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MULTI-PROXY TREE-RING DATING DURING THE YOUNGER DRYAS

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ABSTRACT

The world's longest tree-ring chronology comprises thousands of oak and pine series from Germany and continuously covers the Holocene back to 12,325 cal BP. A lack of relict wood from the Younger Dryas cold reversal ca. 12,900–11,700 cal BP, however, challenges the extension of this absolutely dated ring width record further back in time. Here, we combine 646 high-resolution stable oxygen isotope and 795 radiocarbon measurements from subfossil pines that grew during the Younger Dryas at three different sites near Zurich, Switzerland, to extend the record. Coherency of the oxygen isotope variations secures internal crossdating, and radiocarbon wiggle-matching places the final 425-year-long ring-width chronology between 12,716 and 12,292 cal BP with an uncertainty of ±8 years. Our study describes an important step towards annual dating precision further into the Late Glacial period.

Keywords: Late Glacial, European tree-ring chronology, crossdating, stable oxygen isotopes, radiocarbon, AMS dating, wiggle-matching.

INTRODUCTION

The world's longest tree-ring chronology reaches back to 12,325 cal BP (Figure 1a) and consists of thousands of oak and pine series from southern Germany (Becker 1993; Friedrich *et al.* 2004; Reinig *et al.* 2018a). This unique composite of living, historical, archaeological, and subfossil wood covers the Holocene and terminates in the second half of the Younger Dryas (YD; ca. 12,900–11,700 years ago BP), the last cold spell of the Late Glacial period (Brauer *et al.* 1999, 2014). Scots pine (*Pinus sylvestris* L.) trees that were collected at several sites in Zurich, Switzerland, hold great potential to extend the absolutely dated record beyond the YD and achieve linkage to the

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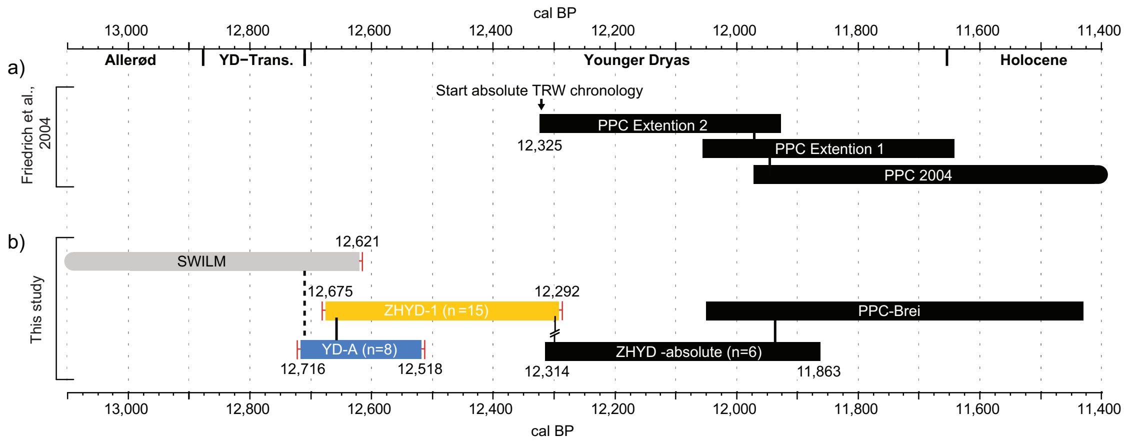

Figure 1. Temporal framework of the Swiss and German Younger Dryas TRW chronologies. (a) Absolutely dated German Preboreal Pine Chronology (PPC) and its extensions (black bars) prolonging into the YD (Friedrich *et al.* 2004). (b) Swiss *ZHYD-absolute* chronology crossdated against the absolute German Breitenthal chronology (PPC-Brei; black bars) reaching back to 12,314 BP; floating *ZHYD-1* (yellow) and *YD-A* (blue) TRW extensions dated into YD; and grey bar indicates the position of the floating Late Glacial Swiss chronology (SWILM, Kaiser *et al.* 2012). Red error bars denote the radiocarbon dating uncertainty of the floating chronologies.

floating Swiss Late Glacial Master Chronology (SWILM, Kaiser *et al.* 2012). So far, the Swiss YD samples have been grouped into three distinct periods spanning from ca. 13,160 to 11,950 BP through a combination of tree-ring width (TRW) crossdating and radiocarbon (^{14}C) wiggle-matching (see Reinig *et al.* 2020 for details). However, juvenile growth disturbance, low sample size, and enhanced wood decay in the outer sections of these samples impeded absolute crossdating (Reinig *et al.* 2018b). The combination of dendrochronological and ^{14}C dating allowed the linkage of the youngest record, Zurich-Younger-Dryas-absolute (*ZHYD-absolute*, n = 6; 12,314–11,863 BP), to the absolute chronology from Breitenthal, ca. 160 km northeast of Zurich (PPC-Brei; see Friedrich *et al.* 2004 and Reinig *et al.* 2020 for details). The two older records, the Zurich-Younger-Dryas-1 (*ZHYD-1*; n = 15) and Younger Dryas-A (*YD-A*; n = 8), however, remained floating despite ^{14}C evidence suggesting overlaps between the records (see Reinig *et al.* 2020). No conclusive link between these weakly replicated records at the termination of the Late Glacial period could so far be established.

Recent technological advancements in radioactive and stable-isotope analysis have led to higher measurement precision and new fields of application. Requiring <20 mg of organic material, ^{14}C Accelerator Mass Spectrometer (AMS) measurements (Synal *et al.* 2007; Wacker *et al.* 2010, 2014) of annual or bi-annual resolution have become feasible using the 'MIniCArbonDAtingSystem' (MICADAS). In addition, stable isotope time series of oxygen ($\delta^{18}O$) have demonstrated crossdating utility during periods of low sample replication and poor TRW crossdating success (Roden 2008; Loader *et al.* 2019; 2021, Sano *et al.* 2022). This is related to their climate sensitivity across wide geographic regions (Treydte *et al.* 2007; Labuhn *et al.* 2016; Esper *et al.* 2018; Loader *et al.* 2020; Altman *et al.* 2021; Wieland *et al.* 2022) and strong common variability between individual trees, largely independent of tree size and stand dynamics (Klesse *et al.* 2018; Vitali *et al.* 2021).

Here, we introduce a new multi-proxy dating approach that combines subfossil pine TRW series from Switzerland with high-precision ^{14}C and $\delta^{18}O$ measurements to develop and date a 425-year-long chronology from the YD.

MATERIALS AND METHODS

Approximately 400 Scots pines (*Pinus sylvestris* L.) were excavated between 1973 and 2013 at five sites in the vicinity of Zurich, Switzerland (Kaiser *et al.* 2012; Reinig *et al.* 2018a; Figure 2). For each subfossil sample, TRW was measured at a precision of 0.01 mm on two or more radii after

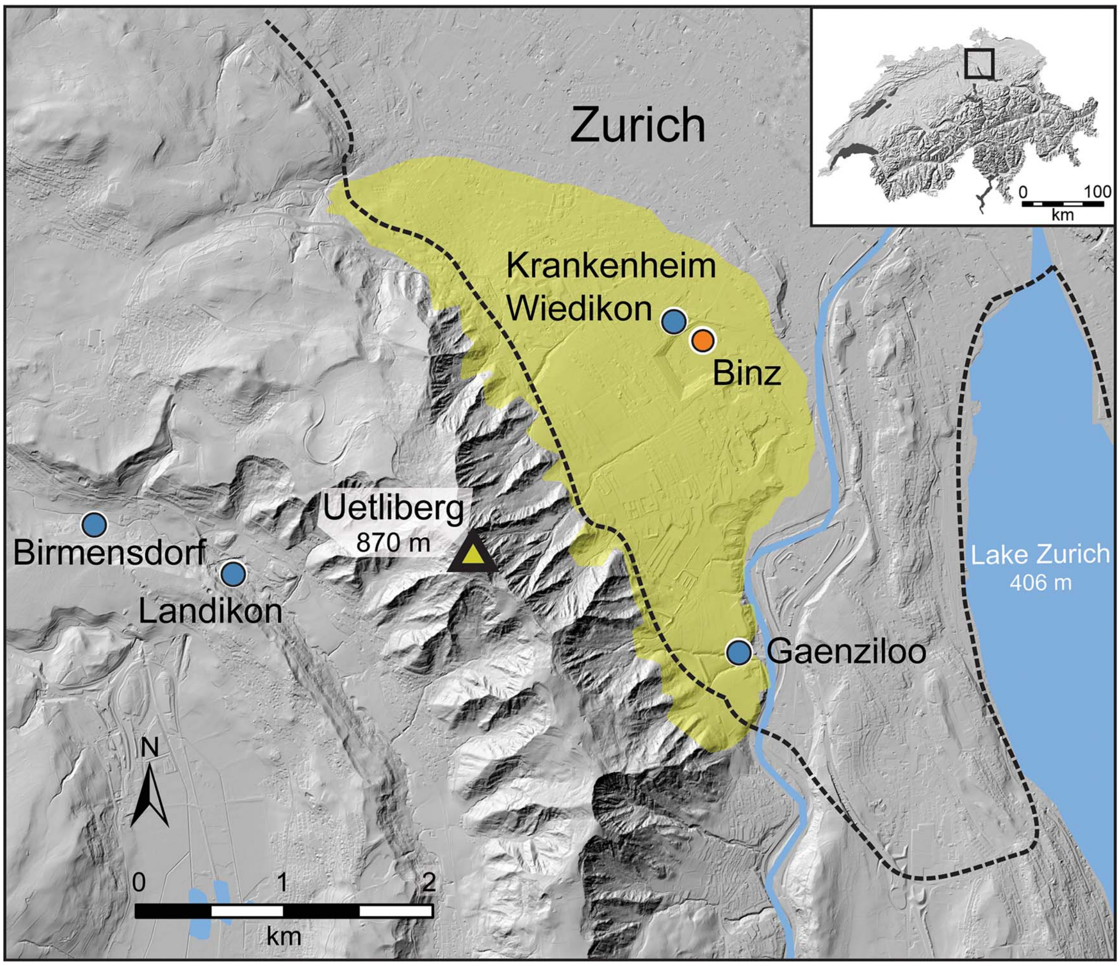

Figure 2. Map of the LG subfossil tree finds in Zurich, Switzerland. The four sites discovered by Kaiser *et al.* (2012; blue dots) are supplemented by the BINZ site from 2013 (Reinig *et al.* 2018b; orange dot). Dashed line indicates the rough city borders of Zurich, whereas the extent of the clay deposit preserving the subfossil wood along the slopes of the Uetliberg is indicated in yellow.

surface sanding to a fineness of 400 grains per inch. Although distributed over almost 2700 years and spanning the Bølling into the Preboreal (ca. 14,200–11,500 years cal BP), most subfossil wood falls into the Allerød (Schaub *et al.* 2008), and only a few trees have initially been radiocarbon-dated to the YD (Reinig *et al.* 2018a). Further dendrochronological assessment of this unique material resulted in tentatively crossdating four pines from the Gaenziloo site (GAEN), three pines from Krankenheim Wiedikon (KHWI), and eight pines from Binz (BINZ) into the floating *ZHYD-1* chronology (Reinig *et al.* 2018a, 2020). The floating *YD-A* chronology comprised eight pines (Kaiser *et al.* 2012) from GAEN. Decayed and heavily disturbed TRW sections were excluded at the outer part of the *YD-A* samples. Secure TRW crossdating between the two chronologies was, however, not successful because of short segment lengths and growth disturbances (Figure 1b).

For this multi-proxy comparison, five Scots pine (*Pinus sylvestris* L.) samples from the *ZHYD-1* chronology (GAEN0027, GAEN0102, BINZ0026, BINZ0073, KHWI0030) and one sample from the *YD-A* record (GAEN0012) (Table 1) were selected for high-resolution ^{14}C and annual δ^{18}O measurements based on sample length and chronology position. Additional ^{14}C measurements

Table 1. Characteristics of the TRW and $\delta^{18}O$ of the selected *YD-A* and *ZHYD-1* trees. SD, standard deviation; Lag-1, first-year autocorrelation; calculated over the common period of both TRW and $\delta^{18}O$ measurements.

					TRW				$\delta^{18}O$			
Tree series	Chronology	Start (ca. cal BP)	End (ca. cal BP)	No. of Years	Mean (mm)	Median (mm)	SD (mm)	Lag-1	Mean (‰)	Median (‰)	SD (‰)	Lag-1
GAEN0012	*YD-A*	12658	12606	53	1.21	1.12	0.40	0.70	26.24	26.25	0.73	0.19
GAEN0027	*ZHYD-1*	12641	12525	117	1.45	1.37	0.58	0.85	25.52	25.62	1.51	0.51
GAEN0102	*ZHYD-1*	12661	12477	185	1.52	1.51	0.57	0.71	27.81	27.92	1.21	0.48
BINZ0026	*ZHYD-1*	12630	12531	100	1.58	1.53	0.60	0.77	27.96	27.94	1.30	0.54
BINZ0073	*ZHYD-1*	12575	12425	151	0.55	0.51	0.25	0.74	27.36	27.38	0.91	0.18
KHWI0030	*ZHYD-1*	12470	12426	45	0.62	0.56	0.20	0.50	27.79	27.72	1.12	0.25

were performed on KHWI0031 from *ZHYD-1* and GAEN0007 and GAEN0008 from *YD-A* (Supplementary Material Table 2), placing the total number of ^{14}C results at 795. Tree rings were manually cut with a scalpel in annual or bi-annual resolution, if feasible (see Supplementary Material Table 2 for details), providing at least 20 mg of organic material for each sample. Special care was taken to prevent contamination from neighbouring tree rings. High-precision ^{14}C AMS measurements were performed at the Laboratory of Ion Beam Physics, ETH-Zurich, on the MICADAS (Sookdeo *et al.* 2019). Holocellulose was extracted using the base-acid-base-acid method (Nemec *et al.* 2010), bleached, and graphitized with an AGE system (Wacker *et al.* 2010). The ^{14}C blanks, standards, and references were continuously cross-checked in accordance with the ETH quality protocol (Sookdeo *et al.* 2019), ensuring the accuracy and comparability of the resulting ^{14}C dates. TRW measurements were used to evaluate the relative position of the new ^{14}C measurements within and between trees, whereas ^{14}C wiggle-matching (Bronk Ramsey 2001) against independent decadal ^{14}C data from New Zealand Kauri trees (Hogg *et al.* 2016) provided the temporal position of the samples during the YD using a χ^2-test (Wacker *et al.* 2014). As the IntCal20 radiocarbon calibration curve (Reimer *et al.* 2020) is predominantly based on Swiss ^{14}C data, no independent calibration was possible.

For the five trees from the *ZHYD-1* chronology (Table 1), as well as for one additional tree from the *YD-A* chronology (GAEN0012; Reinig *et al.* 2020; Kaiser *et al.* 2012), holocellulose was extracted (Boettger *et al.* 2007) from selected rings based on wood quality and temporal placement, and homogenized via ultrasonic treatment (Laumer *et al.* 2009) using a HD3100 sonotrode (Hielscher, Berlin, Germany) for annual $\delta^{18}O$ measurements. The $\delta^{18}O$ values are relative deviations of the $^{18}O/^{16}O$ ratio from the international standard VSMOW in per mil. A total of 646 annual $\delta^{18}O$ values were produced at a precision of <0.2‰, following pyrolysis at 1420°C in an elemental analyzer (PYRO-cube, Elementar, Hanau, Germany) connected to an Isotope Ratio Mass Spectrometer (IRMS, Delta Plus XP) via a Conflo III interface (Thermo Fischer Scientific, Bremen, Germany; Weigt *et al.* 2015).

All resulting TRW and $\delta^{18}O$ measurements were visually and statistically crossdated using *t*-values (t_{BP}; Baillie and Pilcher 1973) and Gleichläufigkeit (Glk) indices, as well as utilizing COFECHA (Holmes 1983). ARSTAN (Cook *et al.* 2007) was used to remove trends from TRW and $\delta^{18}O$ data by applying 50-year cubic smoothing spline (Cook and Kairiukstis 1990) to each series. Pearson's correlation coefficients (r) were calculated to evaluate TRW and $\delta^{18}O$ covariance using R 3.0.1 (R Development Core Team 2018) and the package dplR (Bunn 2008). Detrended TRW and $\delta^{18}O$ series were z-scored to facilitate visual comparison. The annually resolved $\delta^{18}O$ measurements thus provided precise dating, after ^{14}C and TRW established the most likely, however still tentative, placement.

RESULTS AND DISCUSSION

Chronology Development

The combined assessment of TRW, high-resolution ^{14}C, and annual $\delta^{18}O$ measurements allowed for the crossdating of 23 Swiss subfossil trees from *YD-A* and *ZHYD-1* into a single

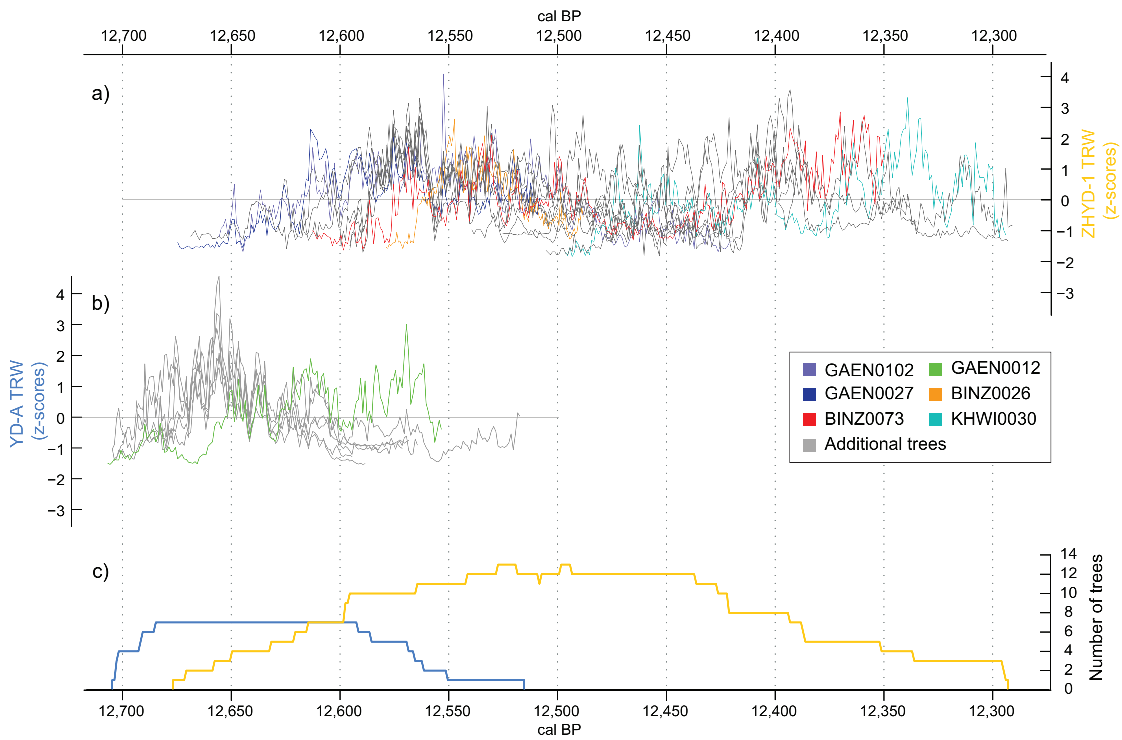

Figure 3. Z-scored TRW measurements of **(a)** the floating *ZHYD-1* ($n = 15$) and **(b)** floating *YD-A* chronology ($n = 8$), and **(c)** their corresponding temporal replication. Colors denote the selected trees used for high-resolution ^{14}C and $\delta^{18}O$ measurements; grey denotes additional trees in the individual records.

425-year-long YD composite chronology. The inclusion of the additional tree-ring proxies beyond TRW was essential to overcome sparse replication, juvenile growth disturbances, and wood decay towards the bark in all samples. The 384-year-long *ZHYD-1* record shows visual and statistical TRW covariance among the 15 individual trees (Figure 3a). The record's inter-series correlation (Rbar) of 0.39, however, suggests partially unsynchronized tree growth among the various sites. The reduced Rbar between distinct sites is likely affected by sample replication. Although the trees of the best-replicated site BINZ ($n = 8$) reach 0.54, Rbar of the less-replicated sites GAEN ($n = 4$) and KHWI ($n = 3$) are 0.29 and 0.35, respectively. It is important to note, however, that given the overall weak sample replication of the individual sites, TRW disturbances within single trees (Figure 3) may bias statistical comparisons. Resolving these issues could only be achieved through sample replication. The BINZ material links the oldest GAEN and youngest KHWI trees in the *ZHYD-1* record. The dendrochronologically obtained *ZHYD-1* crossdating is supported by 635 high-resolution ^{14}C measurements. Wiggle-matching of the ^{14}C dates of the individual trees at their tentative TRW position shows excellent agreement within the ^{14}C uncertainties (typically $<$10 years; Figure 4a). Only a narrow window for wiggle-matching uncertainty remains when compared to the SH Kauri ^{14}C record. The ^{14}C dates from *YD-A* suggest an overlap of ca. 160 years with *ZHYD-1*. With a total of eight trees and a length of 199 years, the *YD-A* record (Kaiser *et al.* 2012) is well-replicated over the initial 140 years (Figure 3b). However, replication rapidly decreases thereafter (Figure 3c), as seen in the increased chronology variability over the most recent 60 years. Additionally, the average growth rate sharply decreases during these final years (Figure 3b). Despite the higher sample replication of GAEN trees in *YD-A* to *ZHYD-1*, Rbar reaches only 0.16. This can be traced back to disturbances and partial decay at the outer section of the samples influencing the

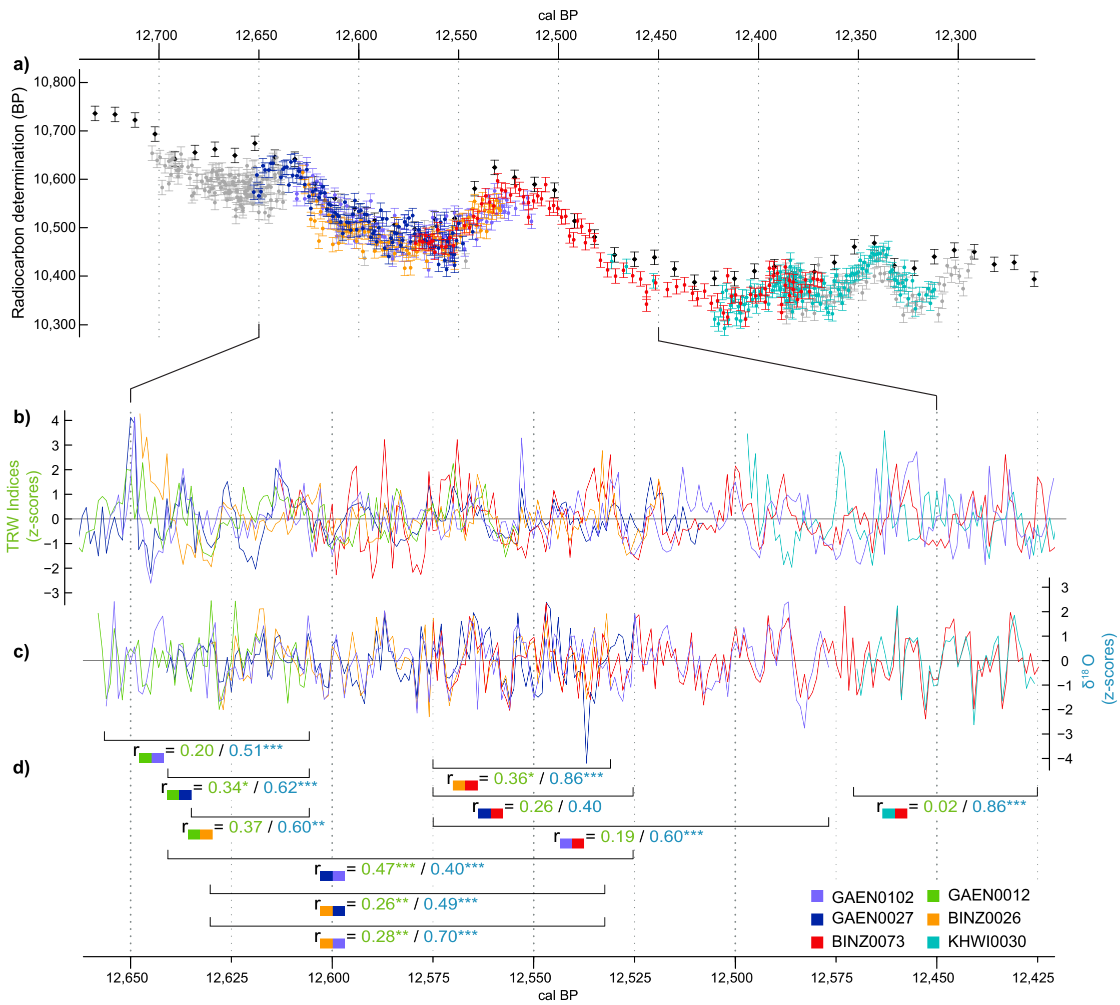

Figure 4. Comparison of ^{14}C, TRW, and δ^{18}O crossdating between trees from *ZHYD-1* and *YD-A*. **(a)** 795 high-resolution ^{14}C measurements from five *ZHYD-1* trees selected for this study and additional three trees from the Swiss YD ^{14}C record (grey; Supplementary Material Table 2) wiggle-matched against the adjusted Southern Hemisphere Kauri ^{14}C record (black diamonds, Hogg *et al.* 2016). **(b)** TRW crossdating position from five trees from *ZHYD-1* and GAEN0012 (*YD-A*) within ^{14}C wiggle-match window (z-scored), **(c)** and their corresponding annual δ^{18}O values (z-scored). **(d)** Comparison of statistical cross-correlations (*r*-values) between TRW (green) and δ^{18}O (blue) over their common period ($p < 0.05$*, $p < 0.01$**, $p < 0.001$***).

TRW patterns (Figure 3b). The youngest 35 years are represented by only one tree (GAEN0008) that bridges the gap to *ZHYD-1*. With a $t_{BP} = 3.0$ and Glk = 58, the TRW link between *YD-A* and *ZHYD-1* is tentative as ^{14}C wiggle-matching does not allow for annual precise placement.

Thus, high-resolution ^{14}C measurements of tree-ring sequences (Wacker *et al.* 2014) have been predominantly utilized to depict single atmospheric ^{14}C events (Büntgen *et al.* 2018), achieve subsequent dating of floating material (Oppenheimer *et al.* 2017), and provide calibration during recent centuries (Brehm *et al.* 2021, 2022). The application of this technique to individual samples to secure dendrochronological crossdating of Late Glacial wood is unique and one of the first attempts reported here. Wiggle-matching to the independent SH ^{14}C Kauri record is applied to support the dating, although the decadal resolution of the Kauri record does not allow for precise positioning, so a dating uncertainty of ±8 years remains.

The $\delta^{18}O$ coherencies substantially exceed those of TRW, supporting the tentative TRW crossdating. Within *ZHYD-1,* the $\delta^{18}O$ data of samples GAEN0102, BINZ0026, BINZ0073, and KHWI0030 show good coherency with means ranging from 27.36‰ to 27.96‰ and variability of 0.91‰ to 1.30‰ between ca. 12,661–12,425 cal BP (Table 1). Lower $\delta^{18}O$ values are observed for GAEN0012 ($\bar{x}$ = 26.24‰) and GAEN0027 ($\bar{x}$ = 25.52‰). GAEN0012 also indicates a lower standard deviation of 0.73‰ whereas GAEN0027 reaches 1.51‰ (Table 1). The latter also shows distinct depletion in ^{18}O of 1.80‰ after ca. 12,559 cal BP (Supplementary Material Figure 1). The detrended $\delta^{18}O$ series of the five *ZHYD-1* trees correlate well at their tentative TRW crossdating positions (Figure 4d, Supplementary Material Table 1). Within *ZHYD-1,* the geographically closer sites BINZ and KHWI are highly correlated ($r > 0.8$, $p < 0.01$), whereas the correlation between BINZ and the remoter GAEN site is weaker. GAEN0027 correlates at $r = 0.49$ ($p < 0.01$) with BINZ0026 over 98 years, whereas the final 49 years of GAEN0027 correlate at $r = 0.40$ ($p = 0.062$) with BINZ0073. Over only 43 years, the two trees from BINZ (BINZ0026 and BINZ0073) correlate at $r = 0.86$ ($p < 0.01$); similarly, BINZ0073 versus KHWI0030 also correlate at $r = 0.86$ ($p < 0.001$) over 30 years. GAEN0102, the longest $\delta^{18}O$ measurement in *ZHYD-1*, underscores the generally good correlation between the individual trees reaching $r = 0.40 – 0.70$ (Figure 4d).

In addition to the strong statistical agreement of $\delta^{18}O$, the visual high-frequency synchronism after detrending and z-scoring further supports the crossdating results (Figure 4c). The same is observed for GAEN0012 from *YD-A*, for which $\delta^{18}O$ variations indicate a secure match to the three trees from *ZHYD-1* (Figure 4c), confirming the former tentative link between the two YD records. The increase in replication to 23 subfossil trees from Zurich will improve the likelihood of future crossdating of subfossil tree finds. Low replication and growth disturbances are common features when dating historical or subfossil wood and challenge secure crossdating. This study demonstrates the strength of high-resolution ^{14}C and $\delta^{18}O$ data during periods of low sample replication and when TRW crossdating is uncertain.

Chronology Implications

The multi-proxy dating approach and the temporal placement of the YD chronology are important steps towards an absolutely dated tree-ring record throughout the Late Glacial. For the first time, the gap between the absolutely dated Swiss YD tree-ring record and the floating SWILM (Kaiser *et al.* 2012) could be securely bridged with additional samples. The new Swiss composite record is ^{14}C wiggle-matched to ca. 12,716–12,292 cal BP with an uncertainty of ± 8 years (2-σ). *ZHYD-absolute,* in combination with the continuous SH ^{14}C Kauri record, to which the floating and absolute Swiss records are firmly aligned, provides a highly resolved and independent ^{14}C reference for YD wiggle-matching. Any additional temporal shift of the floating Swiss record is thus excluded. A common overlapping period of ca. 22 years between the floating and absolute Swiss records is proposed through ^{14}C. This overlap is short and the sample replication low, however, limiting further extensions of the absolute chronology back in time. The excavation of additional samples and measurement of additional high-resolution ^{14}C and $\delta^{18}O$ data are required to secure this linkage further. Wiggle-matching of SWILM ^{14}C evidence to the ^{14}C YD chronology restricts dating uncertainty to only ± 8 years (2-σ).

All high-resolution ^{14}C samples were submitted to the IntCal20 Working Group and are included in the latest calibration curve (Reimer *et al.* 2020). The SH ^{14}C Kauri record spanning across the YD provided temporal guidance for the wiggle-matching to our Swiss record (Reinig *et al.* 2020). The decadal resolution of the SH data is now improved by our high-resolution ^{14}C measurements. These annually resolved YD ^{14}C data represent a crucial anchor point for improved wiggle-matching of YD chronologies and ^{14}C measurements and will foster a more accurate ^{14}C placement in the YD. Proxy records comprising ^{14}C dates can be reassessed and positioned according to this improved accuracy, possibly disentangling proxy discrepancies and depicting a more detailed insight into the Late Glacial environment.

Implemented as an annually resolved, precise crossdating tool in this study, tree-ring δ^{18}O further indicates its potential as an additional climatic proxy as far back as the Late Glacial. Even though the δ^{18}O replication varies strongly over time, the statistically robust high-frequency signal of δ^{18}O likely suggests a common climatic driver. These results are independent of tree stand structure and data correction on the year-to-year variability. Different trees and sites have been shown to display high synchronicity in δ^{18}O on a regional scale in modern samples (Treydte *et al.* 2007; Saurer *et al.* 2012; Esper *et al.* 2018; Klesse *et al.* 2018; Vitali *et al.* 2021). Large-scale weather patterns and temperature fluctuations have been reported to influence the δ^{18}O composition in tree rings, with the covariance being particularly strong in the high-frequency domain (Treydte *et al.* 2007; Esper *et al.* 2018; Vitali *et al.* 2021). Even though the described multi-proxy dating approach is labor-intensive and costly, we see a strong potential for future applications. Römer *et al.* (2023) recently overcame dating uncertainties in TRW and maximum density measurements through a combined stable isotope and ^{14}C approach despite low sample replication in the early part of a chronology. Despite the significant investment, turning to more specialized tree-ring proxies should be considered a supplement or alternative to classical parameters if precise and independent dating is essential. To improve dating success within this study, low-frequency trends within the individual δ^{18}O series have been removed (Esper *et al.* 2010). It is, however, important to note that the records contain low-frequency variability that could represent long-term climate information (Büntgen *et al.* 2021). The local driver of δ^{18}O high-frequency synchronicity and trends requires further exploration. Nonetheless, our results outline the potential to retrieve additional insights into supra-regional climate or source-water forcing, as well as Late Glacial climatic conditions and fluctuations.

CONCLUSIONS

We present a 425-year-long TRW chronology from 23 subfossil pines from Zurich, Switzerland, dated between 12,716 and 12,292 cal BP with an uncertainty of ±8 years (2-σ). A total of 646 annual δ^{18}O values and 795 ^{14}C dates are used to test and verify the initial dendrochronological dating of the YD TRW data. The improved multi-proxy Swiss YD chronology represents an essential step towards an absolute Late Glacial tree-ring record back to ca. 14,226 cal BP, which will further aid the assessment of environmental and climatic changes.

AUTHOR CONTRIBUTIONS

FR initiated the study, and all authors contributed to the discussion and interpretation. FR measured tree-ring width, AS, GG, and LW prepared and measured radiocarbon, and GG, MS, MP, and FR prepared and measured stable isotopes. FR and UB wrote the paper with input from all authors.

DATA AVAILABILITY STATEMENT

All data used in this study are either available in Supplementary Materials or are made available upon request.

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