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Seasonal divergence between soil water availability and atmospheric moisture recorded in intra-annual tree-ring δ¹⁸O extremes

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Abstract

Intra-annual variability of tree-ring oxygen stable isotopes (δ¹⁸O) can record seasonal climate variability and a tree’s ecophysiological response to it. Variability of sub-annual tree-ring δ¹⁸O maxima and minima, which usually occur in different parts of the growing season, may exhibit different climatic signals and can help in understanding past seasonal moisture conditions, especially in Asian monsoon areas. We developed minimum and maximum tree-ring δ¹⁸O series based on sub-annual tree-ring δ¹⁸O measurements of Pinus massoniana at a humid site in southeastern China. We found that interannual variability in minimum tree-ring δ¹⁸O is primarily controlled by the July–September soil water supply and source water δ¹⁸O, whereas the maximum latewood tree-ring δ¹⁸O is primarily controlled by the relative humidity (RH) in October. The maximum of variability of earlywood tree-ring δ¹⁸O records the RH of October of the previous year. We used minimum and maximum tree-ring δ¹⁸O to develop two reconstructions (1900–2014) of seasonal moisture availability. The summer soil water supply (July–September self-calibrated Palmer drought severity index) and the RH in fall show contrasting trends, which may be related to late-growing seasonal warming leading to a high vapor capacity and high atmospheric moisture. Our findings are valuable for research that aims to explore seasonal moisture changes under anthropogenic climate change and the ecological implications of such contrasting trends.

1. Introduction

Tree-ring cellulose oxygen stable isotopes (δ¹⁸O) can provide a reliable annual or sub-annual (seasonal) climate proxy, especially for temperate regions with high humidity and precipitation during the growing season [1, 2], such as the East Asian monsoon regions. Tree-ring δ¹⁸O is determined by the variation of source water δ¹⁸O, evaporative enrichment in leaf water during the transpiration process, biochemical fractionation during sucrose synthesis, and oxygen atom exchanges between organic compounds and xylem water [3–7]. All of these processes are directly or indirectly related to climate conditions. As a result, tree-ring δ¹⁸O can be used to explore the variability in climatic variables, including precipitation (PRE) [8, 9] and atmospheric moisture conditions (i.e. vapor pressure deficit (VPD) and relative humidity (RH)) [10, 11]. In East Asian monsoon regions, for instance, annual mean tree-ring δ¹⁸O has been used to reconstruct the variability in regional precipitation and sea-surface temperature (e.g. [8, 12, 13]).

The use of tree-ring δ¹⁸O, as well the δ¹⁸O of water bodies (i.e. precipitation, rivers, and water vapor) and other δ¹⁸O-based proxies, to explore the hydrological cycle and climate is rooted in climate-driven
variability in precipitation δ¹⁸O and fractionation in proxy δ¹⁸O [14, 15]. Generally, the δ¹⁸O composition of precipitation is impacted by temperature, in which the heavier isotopes are favored under high temperatures, and the effect of the amount of precipitation, in which the portion of heavier isotopes decreases with increasing elevation and the amount of precipitation [14]. In southeastern China, however, intra-annual precipitation δ¹⁸O variability showed neither a local effect of the amount of precipitation nor a temperature effect [16, 17], which challenges the determination of the climatic signals driving δ¹⁸O variability in proxies such as tree rings and speleothems.

Because the timing and duration of formation differ between earlywood (start) and latewood (end of the growing season), intra-annual δ¹⁸O values from different sections within a tree ring are possibly related to different seasonal climate variables [10, 18]. Such intra-annual values, including annual maximum and minimum tree-ring δ¹⁸O, can provide new insights into our understanding of how different climate variables affect tree physiological processes and mechanisms on a sub-seasonal scale [9, 19, 20]. For example, minimum tree-ring δ¹⁸O mainly tracks minimum precipitation δ¹⁸O and can therefore provide a biomarker for crossetting in tropical regions [20, 21] and for specific climatic events, such as tropical cyclones and El Niño years [22, 23]. Maximum tree-ring δ¹⁸O may reflect the magnitude of the leaf-level δ¹⁸O fractionation due to its strong relationship with RH and water demand [2, 4]. Nevertheless, analyses of intra-annual δ¹⁸O variability and the climatic interpretation of the values of tree-ring δ¹⁸O extremes have been limited to a few studies at multi-decadal scales only [9, 12]. The study of intra-annual tree-ring δ¹⁸O extremes can therefore help us to interpret climatic signals in δ¹⁸O-based proxies and to detect seasonal climate changes.

We analyzed tree-ring δ¹⁸O of Pinus massoniana from the Hengshan Mountains in southeastern China at sub-annual resolution. We determined multiple sequential sections per ring, which allowed us to analyze interannual variability in the minimum and maximum tree-ring δ¹⁸O over the past 115 years (1900–2014). We hypothesize that annual minimum and maximum tree-ring δ¹⁸O have different climatic signals controlled by source water variability or the atmospheric moisture-demand environment, as those are the most important drivers of tree-ring δ¹⁸O variability. We then used our series of tree-ring δ¹⁸O extremes to reconstruct seasonal moisture variability. Our study aims to improve our understanding of the limiting factors driving seasonal- to decadal-scale variability of the value of tree-ring δ¹⁸O extremes, as well as the effect of warming trends on the seasonal moisture balance over the 20th century.

2. Data and methods

2.1. Sampling site and climate

We collected tree-ring samples from Pinus massoniana, a widespread conifer species, near the Zhurong Peak (112.7°E, 27.27°N, 603 m a.s.l.) at a natural reserve in the Hengshan Mountains in southeastern China (figure 1(a)). The site is located at a slope of ca 20 degrees without obvious evidence of anthropogenic land use and with limited tree-to-tree canopy competition. The soil type at the site is gleysols in the world reference base for soil resource 2014 (equivalent to a silty clay loam soil listed by the U.S. Department of Agriculture) with a soil depth of about 50 cm [24]. Dendrometer and dendro-anatomy experiments at nearby sites indicate that the regional Pinus growing season lasts from late March to early November [25, 26].

We used monthly meteorological data from the nearby Nanyue station (112.75°E, 27.25°N, 1130 m a.s.l.; 1953–2014) from the China Meteorological Data Service Center (http://data.cma.cn/en). We included monthly mean, maximum, and minimum temperature, PRE, monthly evaporation (EVP), monthly RH, and monthly sunshine hour duration (SSD) in our analysis. We calculated monthly VPD using monthly RH and mean temperature [27]. To study the relationship between tree-ring δ¹⁸O and water availability for soil, we used monthly self-calibrated Palmer drought severity index (scPDSI) values derived from the Climatic Research Unit (CRU) 4.0 dataset [28] (1901–2014) for the region (112.5°–113°E, 27°–27.5°N).

Our study site is located in a region with a monsoon climate [29], which is characterized by a wet spring (March–May) and relatively dry autumn (October–November). Temperatures and SSD are higher and precipitation is lower in July–August compared to spring (March–May) (figures 1(b) and (c)).

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2.2. Tree-ring stable isotope analysis

We extracted two cores per tree from 36 trees using a 12 mm increment borer. We sanded the cores, measured the tree-ring width, crossdated the tree-ring series, and checked the dating results using standard dendrochronological methods [30]. The tree-ring cellulose δ¹⁸O procedure and measurements are labor-intensive, time-consuming, and expensive. Moreover, reliable tree-ring δ¹⁸O chronologies have been developed from as few as four trees [1, 31]. We therefore selected five crossdated cores from four mature trees (table S1; 110–180 years; one tree with one core for 1901–2006 and another core for 2007–2014) without missing rings and developed a subannual isotope chronology from 1900–2014 for each core. We discarded the earliest 20–80 years of the rings of each core to avoid potential juvenile effects [32].
Figure 1. Location, climate diagrams, and monthly precipitation (PRE) δ¹⁸O pattern of the study site. (a) The map shows the locations of the sampling site, the meteorological station, the Global Network of Isotopes in Precipitation (GNIP) site (Changsha), and the Isotope-incorporated Global Spectral Model (IsoGSM) gridpoint. (b) PRE and mean temperature. (c) Monthly sunshine duration hours (SSD) and RH. Climate data (1953–2014) are from the Nanyue meteorological station. (d) PRE δ¹⁸O from the IsoGSM model and from the Changsha station in the GNIP network for their common period of 1988–1992.

Despite a reported lack of age-related trend in tree-ring δ¹⁸O [32–34]. For each of the five cores, we systematically split each ring into multiple and sequential 200 µm thin sections, using a rotary microtome (HM340, Thermo Scientific, Waltham MA, USA). Sections of 100 or 150 µm were used for some of the narrowest rings. This thin sectioning method yielded between 4–42 sections per ring (figure S1). We noted for each thin-sectioned sample whether it was derived from earlywood or latewood. We then extracted α-cellulose [35] and measured the δ¹⁸O of the α-cellulose (uncertainty ≤ 0.2%; supplementary material S2).

2.3. Statistical analyses

For each ring of each core, we assigned a proportional position to each thin-sectioned sample relative to the start of the ring, by dividing the relative position of the sample in the sequence of sub-annual sections by the total number of sections that the ring was split into. We then determined for each ring the mean δ¹⁸O, and the magnitude and the position of the maximum and minimum of the sub-annual δ¹⁸O values, as well as of the maximum δ¹⁸O for earlywood and latewood separately. For the time series (1900–2014) of each of these five tree-ring δ¹⁸O parameters, we evaluated the coherency between the five cores using the mean correlation between all pairs of series (Rbar) and expressed population signal (EPS) with 35 year lags over 15 year running windows in the ‘dplR’ package [36, 37]. We then averaged the tree-ring δ¹⁸O series from the five cores for each of the five tree-ring δ¹⁸O parameters separately. Finally, we assessed linear trends and calculated the correlations with each other for the five tree-ring δ¹⁸O parameter series. The maximum latewood tree-ring δ¹⁸O from the current year and the maximum earlywood tree-ring δ¹⁸O from the following year shared a strong common signal (r = 0.82; 1901–2014); we thus averaged these two maxima as a maximum composite tree-ring δ¹⁸O time series.
We used Pearson’s correlation analysis ($p < 0.05$) to evaluate the climate signal in the six tree-ring $\delta^{18}O$ series (the five averaged and one maximum composite tree-ring $\delta^{18}O$ series) using the R package ‘treeclim’ [38]. We also calculated partial correlations using the ‘seascorr’ function [38] to evaluate the climatic signal while controlling the influence of a variable at various seasonal windows.

We calculated Pearson correlation coefficients between the six tree-ring $\delta^{18}O$ series and monthly and seasonal precipitation $\delta^{18}O$ data from the 20th Century Isotope Reanalysis (IsoGSM) model simulation (1953–2010) [15] at the nearest grid point (112.5°E, 27.6°E; supplementary material S3). We validated IsoGSM precipitation $\delta^{18}O$ data by comparison with observations at the Changsha site (113.1°E, 28.2°E) from the GNIP database (1988–1992). The modeled and observed precipitation $\delta^{18}O$ showed coherent intra-annual variability (figure 1(a)).

To detect the main controlling factors of the variability for the tree-ring $\delta^{18}O$ parameters, we used a stepwise multivariate regression model (supplementary material S4) and decomposed the contributions of the variables using the commonality analysis in the R ‘yhat’ package [39]. We then determined the main controlling factors of the minimum and maximum composite tree-ring $\delta^{18}O$ based on their contributions.

### 2.4. Tree-ring $\delta^{18}O$-based climate reconstruction

We used two linear regression models to reconstruct climate variability using two tree-ring $\delta^{18}O$ parameters (annual minimum $\delta^{18}O$ and maximum composite $\delta^{18}O$) as independent variables and climate targets (July–September scPDSI and the RH in October, respectively) as dependent variables. Climate targets were selected based on the strongest correlations with the tree-ring $\delta^{18}O$ parameters, as well as reasonable mechanisms. For both reconstructions, we applied a split-period cross-calibration and verification by partitioning the target observation data into two periods (1953–1983 and 1984–2014). Reconstruction skills were assessed by adjusted explained variance ($R^2_{adj}$), reduction of error (RE), and coefficient of efficiency (CE) [30]. We also compared multidecadal variability and trends of the two reconstructions using 20-year and 90-year locally estimated scatterplot smoothing (LOESS) methods.

### 3. Results

#### 3.1. Position and temporal variability of the maximum, minimum, and mean tree-ring $\delta^{18}O$

The annual minimum tree-ring $\delta^{18}O$ values were evenly distributed between earlywood and latewood tree rings and were mostly located in the central part of the tree ring (figure 2(a)), which often involves the transition from earlywood to latewood. In southeastern China, this transition typically happens between July and September [25, 26, 40], when precipitation $\delta^{18}O$ is low (figure 1(d)).

The maximum tree-ring $\delta^{18}O$ values showed a bimodal sub-annual distribution, with some rings showing an annual maximum early in the earlywood and other rings late in the latewood, and the maximum values were on average 5% higher than the minimum $\delta^{18}O$ values (figures 2(b) and (e)). The maximum earlywood $\delta^{18}O$ typically occurred at the start of the growing season (March–April; figure 2(c)), corresponding to high precipitation $\delta^{18}O$ (figure 1(d)) [17]. The maximum latewood $\delta^{18}O$ occurred near the ring boundary (figure 2(d)).

All five tree-ring $\delta^{18}O$ parameter series (minimum, maximum, mean, maximum earlywood, and maximum latewood) showed a strong coherence between trees (figure S2), with $Rbar$ values ranging from 0.34–0.83, except for the maximum earlywood $\delta^{18}O$ for the periods 1908–1942 and 1962–1996 (table S2). EPS values were higher than 0.72 throughout and reached 0.92 for the annual mean and minimum tree-ring $\delta^{18}O$ series.

The five tree-ring $\delta^{18}O$ parameter series were significantly ($p < 0.05$) correlated with each other (figure S3), but differed in their long-term trends (figure 2(e)). Correlations were weak between the minimum and maximum $\delta^{18}O$ time series ($r = 0.24–0.31$), as well as between the maximum earlywood $\delta^{18}O$ and the maximum latewood $\delta^{18}O$ ($r = 0.34$) of the same ring. However, the maximum latewood $\delta^{18}O$ was strongly correlated with the maximum earlywood $\delta^{18}O$ of the following year ($r = 0.82$). All (annual, earlywood, and latewood) maximum $\delta^{18}O$ series showed decreasing trends over time ($-0.017% -0.011%$, and $-0.016%$ per year, respectively, $p < 0.05$), but the annual minimum $\delta^{18}O$ showed a gradual increase ($0.011%$ per year, $p < 0.05$).

#### 3.2. Climatic signals in tree-ring $\delta^{18}O$ series

Most tree-ring $\delta^{18}O$ parameters were negatively impacted by water availability, and less affected by temperature, but they showed differences in the seasonality of their responses. Specifically, the annual minimum and mean tree-ring $\delta^{18}O$ series were significantly ($p < 0.05$) negatively correlated with monthly and seasonal scPDSI from April–November ($r = -0.37$ to $-0.67$; figures 3(a) and (b)), with the RH in July and August ($r = -0.25$ and $-0.36$), and with PRE from April–August ($r = -0.26$ to $-0.38$) and October ($r = -0.30$). They were significantly ($p < 0.05$) positively correlated with SSD in July ($r = 0.32$) and August ($r = 0.30$), EVP in August–October ($r = 0.28–0.40$), and VPD in August ($r = 0.26$) to October ($r = 0.36$). The annual minimum tree-ring $\delta^{18}O$ showed the strongest correlations with July–September scPDSI ($r = -0.65$) (figures 3(a) and S4), and this correlation is significant even after removing the influence of precipitation (figure 4(a)). The mean tree-ring $\delta^{18}O$
showed similar but slightly weaker climate response patterns compared to the annual minimum tree-ring $\delta^{18}O$, with the strongest correlation with scPDSI ($r = -0.55, p < 0.05$) and RH ($r = -0.55, p < 0.05$) in October. It also showed a significant correlation with July–September scPDSI ($r = -0.52, p < 0.05$; figure 2(b)).

The annual maximum tree-ring $\delta^{18}O$ showed weak climate signals, with the strongest negative correlation ($p < 0.05$) with the RH in October of the previous year ($r = -0.46$) and the current year ($r = -0.55$; figure 3(c)). The maximum earlywood tree-ring $\delta^{18}O$ was significantly ($p < 0.05$) correlated with the previous year’s climate, particularly of October, including the scPDSI from October–December ($r = -0.39$ to $-0.45$), the RH in October ($r = -0.66$), and SSD, VPD, and EVP in October ($r = 0.62, 0.64$, and 0.59, respectively), but was weakly correlated with climatic variables in the current year (figure 3(d)).

The maximum latwood and composite (maximum latwood + maximum earlywood of the following ring) tree-ring $\delta^{18}O$ were influenced primarily by climate in the late growing season. The maximum latwood $\delta^{18}O$ was strongly ($p < 0.05$) correlated with climate in October, including RH ($r = -0.67$), VPD ($r = 0.63$), SSD ($r = 0.59$), EVP ($r = 0.54$), and PRE ($r = -0.36$; figure 3(e)). Correlations with scPDSI, however, were weak ($r = -0.29$ to $-0.35, p < 0.05$). The maximum composite tree-ring $\delta^{18}O$ showed a strong correlation ($p < 0.05$) with climate variables in the RH in October ($r = -0.68$), VPD ($r = 0.66$), SSD ($r = 0.61$), EVP ($r = 0.59$), and PRE ($r = -0.37$; figure 3(f)). The correlation between the maximum composite $\delta^{18}O$ and the RH in October was the strongest compared to other monthly and seasonal climate variables (figures 3(f) and S4b) and a partial correlation was strongly significant even after removing the influence of precipitation (figure 4(b)).

### 3.3. Relationships of precipitation $\delta^{18}O$, climate variables, and tree-ring $\delta^{18}O$

Source water (precipitation) $\delta^{18}O$ had a stronger influence on minimum interannual tree-ring $\delta^{18}O$ variability than on the maximum earlywood and latwood $\delta^{18}O$ variability (figures 5 and S5). Its influence on the minimum tree-ring $\delta^{18}O$ was the strongest from May–August ($r = 0.60$;
Figure 3. Climatic response of (a) annual minimum, (b) mean, and (c) maximum tree-ring $\delta^{18}$O and maximum tree-ring $\delta^{18}$O from (d) earlywood, (e) latewood, and (f) composite (maximum latewood tree-ring $\delta^{18}$O from the current year and maximum earlywood tree-ring $\delta^{18}$O from the following year) series. Only the significant ($p < 0.05$) Pearson's correlation coefficients are shown in panels. The monthly climate data cover the period from 1953–2014. In the x-axis, the lowercase letters represent the months of the previous year and the capital letters represent the months of the current year. JJA, the seasonal mean value from June–August; JAS, the seasonal mean value from July to September; A-N, the seasonal mean value from August–November, and O–J, the seasonal mean value from October of the previous year to current January. The climate variables include mean (TEM), maximum (TMAX), and minimum (TMIN) temperatures, PRE, monthly self-calibration Palmer drought severity index (scPDSI), monthly RH, monthly VPD, monthly evaporation (EVP), and monthly sunshine hour duration (SSD).

Figure S5(a)). Fifty percent of the total variance of the annual minimum $\delta^{18}$O in tree rings can be explained by a multiple regression model including May–August precipitation $\delta^{18}$O, July–September scPDSI, and July–September SSD (figure 5(a)). July–September scPDSI had the highest unique contribution (29.5%), whereas the joint contribution from July–September scPDSI and May–August precipitation $\delta^{18}$O explained about 29.4% of the variance.

Variance in the maximum composite $\delta^{18}$O, on the other hand, was primarily determined by the RH in October, with a total of 47% explained variance. Other climate variables, such as October...
Figure 4. Correlations and partial correlations of (a) annual minimum tree-ring $\delta^{18}O$ and (b) maximum composite tree-ring $\delta^{18}O$ with climate. In panel (a), simple correlations (top) of minimum $\delta^{18}O$ with precipitation (primary) and partial correlations (down) with scPDSI (secondary, after controlling precipitation). In panel (b), simple correlations (middle top) of maximum composite $\delta^{18}O$ with scPDSI (primary) and partial correlations (bottom) with RH (secondary, after controlling scPDSI). Lowercase letters on the x-axis represent months of the previous year and capital letters represent months of the current year. For seasonal correlations, the month indicates the last month of the season. The black bars represent significant ($p < 0.05$) correlation coefficients.

PRE, SSD, and VPD, were also significantly correlated with the maximum composite $\delta^{18}O$, but their strong correlation with RH prevented them from being included in the multiple regression model (figure 5(b)).

3.4. Differing trends in scPDSI and RH

Based on the results of climate response analysis and the multiple linear regression analysis (section 3.3), we used annual minimum $\delta^{18}O$ to reconstruct July–September scPDSI and the maximum composite $\delta^{18}O$ to reconstruct the RH in October (figures 6(a) and (b)). Both reconstructions showed good skill, with 42% of the variance explained for July–September scPDSI and 47% for the RH in Octoberover the calibration period (1953–2014). All RE and CE values were positive (table 1).

However, our July–September scPDSI reconstruction showed only a weak relationship with the CRU instrumental dataset over the pre-calibration period (1901–1952; $r = 0.42$, $p < 0.05$), with strong offsets between instrumental and reconstructed data from 1920–1950 (figure 6(c)). This may be caused by the degradation of the accuracy of the CRU data due to limited available observation stations prior to 1950 [28].

Our scPDSI reconstruction showed an increase from 1900–1952 (0.03 yr$^{-1}$, $p = 0.02$), but an overall decrease from 1900–2014 (−0.01 yr$^{-1}$, $p < 0.001$) and since 1953 (−0.014 yr$^{-1}$, $p = 0.2$), which agreed with the variability in CRU scPDSI (figure 6(c)). Our RH reconstruction, on the other hand, showed a significant increase ($p < 0.05$) over the entire period (1900–2014; 0.06% yr$^{-1}$, $p < 0.001$), as well as over both subperiods (1900–1952: 0.17% yr$^{-1}$, $p = 0.009$; and 1953–2014: 0.09% yr$^{-1}$, $p < 0.001$) (figure 6(d)). The scPDSI and RH reconstructions showed stronger coherent variability during the early period (1900–1952: $r = 0.51$, $p < 0.05$), than the later period (1953–2014: $r = 0.27$, $p < 0.05$) over which they showed diverging trends. Also at the decadal scale the
Figure 5. The multiple variables regression relationships and commonality analysis (a) between annual minimum tree-ring δ^{18}O and environmental variables, and (b) between maximum latewood tree-ring δ^{18}O and environmental variables. In panel (a), the climatic variables (RH, PRE, SSD, and scPDSI) are seasonal means from July–September. The PRE δ^{18}O is the seasonal mean precipitation δ^{18}O from May–August. In panel (b), the climatic variables are in October. The meaning of the numbers is indicated in the left column. The numbers in the middle of the directional edges are beta weighted coefficients in the model. The directional edges indicate regression parameters (causal relationships) and their unique contribution (%) to tree-ring δ^{18}O. The bidirectional edges and number (%) indicate a common contribution between independent variables. The colored (gray) directional edges are significant (not significant) in the final model. The bidirectional dashed edges indicate the Pearson correlation (blue, negative correlation; orange, positive correlation). The thickness of the line indicates the magnitude of the relationships.

Table 1. Statistics of the split-period cross calibration and verification of the July–September scPDSI and the RH in October reconstructions. The statistics include adjusted explained variance (R^2_adj), reduction of error (RE), coefficient efficiency (CE), and root mean square error (RMSE).

| Target parameters | Calibration (1953–1983) | Verification (1984–2014) | Calibration (1953–1983) | Verification (1984–2014) | Whole period (1984–2014) |
|-------------------|-------------------------|--------------------------|-------------------------|--------------------------|--------------------------|
| July–September scPDSI | R^2_adj | RE | CE | R^2_adj | RE | CE | R^2_adj | RMSE |
| Annual minimum δ^{18}O | 0.57 | 0.27 | 0.23 | 0.23 | 0.56 | 0.54 | 41.9 | 1.39 |
| October RH | Maximum composite δ^{18}O | 0.62 | 0.14 | 0.13 | 0.39 | 0.53 | 0.52 | 47.4 | 5.138 |

coherence between both reconstructions was stronger in the first half of the 20th century (figures 6(c) and d).

4. Discussion and conclusion

4.1. Tree-ring δ^{18}O parameter coherency

High Rbar and EPS values indicate that the maximum, mean, and minimum tree-ring δ^{18}O series from different trees contain common signals and can produce reliable site chronologies. Previous studies indicated that the four to five trees can establish a site δ^{18}O chronology with an EPS value over 0.85 [31], which is in line with the Rbar and EPS values of our mean and minimum tree-ring δ^{18}O chronologies (table S2). The lower EPS values of the maximum tree-ring δ^{18}O series may be caused by the low sample replication [37, 41] and by the fact that the maximum δ^{18}O values are derived from different parts of the ring (figure 2). Coherent variability between trees in tree-ring δ^{18}O extremes implies that they may have some common climatic signals.

4.2. Climatic response of tree-ring δ^{18}O series

All tree-ring δ^{18}O parameters increased with low RH, PRE, and scPDSI, but with high VPD, EVP, and SSD, which suggests that soil and atmospheric moisture conditions are the main climatic drivers of tree-ring
\(\delta^{18}O\) variability (figure 3). Dry conditions typically lead to \(^{18}O\) enrichment in leaf water and tree-ring cellulose [2, 4–6]. Our results are thus in line with tree-ring \(\delta^{18}O\) fractionation models [3, 4, 6], observations [2, 6], and dendroclimatological studies in South and East Asia [9, 12, 22]. In addition to this, the radial stem growth of pine in this region is influenced by late-summer moisture [25], which further supports our results.

The climate response of the parameters of the tree-ring \(\delta^{18}O\) extremes support our hypothesis that the minimum and maximum tree-ring \(\delta^{18}O\) record different climate signals. Variability in the minimum \(\delta^{18}O\) was primarily determined by source-water \(\delta^{18}O\) and scPDSI, whereas variability in the maximum composite \(\delta^{18}O\) was primarily determined by RH (figures 3 and 5). The sub-annual minimum \(\delta^{18}O\) occurs in the central part of the ring, which is formed from June–September [25, 40], corresponding to warm and moist climate and low precipitation \(\delta^{18}O\) period (figures 1(b) and (d)). Pine, as a shallow-rooted species in subtropical forests [42], mainly uptake source water derived from precipitation. Trees may use water from the period before tree-ring formation and tree-ring \(\delta^{18}O\) values record antecedent precipitation \(\delta^{18}O\) [2, 43]. As a result, May–August

**Figure 6.** The linear regression (a) between annual minimum tree-ring \(\delta^{18}O\) and July–September scPDSI, and (b) between maximum composite tree-ring \(\delta^{18}O\) and the RH in October with the confidence intervals at \(p = 0.05\) (shaded). Comparison between observations and reconstructions for (c) July–September scPDSI and (d) RH in October. The thick (thinner) line is the 90 yr (20 yr) LOESS reconstruction with one standard error (shaded) in panels (c) and (d) to emphasize multi-decadal variability and trends. The vertical dashed lines indicate the dividing year (1984) between the calibration and verification periods. \(r\) is the Pearson correlation between the observation and the reconstruction during the calibration and verification periods.
precipitation $\delta^{18}O$ could be source water $\delta^{18}O$ for tree growth and positively affected the minimum tree-ring $\delta^{18}O$ variability (figures 5 and S6). This result is also supported by the fact that at humid sites (PRE > 1800 mm yr$^{-1}$) such as ours, trees use source water that isotopically resembles summer precipitation [43]. July–September scPDSI, however, negatively affects the minimum tree-ring $\delta^{18}O$ (figure 5) by influencing the water availability and soil water source $\delta^{18}O$. Specifically, limited soil water supply (i.e. low scPDSI), may result in a low water transportation rate from soil to trees [43] and increases the uptake of precipitation from past months [43, 44]. As a result, a low scPDSI may lead to the use of relatively more soil water from spring precipitation (with higher $\delta^{18}O$) as source water for trees (figure 1(c)) and thus high source water $\delta^{18}O$. At the same time, low scPDSI indirectly results in high enrichment in soil water source $\delta^{18}O$ through linking to temperature, evaporation, precipitation, and RH [45]. scPDSI variability involves variability in precipitation and RH, which negatively affects source water $\delta^{18}O$ (figure 5) even though no such effect on intraannual precipitation $\delta^{18}O$ variability is visible [17], and as a consequence, scPDSI covaries with precipitation $\delta^{18}O$ (figure 5). In addition to this, scPDSI captures moisture variability over a longer (multi-month) period compared to RH [46], and may therefore be more strongly related to the minimum tree-ring $\delta^{18}O$. Under these circumstances, according to the mechanism model [6] and our statistical model, the minimum tree-ring $\delta^{18}O$ variability is determined by source water $\delta^{18}O$ and by scPDSI (figures 3 and 5).

Tree-ring $\delta^{18}O$ maxima occurred at the beginning and end of the annual ring (figures 2(a)–(c)). They are related to heavier precipitation $\delta^{18}O$ in spring (March–May) and fall (October–November) [17], as well as relative drier fall conditions (October–November; RH 80% and PRE 130 mm) compared to the spring and summer months (figures 1(b) and (c)). The percentage of exchange with unenriched source water during cellulose synthesis is about 40% according to tree-ring $\delta^{18}O$ process model [4, 6, 7] and a 10% reduction in RH can thus result in an ~4% increase in $\delta^{18}O$ enrichment at the leaf level and thus no more than 2.5% in the tree-ring cellulose. Thus, in order to obtain a 5% increase from the minimum $\delta^{18}O$ to the maximum $\delta^{18}O$ in the cellulose (figure 2(e)), the source water $\delta^{18}O$ needs to increase substantially, as is shown in figure 1(d). Our results contrast with pine in North American monsoon areas [10, 19], where tree-ring $\delta^{18}O$ maxima values are mainly explained by high VPD during the nonmonsoon season, but confirm the results in other east and south Asian monsoon regions [12, 22].

The maximum earlywood $\delta^{18}O$ variability is influenced by the climate of the previous fall (figure 3), which may reflect the post-photosynthetic effects in the tree-ring $\delta^{18}O$ downstream metabolism or legacy effects of the previous year’s climate [2, 5]. Other reasons for lag effects may be water pool storage from one to the next year and that the source water used for earlywood formation is similar to that used for latewood formation of the previous year, especially in dry conditions [2, 43].

The maximum latewood $\delta^{18}O$ occurred at the end of the growing season (October–early November) [25, 40], when tree growth slows down or even stops [25, 26, 40] and precipitation $\delta^{18}O$ is high (figure 1(d)), which is similar to the results in pine from the Southeast Asian montane forest [9]. The maximum latewood $\delta^{18}O$ variability was primarily impacted by the RH in October (figures 3–5 and S6) [25, 40] because high atmospheric demand (i.e. low RH) during the transpiration process can lead to a high $\delta^{18}O$ enrichment at the leaf level during this period [1–5]. With the maximum latewood tree-ring $\delta^{18}O$ of one ring and the maximum earlywood tree-ring $\delta^{18}O$ of the following ring both influenced by the RH in fall of the same year, we developed a composite chronology that combines the maximum tree-ring $\delta^{18}O$ of the latewood and subsequent earlywood ring. This maximum parameter of the composite tree-ring $\delta^{18}O$ was primarily determined by the RH in October (figure 3), which synthesizes the mechanisms described above.

### 4.3. Divergence between water availability and atmospheric moisture

We found differing trends in our time series of tree-ring $\delta^{18}O$ extremes, with the minimum $\delta^{18}O$ increasing over the 20th century, but all the maximum $\delta^{18}O$ parameters showing decreasing trends (figure 2(e)). Whereas age effects may cause trends in tree-ring width time series, tree-ring $\delta^{18}O$ are typically less affected by age-related trends [31–34]. We did not remove potential age-related trends from our time series because detrending can remove low-frequency climatic information [32, 33] and because nonclimatic trends are removed by averaging individual series [32, 33] and by removing potential juvenile effects. Given that our tree-ring $\delta^{18}O$ time series showed different trends for the maximum and minimum parameters, but no trend in mean $\delta^{18}O$, age-related trends are unlikely to have affected our results and the trends we found mainly result from climate.

Zhu et al. [9] attributed similar trend differences between maximum and minimum tree-ring $\delta^{18}O$ in Thailand to a decreasing contribution of fog water to trees in response to warming and deforestation. At our site, however, there is no evidence of fog water contribution because there is no trend in cloud cover (figure S6) and no deforestation. Furthermore, precipitation and water vapor $\delta^{18}O$ at our site showed no significant increasing or decreasing trends (figures S7 and S8). The trends in the minimum and maximum tree-ring $\delta^{18}O$ series are therefore likely caused by a trend in May–September scPDSI,
representing soil water supply, and variability of the RH in October, representing atmospheric moisture, respectively.

Our minimum δ\textsuperscript{18}O-based July–September scPDSI reconstruction, as well as the instrumental July–September CRU scPDSI time series, showed decreasing trends from a wetter period in the first half of the 20th century to more average conditions in the second half (figure 6(c)). This decreasing trend suggests increasing growing season drought stress. Our maximum δ\textsuperscript{18}O-basedon the reconstruction of the RH in October, on the other hand, showed an increasing trend since 1900 (0.6% yr\textsuperscript{-1}). In addition to different trends, the two tree-ring δ\textsuperscript{18}O time series also showed reduced co-variability since the 1950s (figure 2(e)). Both trends over the second half of the 20th century may be related to warming (figure S9). By stimulating evaporation, increasing spring and July–September temperatures can lead to increases in water demand and decreasing soil water availability [47] (figure S9). The growing season in southeastern China extended over the 20th century, with a delayed end of the growing season by 1.9–4.8 d per decade, especially in recent years (1980 through the 2000s) [48]. Fall (October) warming, on the other hand, may lead to a lengthening of the growing season and increased moisture holding capacity in the atmosphere [49] and thus atmospheric water vapor. This is important for tree-growth forecasts in humid regions such as southeastern China, where plants usually have poor adaption to water shortages [50] and hot summer droughts are more common [47]. If trees in such regions adapted to more humid fall conditions, they could be more vulnerable when the soils dry out.

Our results reveal different climatic signals in sub-annual maximum and minimum δ\textsuperscript{18}O through different mechanisms, even though tree-ring δ\textsuperscript{18}O variability is also influenced by other ecophysiological processes (e.g. post-photosynthetic processes) [5, 7]. Different climatic signals in seasonal tree-ring δ\textsuperscript{18}O extremes imply that the climatic signal in annually averaged tree-ring δ\textsuperscript{18}O may be mixed and therefore weakened. Sub-annual tree-ring δ\textsuperscript{18}O measurements can therefore result in stronger climatic signals in regions with precipitation δ\textsuperscript{18}O seasonality [9, 12], where tree-ring width fails to record strong climatic signals. Our results further illustrate that inter-annual variability in tree-ring δ\textsuperscript{18}O extremes can provide reliable climate proxies in humid regions. Intra-annual tree-ring δ\textsuperscript{18}O extremes can further be used to detect climatic extremes, and this method may apply to other δ\textsuperscript{18}O-based proxies. We further found contrasting trends between summer soil moisture (scPDSI) and the RH in fall over the 20th century. This information is valuable for our understanding of how seasonal moisture is changing under anthropogenic climate change and the ecological implications of such trends.

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Data availability statement

Data and code in this study can be found in https://github.com/GuobaoXu/Tree-ring-max-and-min-oxygen and the Menderley data (doi: 10.17632/dynh2rd7fm.1). The meteorological data can be downloaded from http://data.cma.cn/en. The climate data of the scPDSI and cloud cover can be found in the CRU dataset. The precipitation δ\textsuperscript{18}O at the Changsha station can be found in the GNIP database (https://www.iaea.org/services/networks/gnip).

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