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Multidecadal storage effects on the water-isotopic composition of ice cores

Kevin S. Rozmiarek[1,2], Valerie Morris[1], Brooke M. Chase[1,3], Samantha P. Wainright[1], Bruce H. Vaughn[1], Rylan Abel[1], Bradley R. Markle[1,2], and Tyler R. Jones[1]

[1]Institute of Arctic and Alpine Research, University of Colorado Boulder, Boulder, CO 80303, USA
[2]Department of Geological Sciences, University of Colorado Boulder, Boulder, CO 80303, USA
[3]Department of Environmental Studies, University of Colorado Boulder, Boulder, CO 80303, USA

Correspondence: Kevin S. Rozmiarek (kevin.rozmiarek@colorado.edu)

Abstract. The National Science Foundation Ice Core Facility (NSF-ICF) in Denver, Colorado utilizes a large walk-in freezer to store archival samples of ice cores that have been collected in polar and high-altitude regions since the 1950s. When new scientific questions arise, archival ice is allocated to research groups to perform new analyses, often using new technologies that were not available in the past. One common measurement on ice cores is water isotopes, a proxy for condensation temperature and regional atmospheric circulation. In recent years, numerous research groups have resampled archival ice cores for water isotopes, yet it is untested whether cores exposed to storage conditions for several decades have undergone isotopic fractionation. In this study, we characterize water-isotopic fractionation vs. radial distance from the surface edge of an ice core for samples originally recovered from 1962–2004. Storage effects, which result from vapor exchange between the stored core and its storage environment, show a time-dependent enrichment (0.082 and 0.010 ‰ yr^{-1} for δ^2H and $\delta^{18}O$, respectively) confined to the outer 1 cm, with no detectable change closer to the core center. A recent reanalysis of the Dye 3 ice core (southern Greenland), originally drilled in 1981, showed an average enrichment of 0.43 ‰ in $\delta^{18}O$ compared to the original analysis. This magnitude of enrichment is comparable to the expected enrichment by its storage age from empirical results of the ensemble of cores, indicating that the Dye 3 resampling may have been affected by storage effects. Expressed in paleoclimate terms, this offset corresponds to an apparent warming of 0.6–1.3 °C, depending on the isotope–temperature calibration, or to approximately 60–70 m of apparent surface elevation change. Such offsets largely cancel in analyses of relative change within a single, consistently sampled record, but can bias studies that compare absolute isotope values between cores, such as ice-core reconstructions of ice-sheet elevation, or that splice reanalyzed data onto earlier records. Based on these results, we develop recommendations for long-term storage and resampling of ice cores for water-isotopes, relevant to any ice core storage facility worldwide.

1 Introduction

Ice cores from Greenland, Antarctica, and high-altitude glaciers preserve records of past climate. (Rasmussen et al., 2014; Brook and Buizert, 2018; Bohleber et al., 2018). Following recovery, portions of many ice cores are analyzed, while others are retained for future investigations, including analyses enabled by new measurement methods. This approach preserves material

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for subsequent research (Souney et al., 2021). The Ice Memory Foundation extends this archival approach to endangered mountain glaciers by preserving ice cores in Antarctica for scientific investigations over the coming centuries (Ice Memory Foundation, 2026). At the National Science Foundation Ice Core Facility (NSF-ICF), some ice cores have been in storage for six decades, which could conceivably result in alterations to the ice and/or its chemistry. Storage-related alteration is already documented for some trapped gases: post-coring gas loss can change O_2/N_2 and Ar/N_2 ratios, particularly in the outer portions of stored ice cores (Oyabu et al., 2021). Investigators must evaluate the validity of new measurements on archival ice cores to ensure there are no storage-induced alterations to the ice compared to when that ice was originally recovered; otherwise they risk consuming not just expensive ice, but more importantly, ice collocated with a suite of other climatic measurements.

One important measurement performed on ice cores is the determination of the isotopic composition of water, which provides information about the hydrologic cycle (Dansgaard, 1964), source and site temperature (Dansgaard et al., 1982; Markle and Steig, 2026), and atmospheric circulation (Jones et al., 2018, 2023). Water-isotope measurement methodology has changed substantially over the past few decades. The introduction of continuous-flow optical systems (e.g., Gkinis et al., 2011; Jones et al., 2017) has transformed water-isotope analysis from discrete measurements of small subsections of ice (e.g., 5 cm samples measured one at a time) to continuous measurement of meter long sticks of ice stacked on top of each other, yielding millimeter-scale resolution records. The new technology and methodology, and resulting ability to measure in high-resolution, has resulted in new scientific projects that are utilizing archived ice cores to unlock new high-frequency information about the climate system (Jones et al., 2023).

The geographically diverse collection held at NSF-ICF then provides opportunities to revisit existing ice-core records using new analytical methods, making the preservation of archived samples relevant to a broad range of future investigations. Cores are stored in sealed plastic bags within cardboard cylinders with a reflective foil-like outer surface. These are placed on racks for long-term storage at temperatures well below freezing ($-36 \pm 2\,^{\circ}\mathrm{C}$ at NSF-ICF). However, frost and ice crystals routinely seen on old, archived cores indicate that exchange between the surface of the ice and water vapor in the bag headspace occurs over the multidecadal storage time of each core. Water molecules may exchange continuously between ice and water vapor in the bag headspace, including at saturation when sublimation and deposition fluxes balance. Consequently, little or no net mass loss does not exclude isotope change when the ice and vapor are isotopically out of equilibrium. Frost within storage bags indicates net deposition at some locations, supplied by redistribution from the core and/or entry of external moisture. Because the headspace may also intermittently be undersaturated with respect to ice due to core handling, the core surface slowly sublimating and redistributing across the interior of the bag. Our observations do not distinguish the relative contributions of these processes; instead, in this paper we investigate their possible cumulative imprint on ice-core water isotopes during storage and evaluate its implications for paleoclimate interpretation.

2 Methods

We investigate whether the water-isotope signal in archived ice cores is fundamentally changed during storage. We measure radial isotope profiles (from the ice core center to one of its edges, Fig. 1) from an ensemble of archived ice cores drilled

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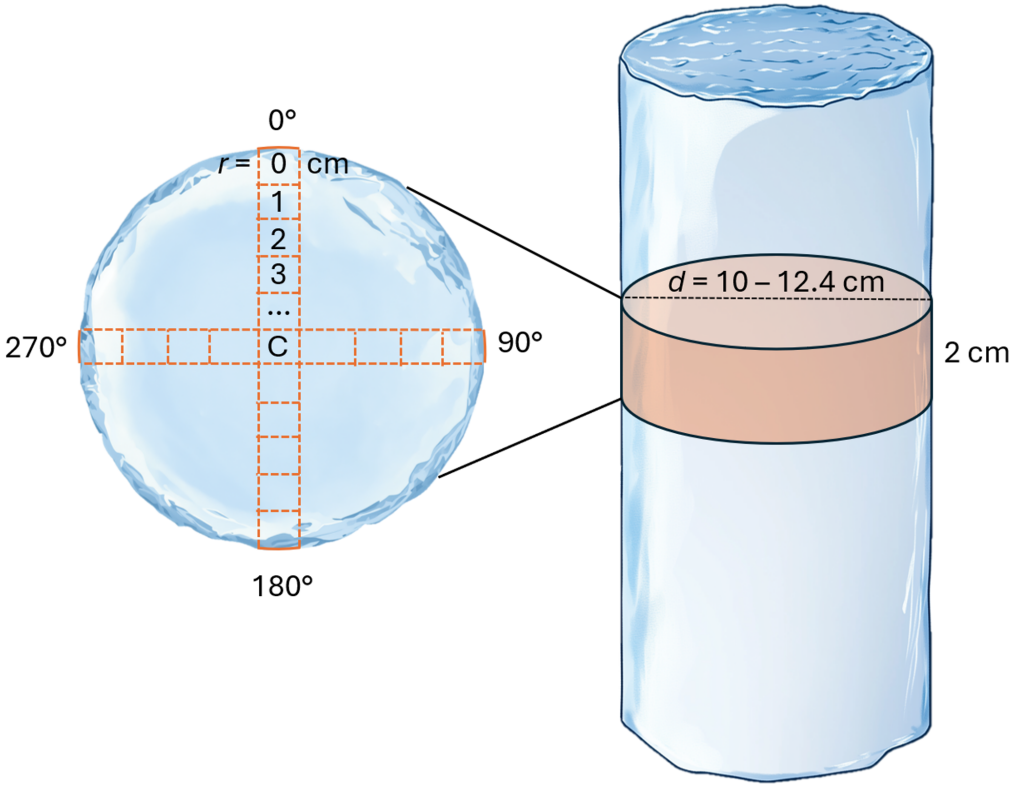


Figure 1. Schematic overview of core subsampling for cores described in Table 1. For each core, a 2 cm tall puck was selected and cut with diameter 10-12.4 cm. Each puck was additionally subsampled in a cross with directions labeled by angles. Subsamples are taken as 1 cm × 1 cm × 2 cm cuts inwards to a center piece of at least 1 cm × 1 cm size. Subsampled cuts are identified by their angle and by their radius away from the edge such that the first cut is $r = 0$ (distance 0–1 cm from the edge), $r = 1$ represents 1–2 cm away from the edge, etc.

between 1962 and 2004. This allows us to characterize the time dependence and penetration depth of storage-induced isotopic changes. We then test our results against a recent reanalysis of the Dye 3 core using the original Dye 3 water isotope record (1981; Dansgaard et al., 1982) compared to a newer high-resolution resampling of the same ice (Buizert et al., 2024). Together, these lines of evidence provide constraints on storage-induced isotopic change, clarify its relevance for resampling of archival cores, and motivate practical recommendations for ice-core storage, handling, and resampling strategies.

2.1 Water isotopes

Water isotopes are expressed in δ notation, a function of isotopic ratios (Craig, 1961). Water isotope ratios comprise the ratio of rarer, heavier isotopes relative to their lighter and more common counterparts, e.g. $^{18}O/^{16}O$ or $^{2}H/^{1}H$ (commonly D/H, where D is deuterium). From these ratios, notation expresses their value relative to internationally recognized primary reference materials, Vienna Standard Mean Ocean Water (VSMOW2) normalized to Standard Light Antarctic Precipitation (SLAP2). To

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tie measurements to primary reference materials, a suite of secondary reference waters is maintained and rigorously calibrated to VSMOW2 and SLAP2. Secondary reference waters are stored in accordance with guidelines described in IAEA technical note no. 43 (International Atomic Energy Agency, 2012).

$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right] \tag{1}$$

In δ notation (Eq. 1), δ^2H and δ^{18}O can be thought of as deviations from primary reference materials (standards) expressed in parts per thousand (‰) following Coplen (2011). We also express relative differences in δ^2H and δ^{18}O as second order isotope parameter $d_{\ln}$ (logarithmic deuterium excess) calculated as:

$$d_{\ln} = \delta'^{2}\text{H} - \left(A \times (\delta'^{18}\text{O})^2 + B \times \delta'^{18}\text{O} \right), \tag{2}$$

where $\delta'_x = \ln(1 + \delta_x)$ and $A = -28.5$ and $B = 8.47$. Note that coefficients are expressed natively and not in ‰ (Markle and Steig, 2022).

2.2 Core subsampling

We collected samples from an ensemble of six ice cores that were originally recovered from 1962–2004; each core recovery age is roughly spaced one decade apart in time. For each core, we selected a 2 cm thick "puck" of ice below the bubble close-off depth. We attempted to make each puck of similar ice depth (closest available to 100 m). Cores were selected from the NSF-ICF "deaccessed cores" list (i.e., cores that are slated to be removed from the archive inventory in the near future for varying reasons), listed in Table 1.

2.3 Water isotope analysis and calibration

Pucks were brushed and subsampled along the diameter of the puck in 1 cm × 1 cm × 2 cm cuts. As each core has a different diameter, we define the outer edges of cores as $r = 0$ and the center piece is denoted C. As such, radius $r = 0$ represents the discrete sample from 0–1 cm inwards from the edge, $r = 1$ represents 1–2 cm, and so on. Pucks were sampled along the perpendicular diameter such that the final cutting pattern was a cross. A diagram of subsampled cuts can be seen in Fig. 1.

Discrete ice samples were melted and transferred to 2 mL glass vials, which were then analyzed on a Picarro L2130-i cavity ring-down spectrometer (CRDS) coupled to an HTC PAL autosampler injection system (CTC Analytics) and Picarro V1102-i vaporization module. Calibration of the CRDS was performed following Jones et al. (2017). Individual vials were subsampled for six total injections, where only the last three injections are averaged to avoid memory effects (Schauer et al., 2016). The first standard deviation of the last three injections is 0.1 ‰ for δ^{18}O and 1.3 ‰ for δ^2H. Additional details on the calibration scheme can be found in Jones et al. (2017). Measurements were performed at the Institute of Arctic and Alpine Research's Stable Isotope Lab at the University of Colorado Boulder.

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2.4 Dye 3 reanalysis

To contextualize the potential impact of storage effects on a full ice core, we investigated the recent resampling of the Dye 3 ice core for water isotopes; this new record was first presented in Buizert et al. (2024). The Dye 3 sections used in that reanalysis are archived in Copenhagen, Denmark, rather than at NSF-ICF; many U.S. sections were stored in Buffalo, New York, before being shipped to Copenhagen (Buizert et al., 2024). Their storage temperatures, bagging, and handling histories therefore may differ from those of the cores sampled here. The new record was measured in Copenhagen with the University of Colorado continuous-flow system (Jones et al., 2017) on the Danish 0.55 m archive sections (Buizert et al., 2024). The resampled Dye 3 water-isotope record includes data obtained from different sections of ice that were left over from the original core. Samples taken at the outer edge of an available archived section of ice ($r = 0$) had visible hoarfrost, which was scraped away prior to instrumental analysis. Whenever possible, samples were instead obtained several centimeters interior to the available archived section of ice; however, the depths at which this was done were not recorded, so the exact exposure history of the sampled ice is unknown. Because the resampled record mixes surface-exposed and interior ice in an unrecorded proportion, we cannot reconstruct the exposure history along the core or isolate the storage signal directly. We can, however, estimate a plausible scale for the storage contribution under specified sampling assumptions. If the edge-to-interior contrast in water isotopes measured in the pucks is representative of Dye 3's offset and the interior ice is unaffected, mixing exposed and interior ice would reduce the measured storage anomaly relative to that of a fully exposed sample. Because the proportion and exposure history of these components are unknown, the puck relationship provides a conditional comparison rather than a strict upper bound on potential storage water isotope offsets in the Dye 3 reanalysis.

We compared the original and reanalyzed δ^{18}O records over their overlapping interval, 1779.850–1919.450 m. After removing missing isotope values, we linearly interpolated the available reanalysis measurements to the 2,793 original measurement depths, spaced at 0.05 m. We retained differences lying strictly within three standard deviations of the initial mean difference, excluding 25 comparisons and retaining 2,768 pairs. The reported mean and standard deviation describe these retained reanalysis-minus-original differences.

3 Results

In this section, we review the evidence for changes in water-isotope compositions in ice cores during long-term storage at the NSF-Ice Core Facility. The evidence falls into two categories: (1) qualitative observations of ice-core storage and handling procedures and (2) empirical observations across multiple ice cores that have been stored for varying lengths of time. Together, these lines of evidence build towards recommendations for proper storage conditions of ice cores that minimize surface–vapor exchange of water–isotopes within storage tubes.

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Table 1. Descriptors for each core sampled for a puck, separated approximately by a decade back to Camp Century. Cores are selected to have approximately the same depth with best available ice past ice close-off depth. Precise depth/age scales exist for GISP2 (Seierstad et al., 2014), South Pole (Winski et al., 2019), and Siple Dome (Buizert et al., 2021) but are incomplete or missing for Camp Century, Byrd Station, and Dominion Range.

Core name	Location	Latitude	Longitude	Depth (m)	Age (before 1950)	Diameter (cm)	Year drilled	NSF core ID
Camp Century	Greenland	77.16667	-61.13333	66.19–66.21	–	12.4	1962	CC 62
Byrd Station '71	Antarctica	-80.01667	-119.51667	637.27–637.29	–	11.4	1971	BYRD 71
Dominion Range	Antarctica	-85.25	166.16667	115.06–115.08	–	10	1984	DOMINION
GISP-2 H	Greenland	72.58333	-38.46667	189.97–189.99	648	10.2	1992	GISP2H
Siple Dome J	Antarctica	-81.65883	-148.812	105.975–105.995	786	10	1997–1998	SDMJ
South Pole 04 hole 6	Antarctica	-89.95	-17.53333	99.615–99.635	779	10.2	2004	SP04-C6

3.1 Ice-core storage and handling procedures

At NSF-ICF in Denver, Colorado, ice cores are stored on warehouse racks within a walk-in freezer. The storage temperature is maintained by active refrigeration, with a defrost cycle occurring at 08:00 and 20:00 LT daily. To maintain structural integrity and prevent frost heave of the freezer's foundation, heaters are installed within the concrete floor. The space is divided into two areas: "cold storage", where cores are stored long term, and the "examination room" where cores are processed (e.g., ice cutting using bandsaws) or analyzed for varying physical properties (e.g., electrical conductivity). The cold storage is held at $-36 \pm 2\,^{\circ}\mathrm{C}$, while the examination room is held at $-24 \pm 2\,^{\circ}\mathrm{C}$. Archived ice cores are stored in plastic bags, which are either heat-sealed (Fig. 2b) or stapled (Fig. 2c) shut, and are stored within aluminum-wrapped cardboard tubes.

Frost accumulates within both the examination room and cold storage (Fig. 2d), which likely originates from moisture input from air exchange with the outside warehouse environment or from air infiltration and defrost during the refrigeration cycle. However, NSF-ICF curators have observed that ice left exposed to the air in cold storage will eventually sublimate until it disappears, suggesting that the air outside storage tubes tends to be unsaturated with respect to ice. Within the ice-core storage tubes, frost accumulates within the plastic bags where ice cores rest (Fig. 2a). This implies that vapor exchange occurs within sealed bags that sit within the tubes even if bags don't interact with the outside unsaturated environment.

In preparing and cutting ice cores for water-isotope analyses, ice cores are left to relax in the examination room overnight to prevent fracture. Then, the top 1 mm of cores along with surface frost is scraped off and brushed away. Ice is then cut into samples for discrete analysis or into sticks for continuous-flow analysis. Opening the storage bags during preparation and sampling allows room air to replace or mix with the bag headspace. The isotopic effect of this air exchange depends on the humidity and isotopic composition of the incoming vapor, as well as subsequent conditions within the resealed bag.

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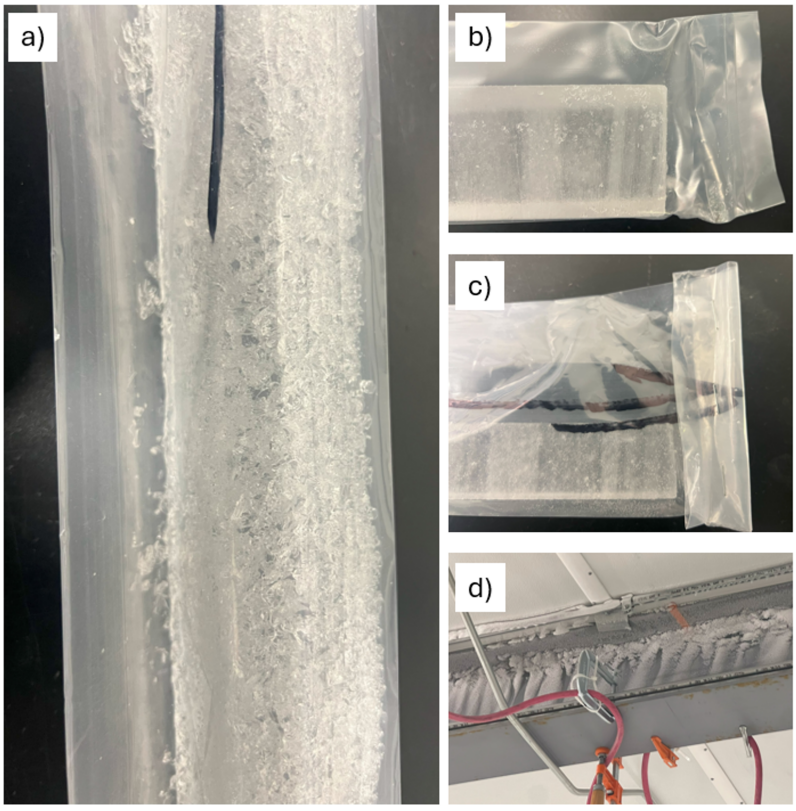


Figure 2. Photos of storage conditions inside the National Science Foundation Ice Core Facility. (a) archived core section with significant hoarfrost exchange settled at the bottom of the core bag. (b) a heat-sealed archived core. (c) a folded and stapled archived core. (d) frost accumulation on surfaces within cold storage from the introduction of vapor during regular use of the facility (Photos from Richard Nunn).

3.2 Empirical evidence for vapor exchange within storage tubes

In Fig. 3a,c, and e, we document the δ^{18}O, δ^{2}H, and $d_{\ln}$ anomaly between the center piece "C" and the edge piece of ice cores that have experienced varying amounts of storage time ($r = 0$, Fig. 1). In both δ^{18}O and δ^{2}H, the edge piece is enriched (more heavy isotopes) relative to the center piece, consistent with vapor exchange between the ice and air. The sign of these offsets does not require net mass loss from the ice to vapor, but do indicate exchange. These differences do not establish whether the affected ice experienced net mass loss, net deposition, or isotope exchange with little net mass transfer. This enrichment increases with longer storage times ($0.010\,‰\,\mathrm{yr}^{-1}$ and $0.082\,‰\,\mathrm{yr}^{-1}$ in δ^{18}O and δ^{2}H, respectively). Enrichment exceeded water isotope measurement uncertainty by the 16-year mark, as indicated by the red dashed lines. Differences in $d_{\ln}$ remain within measurement uncertainty and therefore do not provide a conclusive constraint on the mechanism responsible for the observed enrichment.

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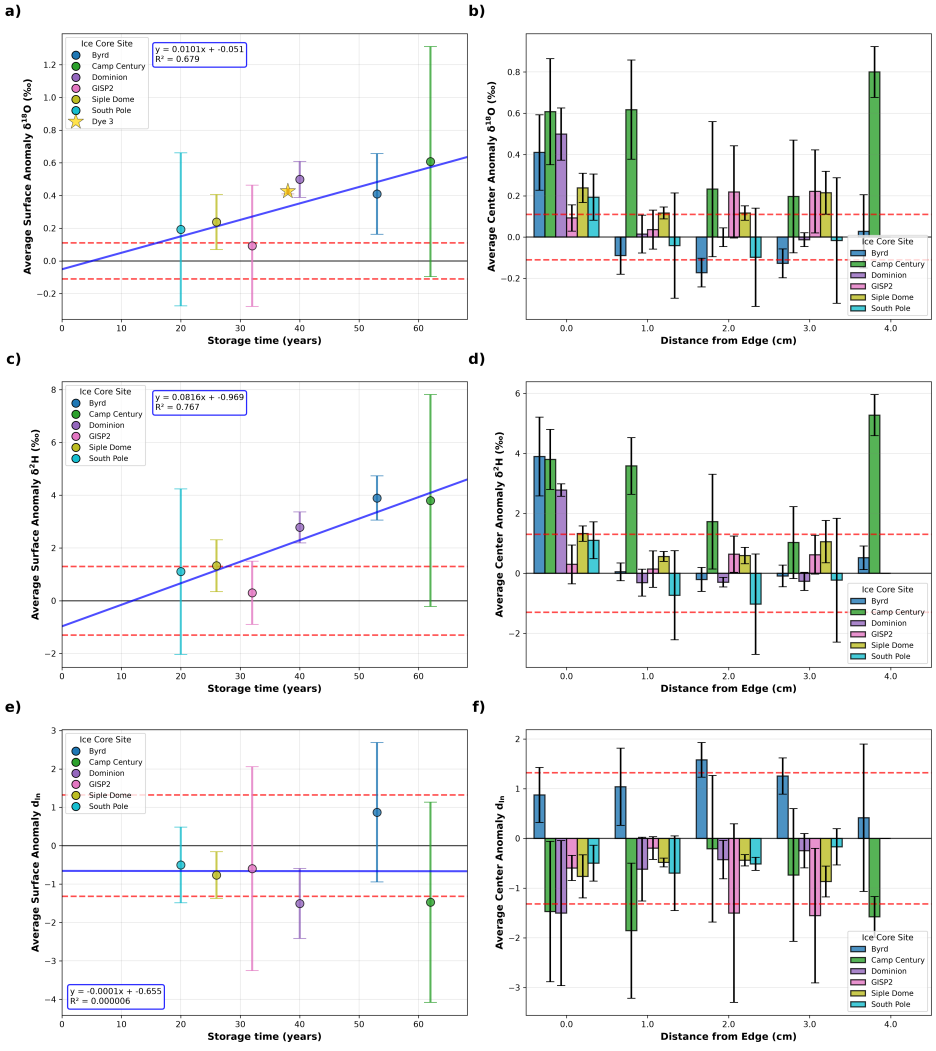


Figure 3. Results from subsampled pucks from all cores. In a), c) and e) are shown the δ^{18}O, δ^{2}H and $d_{\ln}$ differences against the center piece of pucks as a function of storage age of the puck (i.e. age from drilling to 2024 analysis). The four edge pieces are averaged for the anomaly and plotted with the standard deviation of those values. In δ^{18}O and δ^{2}H a linear interpolation is shown with equations on each respective plot. In red dashed lines are the limits of reported uncertainty for continuous-flow water isotope analysis of ice cores in Jones et al. (2017). In e), $d_{\ln}$ measurement uncertainty is determined from propagated error between δ^{18}O and δ^{2}H. In b), d), and f), are shown the anomalies for each core puck as a function of distance from edge as shown in Fig. 1. Error bars for each core are determined by the first standard deviation of all subsampled pieces not exposed to the edge. This can be interpreted both as the uncertainty of selection of the center piece as the storage-unaffected "true value" of the core and as the internal repeatability of any given puck. Each core is represented both by a different color and symbol.

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It is not necessarily true that the center piece best represents the unmodified isotopic composition of the ice, as different cores may exhibit different levels of internal variability, both from measurement uncertainty from the CRDS and its calibration (Sect. 2.3) and isotopic horizontal spatial heterogeneity unrelated to storage effects within the sampled puck. To account for internal variability, we represent the first standard deviation of all non-edge pieces ($r > 0$) as error bars (Fig. 3b,d, and f). Notably, the internal variability varies substantially across cores, with δ^{18}O standard deviations of Dominion and Siple Dome being similar to that of the isotopic measurement uncertainty (0.05 and 0.08 respectively) and GISP2, South Pole, Byrd, and Camp Century being above measurement uncertainty (0.18 ‰, 0.23 ‰, 0.23 ‰, 0.34 ‰, 2–3 times measurement uncertainty). The reason for this variability across cores is not clear, but a likely contributor is layer inclination: if annual layers are tilted relative to the core axis at depth, individual 1 cm × 1 cm subsamples may cross layer boundaries and represent climatically-distinct ice, producing horizontal isotopic heterogeneity that exceeds measurement uncertainty. Confirming this interpretation would require sampling multiple pucks from different depths with high-resolution orientation within each core (e.g., Kirkpatrick et al., 2025), which is outside the scope of the present study.

Isotopic differences with the center ice piece above measurement uncertainty in δ^{2}H, δ^{18}O, and $d_{\ln}$ do not appear deeper than the edge piece beyond the outer 1 cm (Fig. 3b,d, and f). The exception is Camp Century, whose core was significantly fractured internally, perhaps permitting exchange deeper towards the core center. The absence of detectable enrichment beyond 1 cm depth indicates that the isotopic imprint of surface exchange is confined to the outer 1 cm under storage conditions at NSF-ICF.

3.3 Enrichment between past and present measurements of the Dye 3 core

A recent resampling of the Dye 3 ice core, which had been in storage for 38 years since the original water isotope record was measured, provides an opportunity to evaluate whether long term storage can affect the water isotope measurements of an entire core (Buizert et al., 2024). The resampling of Dye 3 had a mixture of core that was exposed to storage conditions and scraped vs interior core that was not exposed to storage conditions. Scraped ice removes outer flakes but may not necessarily remove all ice affected by storage conditions. The relative amount of scraped and interior core was not recorded during resampling. The core was resampled from depth 1779.850 to 1919.450 m. Average enrichment between the reanalysis and original analysis is 0.43 ‰ in δ^{18}O, but with high variability of enrichment across the entire core (0.71 ‰, first standard deviation). The average enrichment of Dye 3 (0.43 ‰) is comparable to the expectation of storage-exposed enrichment determined from an interpolation of enrichment across all pucks in this study and storage time (0.33 ‰, Fig. 3a).

4 Discussion

4.1 Isotopic enrichment of ice core surfaces in long-term storage

The empirical relationship between storage time and observed edge-to-center difference demonstrates the impact of surface exchange. Using only the outer centimeter as a sample, core pucks showed continuous enrichment over time that exceeded

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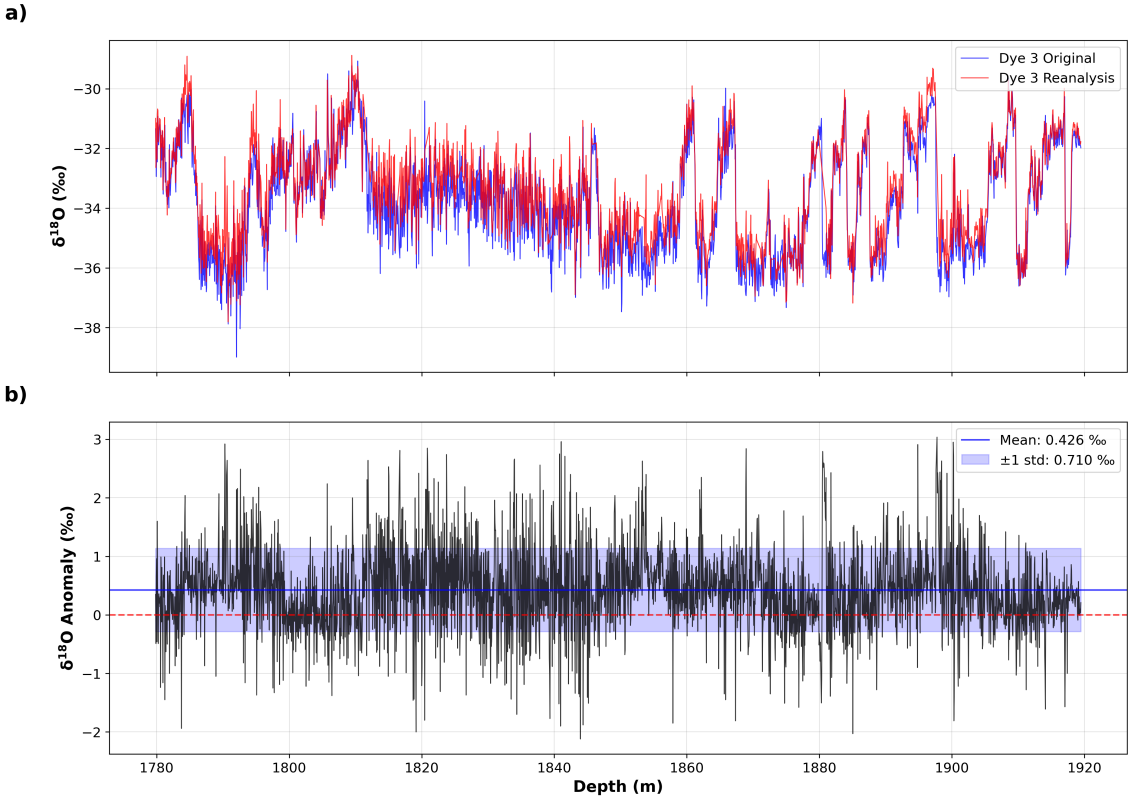


Figure 4. (a) comparison of δ^{18}O between the original Dye 3 analysis (Dansgaard et al., 1982) and modern reanalysis (Buizert et al., 2024) for their overlapping depth. Reanalysis data is linearly interpolated to match original analysis depth points. (b) δ^{18}O anomaly (reanalysis − original analysis) including mean (blue line) and first standard deviation (shaded blue region). Origin shown as a dashed red line. Measurements of δ^{2}H were not performed for the original Dye 3 analysis.

the measurement uncertainty of continuous-flow water isotope measurement of the cores (Sect. 2.3). This enrichment was approximately linear as a function of storage time, proceeding at $\sim$0.010 ‰ yr^{-1} in δ^{18}O. Samples deeper than 1 cm within the core did not show the same enrichment compared to the center piece, indicating that 1 cm is a sufficient sampling depth radially inwards for water isotope analysis. This is a meaningful amount of core as removing 1 cm from the outer surface of a 10 cm diameter cylindrical core renders 36 % of the core unsuitable for water isotope reanalysis. Archived cores are often non-cylindrical, and the relationship between penetration depth and surface area will vary according to geometry. It is possible that less than 1 cm of removal is sufficient and that the strongest enrichment is confined to a thinner outer crust. Evaluating radial distances less than 1 cm away from the edge introduces an analytical challenge to our method, as retrieving sufficient ice from a shallower radial extent requires sampling a thicker puck for a discrete water isotope measurement. Sampling over a thicker puck risks averaging across multiple depositional layers. These annual layers contain different accumulation histories, causing larger discrete samples to potentially average over isotopic excursions that skew the isotope average of the piece.

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The accumulation of frost within the NSF-ICF indicates the presence of temperature and humidity gradients. These gradients exist at doors and vents but also throughout the room (Fig. 2). Humidity gradients by themselves are not an issue for archived cores if there is little or no vapor exchange between the freezer and archived cores in their storage bags. Frost accumulation within bags demonstrates net transfer of water to deposition sites, although the relative contributions of redistribution from the core and external moisture input cannot be determined from these observations. Bag sealing methods may further increase the amount of water exchange by allowing vapor transport with the environment outside the storage bag. Heat-sealed bags (Fig. 2b) provide better isolation than stapled bags (Fig. 2c), yet frost accumulates in both. Stapled bags may expose stored archive cuts to the same outside vapor that accumulates on surfaces in storage (Fig. 2d), allowing for outside moisture exchange at the exposed core surface. The extent of this exchange and the depth of the resulting isotope signal into the core surface will determine the relative importance of this effect for water isotope resampling. Even in a perfectly sealed bag never exposed to outside air during its entire storage lifespan, a core will undergo internal vapor exchange with its surfaces. The isotopic signal from the top of the core could potentially migrate to the bottom and in between, potentially attenuating high-frequency isotope signals that would otherwise be preserved. While potentially relevant to high-frequency signal attenuation, evaluating high-frequency signal integrity is not constrained by our radial sampling design and should be a topic for future investigation.

4.2 Isotopic enrichment of Dye 3 in storage

The mean offset in δ^{18}O between the original and modern Dye 3 measurements is consistent with the enrichment expected from the 38 years of storage separating them, based on the puck relationship interpolated in this study (Fig. 3). The offset is not uniform, however: enrichment varies substantially across the resampled depths (0.71 ‰, first standard deviation). Two factors likely drive this variability. First, the radial depth sampled varied along the core (some pieces were scraped edge ice, others interior cuts) so the storage effect differs piece by piece. Second, continuous-flow analysis can draw a variable amount of edge-exposed ice into the melt head, inadvertently mixing surface and interior ice within a single measurement (Jones et al., 2017). Both factors are consistent with the record being a mixture of exposed and interior ice in unknown proportion. If surface exposure status were systematically tracked during sampling, it may be possible to mitigate the first potential cause of variability or to apply a correction to surface-exposed pieces, yielding a more accurate high-resolution water isotope record. To address the second cause, edge pieces cannot be used in analysis, though interior pieces may still exhibit internal variability (Sect. 3).

A competing hypothesis to explain mean enrichment between previous and recent measurements of Dye 3 may be differing water isotope standard ties to VSMOW. There are no continuous instrument standard ties going back in time to the original Dye 3 analysis. Without a chain of calibrations or reference to a common standard, determining if calibration offsets contributed to net enrichment is impossible. Instead, the average of the isotope offset is consistent with the enrichment expected from storage effects derived from our empirical analysis across all pucks. It is then plausible that surface exchange could account for the reanalysis enrichment but ultimately remains inconclusive given variability in the subsampling method of the archive cut during processing combined with an unknown calibration mismatch. Because the resampled record mixes exposed and interior ice, a storage-only explanation would predict a mean offset smaller than the fully exposed value. That the observed offset is

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larger suggests stronger enrichment in the outermost millimeters than the 0–1 cm average resolved by our pucks (Sect. 4.1), an additional calibration offset, or both.

4.3 Implications of storage offsets for paleoclimate interpretation

Ice-core water isotopes are converted to past site temperature through an isotope–temperature slope, the change in δ^{18}O (or δ^{2}H) per degree of temperature (Dansgaard, 1964; Jouzel et al., 1997). Two kinds of slope are used. A spatial slope is derived from the modern relationship between mean isotopic composition and mean annual temperature across many sites, for example 0.67 ‰ °C^{-1} across the Greenland ice sheet (Johnsen et al., 1989), and assumes that this geographic relationship also holds through time at a single site. A temporal slope is calibrated at a single site against an independent paleothermometer, such as borehole temperatures (Cuffey et al., 1995) or the δ^{15}N of trapped air (Guillevic et al., 2013), and describes how isotopes and temperature actually covaried through time. Because surface temperature and precipitation δ^{18}O both decrease with altitude, an analogous isotope–elevation gradient, about 0.6 ‰ per 100 m in Greenland (Johnsen et al., 1989), allows isotopic changes not explained by regional climate to be interpreted as changes in ice-sheet surface elevation (Vinther et al., 2009). Each of these conversions maps an isotope change onto a temperature or elevation change, so any non-climatic isotope offset, including storage enrichment, maps onto an apparent temperature or elevation change in the same way.

The storage effect documented here is an additive enrichment of surface-exposed ice. Its consequence for a paleoclimate record therefore depends on whether an interpretation relies on absolute isotope values or only on relative changes within a single, consistently sampled record. To express the offset in paleoclimate terms, Table 2 converts the fitted edge enrichment (Fig. 3a,c) into apparent temperature and elevation changes using published isotope–temperature and isotope–elevation slopes. These values apply to fully exposed edge ice ($r = 0$). A sample that mixes exposed and interior ice, with an exposed fraction f, carries approximately f times the tabulated bias. Because temperature is inferred by dividing an isotope change by the slope, a smaller slope converts the same isotope offset into a larger apparent temperature change. In Greenland, temporal slopes are lower than the spatial slope, by a factor of approximately two for glacial–interglacial change (Cuffey et al., 1995; Jouzel et al., 1997) and by up to approximately two for Dansgaard–Oeschger (DO) events (Guillevic et al., 2013), and so increase the apparent temperature bias of a given storage offset accordingly. For the 38-year storage interval of Dye 3, the observed mean offset of 0.43 ‰, if attributed entirely to storage, corresponds to an apparent warming of 0.6 °C using the spatial slope, 0.7–1.4 °C using DO-event temporal slopes, and 1.3 °C using the glacial–interglacial temporal slope. For Antarctic cores stored for 60 years, fully exposed ice would be biased warm by approximately 0.4–0.7 °C, depending on isotope species and region (Masson-Delmotte et al., 2008). These magnitudes are not negligible relative to the stated uncertainties of several published multi-core reconstructions, discussed below.

Analyses based on water isotope changes within a single record measured in one campaign are largely insensitive to a uniform offset, which cancels when computing anomalies, transition amplitudes, or trends. The offset matters when (1) absolute isotope values are compared between cores or against modern spatial relationships, (2) newly measured data are spliced onto, or substituted for, an existing record, or (3) the fraction of exposed ice varies along the core, as it did in the Dye 3 resampling discussed above.

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Table 2. Apparent temperature and elevation equivalents of the storage-induced edge enrichment for (a) Greenland and (b) Antarctica. Isotope offsets ($\Delta\delta^{18}$O, $\Delta\delta^{2}$H) are evaluated from the linear fits in Fig. 3a,c ($\Delta\delta^{18}\mathrm{O} = 0.0101\,t - 0.051$; $\Delta\delta^{2}\mathrm{H} = 0.0816\,t - 0.969$, with storage time t in years) and represent fully exposed edge ice ($r = 0$), except for the Dye 3 row ([†]) which is a mixure of interior and storage-exposed ice. Temperature and elevation equivalents are obtained by dividing the isotope offset by the slope given in each column header. Superscript letters in the column headers identify the source of each isotope offset or slope: [a] linear fit in Fig. 3a; [b] linear fit in Fig. 3c; [c] Greenland spatial slope, Johnsen et al. (1989); [d] glacial–interglacial temporal slope at GISP2, Cuffey et al. (1995), see also Jouzel et al. (1997); [e] DO-event temporal slopes, Guillevic et al. (2013); [f] Greenland isotope–elevation gradients, 0.60 ‰ (100 m)$^{-1}$ from Johnsen et al. (1989) and up to 0.72 ‰ (100 m)$^{-1}$ as compiled by Malmierca-Vallet et al. (2020); [g] Antarctic spatial slopes, Masson-Delmotte et al. (2008). Antarctic plateau slopes are for sites above 3300 m a.s.l.

(a) Greenland

Storage time	$\Delta\delta^{18}$O[a]	Spatial[c] 0.67 ‰ °C^{-1}	Glacial–interglacial[d] 0.33 ‰ °C^{-1}	DO events[e] 0.34–0.63 ‰ °C^{-1}	Elevation[f,*] 0.60–0.72 ‰ (100 m)$^{-1}$
(yr)	(‰)	(°C)	(°C)	(°C)	(m)
20	0.15	0.22	0.46	0.24–0.44	21–25
40	0.35	0.52	1.07	0.56–1.03	49–59
38 (Dye 3)[†]	0.43	0.64	1.30	0.68–1.26	60–72
60	0.55	0.83	1.68	0.88–1.63	77–92

(b) Antarctica

Storage time	$\Delta\delta^{18}$O[a]	$\Delta\delta^{2}$H[b]	δ^{18}O, continent[g] 0.80 ‰ °C^{-1}	δ^{18}O, plateau[g] 0.94 ‰ °C^{-1}	δ^{2}H, continent[g] 6.34 ‰ °C^{-1}	δ^{2}H, plateau[g] 9.1 ‰ °C^{-1}
(yr)	(‰)	(‰)	(°C)	(°C)	(°C)	(°C)
20	0.15	0.66	0.19	0.16	0.10	0.07
40	0.35	2.30	0.44	0.38	0.36	0.25
60	0.55	3.93	0.69	0.59	0.62	0.43

[*] Shown as a sensitivity range only: the lower isotopic lapse rates simulated for last-interglacial ice-sheet configurations by Malmierca-Vallet et al. (2020), 0.29–0.49 ‰ (100 m)$^{-1}$, would give 88–148 m for the Dye 3 offset. [†] Observed mean δ^{18}O offset between the reanalysis and the original Dye 3 record (Fig. 4), rather than the regression value. This offset reflects a mixture of exposed and interior ice, may include an inter-laboratory calibration offset (Sect. 4.2), and comes from ice archived in Copenhagen rather than at NSF-ICF (Buizert et al., 2024); the equivalents shown assume it is entirely storage-derived.

Inter-core comparisons of absolute isotope values are the most sensitive application, where reanalyzed ice introduced to an existing ensemble of cores may introduce offsets in interpretation (Vinther et al., 2009; Markle and Steig, 2026). Vinther et al. (2009) synchronized Holocene δ^{18}O records from six Arctic ice cores, including Camp Century and Dye 3, and used uplift-corrected records from the Agassiz and Renland ice caps as a reference temperature history. The residual δ^{18}O at Greenland ice sheet sites was then attributed to surface elevation change. They emphasized that all records were measured in a single laboratory to ensure homogeneity, so that inter-core differences could be interpreted as an elevation signal. A storage offset in reanalyzed ice would violate exactly this condition. Their reconstructed elevation histories carry 1σ uncertainties of $\pm$65 m at Camp Century and Dye 3. Using Greenland isotope–elevation gradients of 0.60–0.72 ‰ (100 m)$^{-1}$ (Johnsen et al., 1989;

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Malmierca-Vallet et al., 2020), the mean Dye 3 offset, if attributed entirely to storage, is equivalent to 60–72 m of apparent elevation change within an affected interval (Table 2a), comparable in magnitude to the stated uncertainty of these reconstructions. A storage-affected reanalysis substituted into such a framework would therefore introduce a bias comparable to the full stated uncertainty, and of fixed sign, with storage-enriched ice reading as an apparently lower surface elevation at the time of deposition. Because the reconstructed surface elevations decrease through the Holocene, these elevation histories are commonly referred to as thinning curves. Vinther et al. (2009) inferred approximately 600 m of surface lowering at Camp Century between 11 and 6 kyr before present and approximately 400 m at Dye 3, and Lecavalier et al. (2017) later revised the Camp Century estimate to approximately 1 km. Such curves are used to constrain and evaluate ice-sheet models of past Greenland mass loss, so an isotope bias propagates into model-based estimates of ice-sheet sensitivity to warming. Camp Century, the oldest core in our ensemble, after approximately 60 years of storage with a fully exposed edge ice would carry an apparent elevation bias of approximately 77–93 m (Table 2a). Similar inter-core residual approaches have been used to identify regional δ^{18}O gradients between Summit and NGRIP (Seierstad et al., 2014), to interpret regional departures from a common East Antarctic signal in terms of local elevation histories (Masson-Delmotte et al., 2011), and to attribute Holocene isotope trends at Byrd partly to ice-sheet thickness change (Steig et al., 2001). These studies relied on measurements of a freshly-drilled core. The concern raised here is prospective and arises if reanalyzed archive ice is merged with, or substituted for, existing records without accounting for storage exposure.

Analyses based on the amplitude of abrupt events across cores are less sensitive, because a uniform offset cancels. Guillevic et al. (2013) combined δ^{15}N-derived temperature changes with δ^{18}O at four Greenland cores over DO events 8–10, obtaining temporal slopes of 0.3–0.6 ($\pm$0.08) ‰ °C^{-1} and stadial–interstadial warmings that differ between sites by several degrees. Buizert et al. (2024) extended this calibration to Dye 3 and Renland. For Dye 3 they averaged the original δ^{18}O record (Dansgaard et al., 1982) with the resampled record examined in this study. If exposure differs systematically between stadial and interstadial ice, however, the offset no longer cancels. As an example, assigning the entire mean Dye 3 offset of 0.43 ‰ as a differential offset across a single transition with the DO 8 warmings of 8.8–11.1 °C reconstructed by Guillevic et al. (2013) would bias the inferred isotope sensitivity by 0.04–0.05 ‰ °C^{-1}, approximately half of their reported uncertainty. Realistic differential offsets are likely smaller, as storage history is unlikely to differ in a reanalysis across such warming transitions.

Glacial–interglacial comparisons across cores are sensitive whenever only part of a record is reanalyzed. Resampling campaigns typically target specific intervals, as for the Dye 3 section resampled for Buizert et al. (2024) (1779.85–1919.45 m), which lies almost entirely below the Holocene–glacial transition at 1786 m (Johnsen et al., 1989). In that case the full offset enters the glacial–interglacial difference at Dye 3, where glacial ice is generally 6–7 ‰ lower in δ^{18}O than Holocene ice (Johnsen et al., 1989), 0.43 ‰ is approximately 6–7 % of that difference. Multi-core comparisons of glacial cooling with independent temperature estimates (Buizert et al., 2021), and model–data comparisons that use glacial isotope changes across cores to constrain ice-sheet topography (Werner et al., 2018), would inherit this bias at affected sites.

Two further characteristics of storage effects could produce artifacts in inter-core studies. First, cores of different ages carry different offsets even when reanalyzed at the same time. At the fitted rate, edge ice from Camp Century (drilled 1962) and GISP2 (drilled 1992) would differ by approximately 0.3 ‰ in δ^{18}O from storage age alone (Fig. 3a). Second, we speculate

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that exposure is unlikely to be random along a core. Intervals of high scientific interest, such as glacial terminations and abrupt events, are the most frequently resampled, leaving smaller archive pieces with a higher surface-to-volume ratio, so a larger fraction of each new sample is likely to be exposed ice in precisely those intervals. Where a reanalyzed section is spliced onto earlier measurements, a near-uniform storage offset would appear as a step at the splice and could be misinterpreted as an abrupt elevation or regional climate change. Because such an offset cannot be distinguished after the fact from an inter-laboratory calibration offset (Sect. 4.2), the most robust safeguard is to record the exposure status of each sample at the time of cutting, as recommended below.

4.4 Recommendations for storage and the resampling of water isotopes of ice cores

With the observation of the multidecadal storage effects on the water-isotopic composition of ice cores, we can develop improved practices both for the storage of cores, new or archived, as well as subsampling strategies for novel high-resolution analysis of existing archives. At the surface-exposed edge, an isotopic gradient persists into the core, even after surface frost is removed. From our analysis, cuts of ice for water isotope analysis should be made at least 1 cm into the ice after approximately 16 years of storage, at which point enrichment becomes greater than current measurement precision. The distance where enrichment is greater than measurement uncertainty may be deeper within the core given longer storage time. Care should be taken with archival pieces with geometries which are not cylindrical, as this storage effect depth may exclude a significant portion of the core. If storage effects are of specific concern, replication of this study using a narrow azimuthal wedge at several depths along a resample is logistically minimal compared to the analysis of the larger full core and could be pursued alongside full core reanalysis. Sampling logs should record, for every sample, whether it includes a previously exposed surface (outer edge or cut end,) and its approximate distance from that surface. Such records would allow storage-affected data to be flagged, excluded, or perhaps corrected, and would allow reanalyzed records to be combined with earlier measurements, or compared across cores, without introducing undocumented offsets.

Sampling around affected ice and preventing exchange in the first place are complementary practices and doing both is most effective at preventing storage effects on ice core water isotopes. Minimizing storage effects can be separated into (1) preventing air exchange within storage and (2) preventing sublimation/deposition exchange at the core surface. Although dependent on temperature and local conditions, the time scale of sublimation is slow compared to the time spent during subsampling and processing, so core-air exchange considerations will only matter to storage. To minimize air exchange, core bags should be meticulously heat sealed between samplings. The common practice of stapling bags should be abandoned for any long-term storage. Any isotopic exchange is magnified on multidecadal time scales. To prevent sublimation/deposition exchange, care should be taken to ensure that cores experience minimal temperature fluctuations during storage. Additionally, temperature within a storage facility must be uniform, otherwise different core sections will experience differing magnitudes of surface exchange due to temperature dependencies on equilibrium fractionation within storage.

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5 Conclusions

With each new community ice core, a section of core is saved as an archive cut, under the assumption that future method developments will open new possibilities for analysis. The advent of high-resolution water isotope measurements warrants the reinvestigation of past cores, but do water isotope records hold up over their time in storage? To test this, we explored the relative contribution of surface effects on a series of ice cores dating back to Camp Century in 1962. We found that the surface or edge of a core is enriched relative to its interior, exceeding measurement precision after approximately 16 years of storage. This enrichment grows at a rate of $0.082\,‰\,\mathrm{yr}^{-1}$ and $0.010\,‰\,\mathrm{yr}^{-1}$ in δ^2H and δ^{18}O, respectively. The sign of these surface alterations, and relative magnitudes between the isotope species, are consistent with surface exchange between the ice and the surrounding vapor. Whether the isotope enrichment can be completely explained by equilibrium conditions or alternatively suggests interaction with, or vapor loss to, the open storage facility air outside the sample bags is not yet clear. We leave modeling of this process to future work.

In a recent reanalysis (2019) of the Dye 3 ice core by Buizert et al. (2024), water isotopes were found to be enriched on average by 0.43 ‰ in δ^{18}O relative to the original analysis. The reanalysis was done with a mixture of surface-exposed and interior core. Though the potential calibration mismatch is unknown, our analysis demonstrates that multidecadal storage effects can plausibly account for a substantial part of the observed enrichment. From this result, and from the ensemble of past cores sampled in this study, we urge investigators to pursue water isotope reanalysis from deeper within the cross-sections of ice cores, at least 1 cm from the core surface after approximately 16 years of storage, with greater depth warranted for cores of longer storage age. To further mitigate post-archival isotopic change, core bags should be heat-sealed between samplings, and the exposure status of each reanalyzed sample should be recorded at the time of cutting so that storage-affected data can be identified and, where possible, corrected. Expressed in paleoclimate terms, the enrichment of fully exposed edge ice corresponds to an apparent warming of approximately 0.2–0.8 °C after 20–60 years of storage using the modern Greenland spatial slope, and roughly twice that using temporal slopes calibrated against independent paleothermometers. The mean Dye 3 offset is equivalent to 0.6–1.3 °C or to 60–69 m of apparent elevation change, comparable to the ±65 m uncertainties of ice-core-derived Holocene elevation histories (Vinther et al., 2009). Analyses of relative change within a single, consistently sampled record are largely robust to such offsets. In contrast, studies that compare absolute isotope values between cores, splice reanalyzed sections onto earlier measurements, or use partially reanalyzed records in glacial–interglacial comparisons are vulnerable to storage-induced bias. Some process questions remain, particularly internal variability of archive cores, which may be addressed by replication of this study across additional archive cuts. The importance of understanding and limiting storage-related alteration extends to initiatives such as Ice Memory, which aim to preserve glacier archives for scientific investigations over centuries (Ice Memory Foundation, 2026).

Code and data availability. Data along with plotting and analysis code are available on Zenodo (Rozmiarek et al., 2026).

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Competing interests. The authors declare that they have no conflict of interest.

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