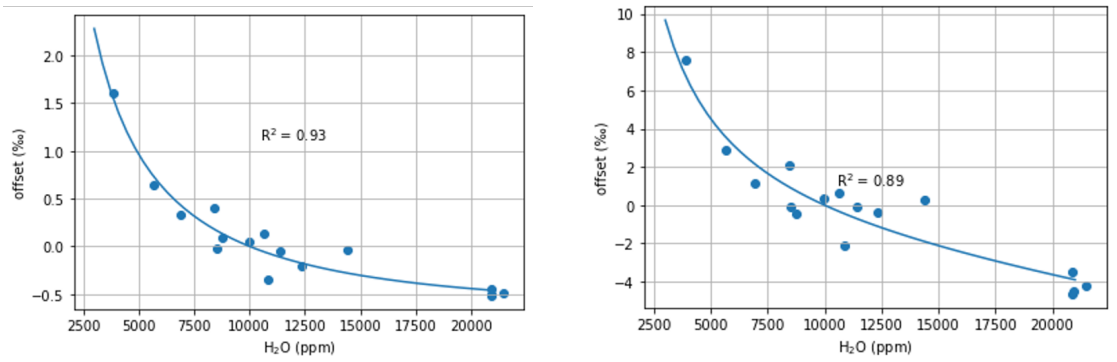
1 Humidity Response of the CRDS Analyzer

1.1 Humidity Response Curves

The response of the Cavity Ring Down Spectrometer L-2130i to different humidity levels regarding water isotope values was investigated. Constant water vapour concentrations, mixed with nitrogen gas, where introduced to the cavity in order to obtain the corresponding water isotope values. The offset values were determined (Figure S1) and used for correction of water isotopic signal when LA-CRDS experiments were performed.



(a) δ^{18}O **(b)** δD

Fig. S1 Charactherization curves for (a) δ^{18}O and (b) δD (18 July 2023) with Picarro L-2130i and autosampler in N_2 mode AP1 standard (Antarctic Precipitation collected at Concordia Station at Dome C, δ^{18}O : -54.56‰ and δD $-$ 424.23‰) was used to estimate the curve. Tie point is set at 10000 ppm (i.e. correction is = 0 at 10000 ppm)

1.2 Humidity Corrected and Raw Data

Water isotope raw data were corrected by applying the humidity curves (Figure S1) derived for each of the δ^{18}O and δD. The values are presented in Figure S2.

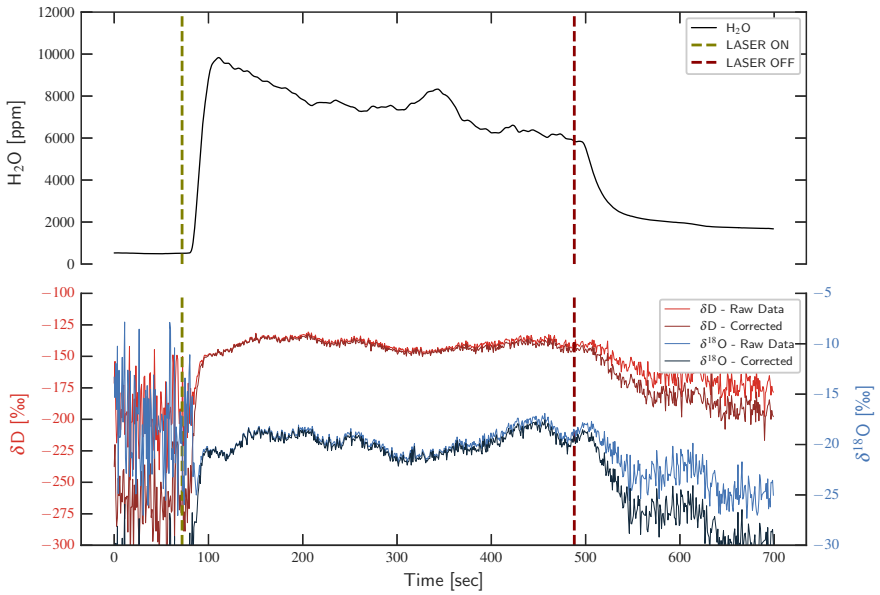


Fig. S2 Water vapour concentration and δD (light red - raw data, dark red - humidity corrected data) and δ^{18}O (light blue - raw data, dark blue - humidity corrected data) signal across a 7-minute LA raster scan of NS water isotope ice standard, marked by dashed lines.

2 Laser Parameters Optimization

For optimizing the laser ablation parameters we used ice isotope standards produced from liquid water isotope standards AP1 (Antarctic Precipitation collected at Concordia Station at Dome C) and NS. Their water isotope values are listed in Table 1. Since spot ablation measurements did not yield detectable water vapour levels with the CRDS, we employed raster scans and optimized the laser's repetition rate to 300 Hz with a dosage level of 9 or higher. Our goal was to ablate enough material, in the vapour phase, to be detected by the analyzer. In the initial test measurements (Fig. S3, AP1 1), after completing one raster scan, the next target area was a clean surface close to the previously scanned one. The laser's initial settings were an 80 µm spot size, 4.5 J cm^{-2} fluence, with a scanning dosage of 9 and flow rates for MFC1 and MFC2 were set at 0.5 L/min each. These parameters resulted in a water vapour peak below 700 ppm. Adjustments were made by increasing the spot size to 150 µm and fluence to 5.5 J cm^{-2}, which significantly increased the water vapour concentration to over 2800 ppm in subsequent peaks. Further modifications involved extending the ablation time to 30 seconds, which improved the water vapour generation to 4200 ppm.

An additional optimization step involved reducing the flow rate from 0.5 L/min to 0.15 L/min in both the ablation chamber and the inner cup (MFC1, MFC2). This modification was critical in doubling the detected water vapour levels (8800 ppm). These conditions were consistently applied in subsequent experiments using the AP1 ice standard (Fig. S3, AP1 2).

Further testing, included maximizing the laser fluence at 11 J cm^{-2} and increasing the ablation duration to 150 seconds. In this case (Fig. S3, AP1 3, Peak 1), the isotopic signal stabilized at a plateau throughout most of the raster scan. Deeper parts of the ice area were scanned by adjusting the laser focus, which was necessary after material removal created a crater. The Analyte Excite LA system employed in this study does not incorporate a traditional objective lens. Instead, it comprises an "exploded" optical design, where the individual components typically found in an objective lens are distributed along the laser beam's path and the optical path of the microscope and camera. This configuration allows the system to maintain a greater working distance while ensuring the delivery of maximum laser fluence over extended travel distances along the Z-axis. This design allowed easy refocusing when sequential ablations at greater depths were investigated. To ensure laser focus post-ablation, the laser head's position was adjusted by approximately 100-150 µm, corresponding to the depth of material removed from the sample surface. This adjustment was facilitated by the microscope/camera system, which is co-axially aligned with the laser, allowing for precise focusing by visually monitoring the sample alignment. In Fig. S3, Δz indicates the depth difference from the initial surface targeted for ablation, starting at $z = 0$. After each ablation scan, Δz increases by 100 µm, indicating the laser's progression into deeper layers. Thus, $\Delta z = 100$ µm after the first pass, $\Delta z = 200$ µm after the second and continues similarly for each subsequent scan. The water level remains relatively similar across the depth profile measurements, indicating that the focus and energy applied are adequate to ablate material, effectively counteracting any surface alterations that could potentially weaken laser-ice coupling during irradiation. However, an increase in baseline water vapour level indicates more extensive ablation, potentially making it challenging to purge residual material before subsequent measurements. This residual water vapour might affect the accuracy of subsequent isotopic readings, which can also be observed in the decreasing trend of the water isotope values of subsequent measurements.

The following measurements were conducted on a more enriched ice standard, NS (Fig. S3, NS 1). Ablation duration of 90 seconds was selected, and the laser fluence was set to 8.7 J cm^{-2}. This resulted in a relatively stable water isotope signal, while no residual vapour was observed in this case. However, for subsequent ablation at greater depths, the water vapour level follows a decreasing trend. This could be attributed to poor focusing, since the altered surface, being less flat than the initial, will appear darker in reflected light, complicating the refocusing process. In addition, the mobilization of the ablated material decreases in efficiency with crater depth, further reducing the water vapour signal. Measurements at higher fluence 9.7 J cm^{-2} (Fig. S3, NS 2) were also performed but the water vapour level, although higher, followed a similar decreasing trend.

For further investigation of parameters such as the laser energy and the sequential ablation of deeper layers of the same area, the laser fluence was set between 7 and 10 J cm^{-2}, the repetition rate was set at 300 Hz, and the spot size was the largest possible (150 µm). The selected duration of the ablation raster scan was 90 seconds across a 4 mm × 4 mm area, to ensure a detectable and relatively stable water vapour signal, while also ensuring the ablated material was effectively removed by the

continuous flow of the carrier gas within a reasonable timeframe between measurements. Dosage levels were maintained between 12 and 20 for a better signal-to-noise ratio. Flow rates for the MFC1 and MFC2 were kept between 0.1 and 0.15 $\mathrm{L\,min^{-1}}$, with lower flow rates and a pressure setting of 15-16 PSI yielding more stable and higher water vapour concentrations.

Table 1: Water isotopic composition of liquid laboratory standards.

Standard Sample	δ^{18}O [‰]	δD [‰]
AP1	-54.56	-424.23
NS	-15.37	-112.62

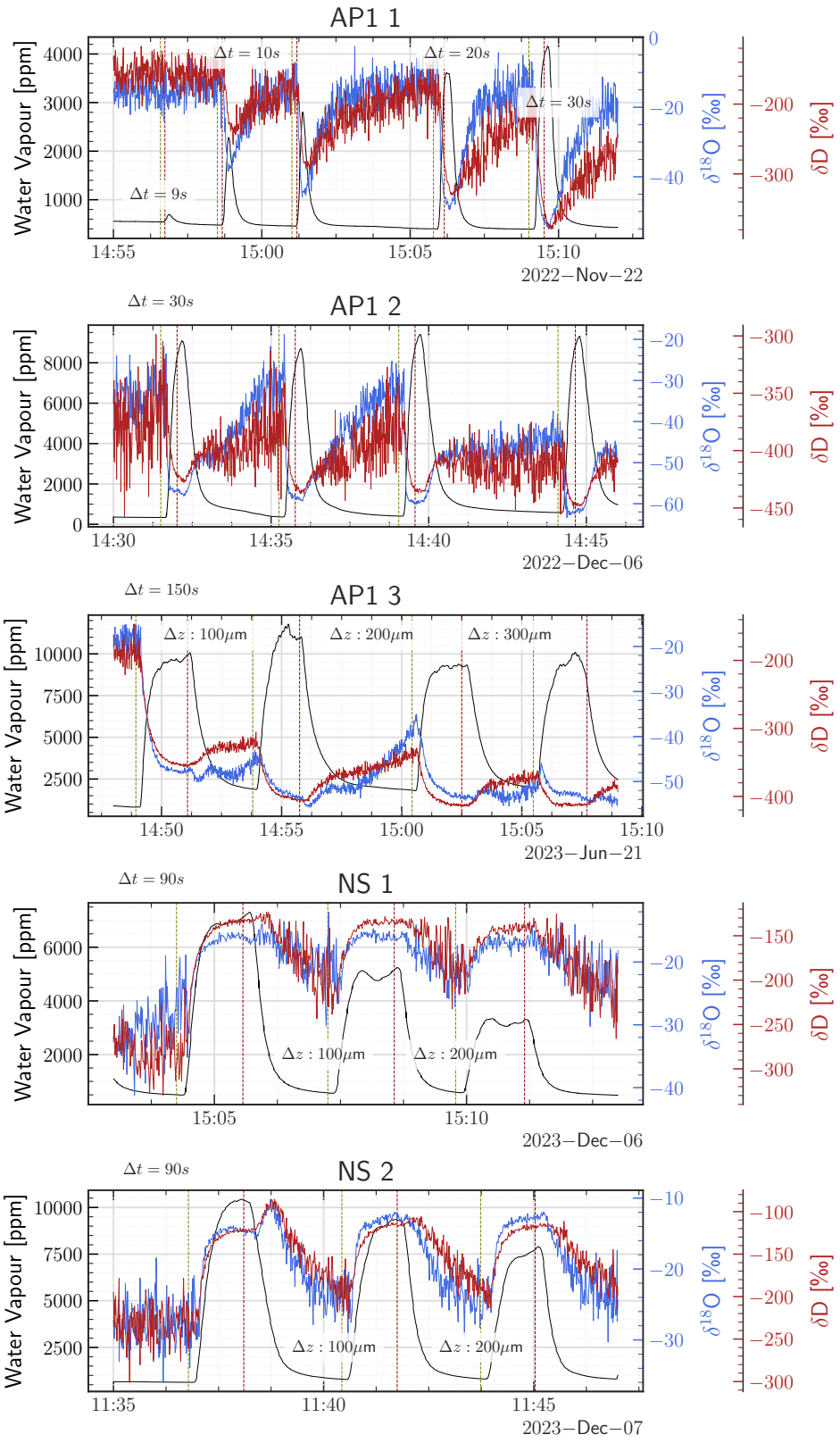
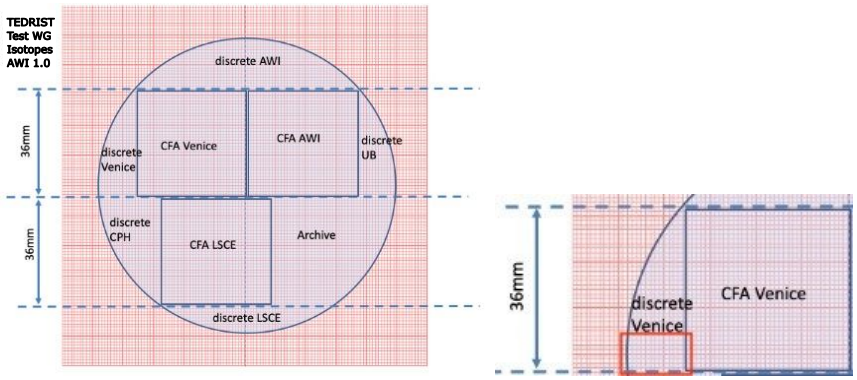


Fig. S3 LA-CRDS: Water vapour peaks detected and corresponding water isotopic values under varying experimental conditions.

3 TEDRIST Ice Core

The TEDRIST (Test Drilling) ice core was drilled at Neumayer Station in Antarctica by the Alfred Wegener Institute (AWI) drill team in January-February 2016, for testing drilling equipment. The processing of the ice core, including cutting (Fig. S4), was carried out at the AWI, and the ice sections were used to test and assess the uncertainty of isotope measurements. This ice core has also been used for intercomparison tests within the Beyond EPICA-Oldest Ice Core (BEOIC) Water Isotope Consortium. In this study, a 5cm length of the core was used to test LA-CRDS technique (Fig. S5).

3.1 Cutting Scheme



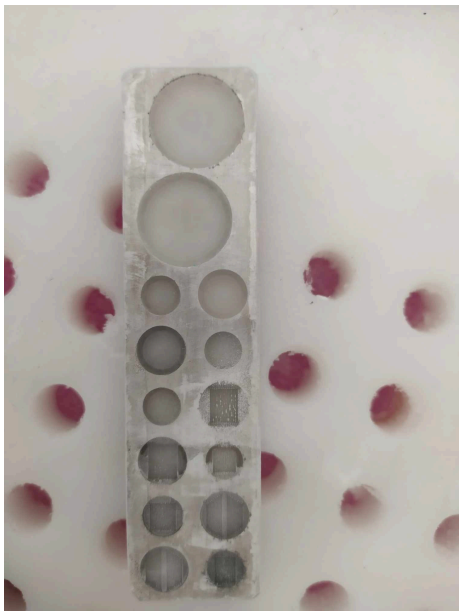
(a) TEDRIST ice core

(b) TEDRIST ice core section for LA

Fig. S4 Cutting scheme for (a) TEDRIST ice core and (b) section cut for LA-CRDS analysis.

3.2 LA-CRDS Measurement

(a) TEDRIST ice core section



(b) Ice standard samples in the metal holder

Fig. S5 TEDRIST ice core section (a) placed in the ablation chamber and water isotope ice standard samples (b) placed in the metal holder. The images show the patterns that were formed on the ice surface as a result of the LA raster scans.