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Progress in Tree-Ring Stable Isotope Research in China

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Abstract: Tree-ring stable isotopes ($\delta^{13}C$, $\delta^{18}O$ and δD) have relatively well-understood fractionation mechanisms, require only small numbers of replicates, and can preserve low-frequency climate signals, making them important proxies for research on past climate change and forest ecology in China. Taking indicator succession and regional expansion as the thread, this paper reviews the development of tree-ring stable isotope research in China since the late 1980s. Early work focused on $\delta^{13}C$ and reconstructed temperature, relative humidity and atmospheric CO_2 concentration at sites such as Mt. Tianmu, Mt. Helan, the Qinling Mountains and western Sichuan; after 2000, $\delta^{18}O$ rapidly became the dominant indicator, and annually resolved series and regional networks were established on the Tibetan Plateau, in the arid Northwest and in the eastern monsoon region, with reconstruction intervals extending from centennial scales to millennia and even to the late Holocene; meanwhile, δD measurement, joint interpretation of carbon and oxygen isotopes, intra-annual high-resolution analysis, and studies of water-use efficiency and isotope process models were gradually developed. This paper summarizes the main findings at three levels—fractionation mechanisms and chronology construction, regional progress by indicator, and applications to ecological processes—identifies constraints such as insufficient mechanistic understanding, uneven spatial coverage, non-stationary signals and inadequate data sharing, and proposes directions including stronger multi-isotope coupling and high-resolution measurement, the development of isotope process models, and the establishment of a unified data platform.

Keywords: Tree rings, stable isotopes, $\delta^{13}C$, $\delta^{18}O$, paleoclimate reconstruction, water-use efficiency.

1. Introduction

Tree rings, with their precise dating, high temporal resolution, wide distribution and ease of sampling, have long served as basic material for the study of past climate change. Width and density indicators can provide reliable series in areas where the limiting factor is single (for example, near the treeline and in arid regions), but their climate signals are often ambiguous in regions where water and heat jointly limit growth, where growth trends are complex, or where dating is difficult in the tropics. Stable isotope ratios offer another pathway: the fractionation of carbon, oxygen and hydrogen during photosynthesis, transpiration and cellulose synthesis is controlled by stomatal activity, water source and photosynthetic efficiency, the series are less affected by age effects, and they can preserve low-frequency information that width indicators tend to lose [1].

The starting point of tree-ring stable isotope research in China can be traced to the systematic introduction of methods and application prospects in the late 1980s [2]. Subsequently, $\delta^{13}C$ of Cryptomeria japonica at Mt. Tianmu was used to reconstruct changes in atmospheric CO_2 concentration [3]; $\delta^{13}C$ of Pinus tabuliformis at Mt. Helan yielded a summer temperature series since 1890 [4]; and work on the western Sichuan Plateau further clarified the climatic significance and limitations of isotope signals in humid regions [5]. Over the past two decades, as α-cellulose preparation and isotope mass spectrometry matured, the research focus shifted from $\delta^{13}C$ to $\delta^{18}O$, sampling sites shifted from scattered distribution to regional networks, reconstruction targets expanded from temperature and humidity to runoff, cloud cover, drought and monsoon intensity, and time spans extended from centuries to millennia [1].

This paper does not attempt to exhaust the literature but, taking indicator succession and regional expansion as the thread, reviews progress at three levels: first the common basis of fractionation mechanisms, sample processing and chronology construction; then the main findings for each region by $\delta^{13}C$, $\delta^{18}O$ and δD; and finally attempts to move from climate reconstruction towards ecological processes and models, together with an assessment of existing problems and future directions.

2. Fractionation Mechanisms, Sample Processing and Chronology Construction

2.1. Basic Controls on Carbon, Oxygen and Hydrogen Isotope Fractionation

Carbon isotope fractionation occurs when CO_2 diffuses through stomata into the leaf and is carboxylated. Rubisco preferentially fixes $^{12}CO_2$, so that photosynthate is depleted in ^{13}C relative to atmospheric CO_2; the degree of fractionation depends on the ratio of intercellular to atmospheric CO_2 concentration, which is determined jointly by stomatal conductance and photosynthetic rate. When water is sufficient and air humidity high, stomata are open, intercellular CO_2 concentration rises and $\delta^{13}C$ becomes more negative; drought, high temperature or enhanced radiation cause stomatal closure and higher photosynthetic rates, making $\delta^{13}C$ more positive. $\delta^{13}C$ therefore carries information on moisture conditions, temperature and radiation at the same time, and its dominant factor varies from region to region [1, 5].

The fractionation chain of oxygen isotopes is longer. Tree-ring $\delta^{18}O$ first inherits the $\delta^{18}O$ of precipitation and soil water, and the source-water signal contains information on moisture source, temperature effect and amount effect; it is then modified by transpirational enrichment in the leaf and during cellulose synthesis, with the degree of enrichment controlled by relative humidity—the lower the humidity, the stronger the enrichment and the more positive the cellulose $\delta^{18}O$ [6, 7]. This means that tree-ring $\delta^{18}O$ records the superposition of two processes, "source water" and "evaporative enrichment":

in monsoon regions it mostly correlates negatively with warm-season precipitation and relative humidity, whereas in westerly regions it reflects regional wet-dry conditions more strongly.

The fractionation process of hydrogen isotopes is similar to that of oxygen but with different fractionation coefficients, and is equally sensitive to source water and transpirational enrichment; because exchange reactions of hydrogen in organic matter are more complex, the construction of δD series depends more on sampling and pooling strategies [8, 9]. The differences in fractionation mechanisms among the three isotopes determine the complementarity of the information they record: $\delta^{13}C$ emphasizes carbon metabolism and water use within the leaf, $\delta^{18}O$ emphasizes source water and atmospheric humidity, and δD provides a constraint between the two.

2.2. α-Cellulose Extraction and Mass Spectrometric Determination

The components of tree rings available for isotope analysis include whole wood, holocellulose and α-cellulose. α-Cellulose is chemically stable with a fixed molecular formula and is less disturbed by lignin and extractives during isotope exchange, and has therefore become the standard medium for $\delta^{13}C$ and $\delta^{18}O$ determination [1]. The routine procedure is as follows: separate the sample ring by ring under a stereomicroscope, grind it, extract resins and pigments with organic solvents, extract α-cellulose by the sodium chlorite–sodium hydroxide method, freeze-dry it, weigh an appropriate amount into a silver capsule, and determine it by high-temperature pyrolysis or combustion in an elemental analyser–isotope ratio mass spectrometry system [10]. Monitored with cellulose standards and replicate samples, the analytical precision is generally better than 0.1‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{18}O$ [5, 10].

In recent years, micro-extraction and the measurement of multiple proxies on a single sample have been gradually promoted, markedly reducing sample loss and opening possibilities for narrow rings, high elevations and buried wood samples; however, the many pretreatment steps and the long turnaround time remain practical constraints on the number of sites and the length of series.

2.3. Replication, Juvenile Effect and Series Reliability

As with width chronologies, isotope series require sufficient replication to ensure an adequate signal-to-noise ratio. Using EPS greater than 0.85 as the criterion, $\delta^{13}C$ generally requires 4 to 6 trees, $\delta^{18}O$ 4 to 5 trees and δD 5 trees; in the arid and semi-arid regions of China, where rings are narrow and the material available per ring is limited, 4 to 10 trees are often used in practice [1]. Pooling strategy also affects the signal: measuring pooled samples from several trees of the same year reduces individual differences but masks individual responses to the local environment, whereas building individual-tree series first and pooling them afterwards makes it easier to identify anomalous individuals and azimuthal differences [11].

Age effects are another issue that must be addressed. $\delta^{13}C$ often shows a positive bias of 1‰ to 2‰ at juvenile stages, lasting from 20 to 200 years, and most studies discard the first 20 to 50 years of the series to avoid juvenile effects; the juvenile effect of $\delta^{18}O$ is weaker, and a decrease of about 1.5‰ within 30 to 40 years has been reported for Pinus in France, so $\delta^{18}O$ series are usually not detrended, which is also an important reason why they preserve low-frequency climate information [1]. On the Tibetan Plateau, researchers have linked living trees with buried wood from tombs and sediments, extending the dating framework back several millennia and providing the material basis for the establishment of long $\delta^{18}O$ series [12, 13].

3. Progress in Tree-Ring $\delta^{13}C$ Research

3.1. Regional Differentiation of Temperature and Humidity Signals

$\delta^{13}C$ was first used for temperature reconstruction. A Pinus tabuliformis series from Mt. Helan reconstructed June–August mean temperature since 1890, revealing a clear outline of twentieth-century warming [4]; a May–July temperature reconstruction from Nanwutai further discussed the commonalities and differences between individual and pooled series [14, 11]. Under arid conditions, the response of $\delta^{13}C$ to moisture is often stronger than that to temperature: higher relative humidity opens stomata and strengthens fractionation, making $\delta^{13}C$ more negative, and a Cryptomeria japonica series from Mt. Tianmu accordingly reconstructed April–June relative humidity since 1648 [15], while a series from the upper Tarim River provided changes in growing-season relative humidity over the past 195 years [16].

Regional comparison shows that the dominant factor of $\delta^{13}C$ changes with the moisture background. In the arid Northwest and on the Loess Plateau, the series mainly record relative humidity, precipitation or drought indices; in the northeastern Tibetan Plateau, $\delta^{13}C$ of Qilian juniper reflects growing-season temperature more strongly; in humid regions such as western Sichuan, temperature and moisture jointly control the signal and a single factor explains only limited variance [1, 5]. This differentiation shows that the climatic significance of $\delta^{13}C$ must be verified site by site, and that transferring interpretations across regions easily leads to distortion.

3.2. Water-use Efficiency and Physiological Response

$\delta^{13}C$ allows the ratio of intercellular to atmospheric CO_2 concentration to be derived, and hence intrinsic water-use efficiency to be estimated. Rising atmospheric CO_2 concentration lowers this ratio and makes $\delta^{13}C$ more positive, so that water-use efficiency increases; drought produces an effect in the same direction through stomatal closure, and the two are difficult to separate directly in long series. Chinese researchers have made many attempts in plantation forests of North China, masson pine in the Southeast and the arid Northwest, generally finding an upward trend in water-use efficiency since the twentieth century, but the magnitude of the increase is closely related to climatic background, tree species and site conditions [1, 5]. To separate the CO_2 fertilization effect from climatic stress, joint constraints from tree-ring width, density and physiological models are needed [17].

Compared with width indicators, $\delta^{13}C$ responds more sensitively to drought years and can capture physiological stress signals that width series miss. Research at Mt. Helan shows that drought significantly raises $\delta^{13}C$ and alters its intra-annual pattern, a feature that can be used to identify extreme years and recovery processes [17].

3.3. Signal Limitations in Humid Regions

Humid regions were among the first areas entered by $\delta^{13}C$ research in China and are also the most constrained. A comparison of Tsuga and Pinus densata on the western Sichuan Plateau showed differences between the $\delta^{13}C$ series of the two species; although the fractionation values after removal of atmospheric CO_2 effects were significantly correlated, the best multiple regression explained only 38.5% of the variance, which is insufficient for climate reconstruction alone [5]. The reason is that neither water nor heat constitutes a strong limitation, stomatal and photosynthetic processes dominate alternately, and together with species-specific physiological differences and local site effects the signal is diluted by multiple processes. Research in this region subsequently shifted more towards $\delta^{18}O$, emphasizing multi-species, multi-azimuth sampling and the joint use of multiple indicators [18, 19].

4. Progress in Tree-Ring $\delta^{18}O$ Research

4.1. Tibetan Plateau: From Point Reconstructions to Long Series

The Tibetan Plateau is the region with the densest $\delta^{18}O$ research in China. Picea and juniper series from the Qilian Mountains revealed the relationship between $\delta^{18}O$ and regional atmospheric circulation, providing a basis for the study of moisture sources in the northeastern plateau [6]; a 400-year $\delta^{18}O$ chronology from southeastern Tibet linked regional hydroclimatic change with the Indian monsoon and the El Niño–Southern Oscillation [20]; a series from western Sichuan showed that $\delta^{18}O$ can record changes in regional cloud cover and tropical sea surface temperature [18]; and another 200-year series from southeastern Tibet further separated the effects of summer monsoon precipitation and local evaporation [21]. Together these studies established the methodological advantage of $\delta^{18}O$ on the plateau—"preserving low frequencies and strong regional consistency".

Work in the Qaidam Basin extended series length to the millennial scale: $\delta^{18}O$ series since 1800 were used to discuss the relationship between basin moisture and the East Asian summer monsoon [22], millennial-scale moisture variations were subsequently reconstructed [23], and Qilian juniper $\delta^{18}O$ was also used to identify drought events [24]. Most representative is a 3476-year annual series built from 17 Qilian juniper trees and 15,028 $\delta^{18}O$ measurements, which shows that 1930–2010 was the driest period of the past 3500 years and links the intensification of twentieth-century drought to anthropogenic aerosols weakening the monsoon and the westerlies [12]. This achievement placed China at the international forefront in ultra-long, annually resolved isotope records.

4.2. Arid Northwest and the Monsoon Margin

$\delta^{18}O$ series in the arid Northwest are notable for recording precipitation and wet-dry changes. A series since 1878 shows that $\delta^{18}O$ varies synchronously with monsoon precipitation and can be used to track moisture transport under westerly–monsoon interaction [7]; work in the Qilian Mountains and the Qaidam Basin indicates that under arid conditions the inheritance of precipitation $\delta^{18}O$ dominates, with the leaf enrichment effect relatively minor [6, 22].

The monsoon margin is another sensitive zone. The line from the eastern Qilian Mountains to Mt. Helan lies near the northern limit of the East Asian summer monsoon, and $\delta^{18}O$ series there are relatively sensitive to changes in monsoon strength and in the position of the precipitation belt; however, the region is affected by both the westerlies and the monsoon, so the uncertainty of signal interpretation is greater and comparison of multiple series is needed for robust conclusions [1].

4.3. Eastern Monsoon Region and Northeast China

In the eastern monsoon region, where humidity is higher and tree growth is controlled by multiple factors, $\delta^{18}O$ nevertheless shows strong usability. A Fokienia hodginsii series from Changting, Fujian, with April–September precipitation as the limiting factor, reconstructed warm-season precipitation in the subtropical region [25]. Rainy-season precipitation in Southwest China is modulated by the Indian monsoon and central Pacific sea surface temperature, and $\delta^{18}O$ series have been used to identify drought events and to discuss the role of the Indian Ocean Dipole [26]; a series from Lijiang, Yunnan recorded changes in large-scale circulation [27]. $\delta^{18}O$ studies in Northeast and North China have mostly focused on temperature and precipitation reconstruction, and in recent years have also begun to discuss moisture sources and the influence of the Siberian High [28]. Overall, $\delta^{18}O$ in the eastern monsoon region mainly reflects warm-season precipitation and relative humidity, and the "amount effect" is the key to its signal formation.

4.4. Regional Networks and Asian-Scale Integration

The limitations of single-site series have driven networked research. Placing multiple $\delta^{18}O$ series from western China side by side shows a clear spatial division of signals between the westerly-influenced and the monsoon-influenced areas, with signals in the transitional belt relatively weak [1]; integration of records at the Asian scale further shows that the moisture signals of the monsoon and westerly regions corroborate each other at large scales, providing a basis for paleoclimate field reconstruction [28]. A central Pacific sea surface temperature reconstruction based on $\delta^{18}O$ of Chamaecyparis formosensis in Taiwan shows that $\delta^{18}O$ records not only local hydrology but also captures the long-term variability of large-scale ocean–atmosphere interaction [29].

5. Tree-Ring δD and Multi-Isotope Coupling

5.1. δD Records

The measurement and interpretation of δD are more complex than those of $\delta^{18}O$, yet provide independent information on humidity and circulation. A combined $\delta^{18}O$ and δD series from the Batang–Litang Plateau reconstructed relative humidity since 1755, with the two isotopes corroborating each other in low-frequency trends [8]. A comparison of δD measurements on pooled versus individual samples in Northwest China showed that pooled samples improve series stability, and the authors accordingly discussed the response to the Arctic Oscillation [9]. Because δD requires larger sample amounts and higher analytical costs, the number of independent δD series in China remains clearly smaller than that of $\delta^{18}O$.

5.2. Joint Interpretation of Carbon and Oxygen Isotopes

Joint interpretation of carbon and oxygen isotopes has been an important direction in recent years. The two are controlled by different processes: $\delta^{13}C$ records the ratio of intercellular to atmospheric CO_2 concentration and water use, whereas $\delta^{18}O$ records source water and leaf enrichment; used together, they can separate source-water changes from physiological responses. In humid regions such as western Sichuan, researchers found that the correlation between $\delta^{13}C$ and $\delta^{18}O$ strengthened in recent decades and discussed the coupling of climate reconstruction and physiological response on this basis [19]. In the Qaidam Basin and the Qilian Mountains, the two isotopes were also used to distinguish the contributions of humidity and temperature signals [23, 24].

5.3. Intra-annual and Sub-Seasonal Resolution

Beyond annual resolution, intra-annual analysis is becoming a new growth point. Differences in $\delta^{18}O$ between earlywood and latewood in Southwest China were shown to be related to the seasonal distribution of monsoon precipitation [30]; a $\delta^{18}O$ profile within the glucose units of α-cellulose from Larix on the southern slopes of the Qinling Mountains pushed the resolution to the sub-annual scale, making it possible to reconstruct the seasonal configuration of temperature and humidity [31]. Combined with sampling techniques such as laser ablation and rotary microtomy, tree-ring isotopes are expected to recover changes in monsoon advance and retreat and in moisture transport at seasonal scales.

6. From Climate Reconstruction to Ecological Processes and Models

6.1. Intra-annual Processes of Tree Growth and Isotope Fractionation

Placing isotope series back into tree physiological processes is a recent shift in research. Intra-annual $\delta^{13}C$ and $\delta^{18}O$ series of Pinus tabuliformis at Mt. Helan show that $\delta^{13}C$ rises from the early growing season and peaks in the middle to late season, while $\delta^{18}O$ declines continuously throughout the growing season; drought significantly raises $\delta^{13}C$ and alters its intra-annual pattern, whereas the intra-annual pattern of $\delta^{18}O$ differs little between wet and dry years [17]. Such results provide direct evidence for explaining the formation of annually resolved series and a basis for separating climatic signals from carbohydrate storage effects.

6.2. Process Models and Parameter Calibration

Isotope process models connect photosynthesis, carbon allocation, growth and fractionation. A domestic team coupled a tree-ring process model with ecological memory effects, improving the simulation accuracy of radial growth in temperate coniferous forests of China [32]; a MATLAB version of the MAIDENiso model was developed together with a MATLAB–C++ collaborative framework, and improved genetic algorithm and MCMC-GA parameter calibration schemes were proposed, markedly improving calibration accuracy and search efficiency [33]. These works turn tree-ring isotopes from "recorders" into tools for testing physiological mechanisms and predicting future responses.

6.3. Global Change Ecology and Deep-Time Applications

At the ecological level, water-use efficiency derived from $\delta^{13}C$ is widely used to assess the effects of rising CO_2 and drought on forest carbon–water relations [1, 17]; $\delta^{18}O$ is used to infer changes in moisture sources and soil water use strategies. Research objects have also expanded from modern living trees to buried and fossil wood, and isotope studies of Cenozoic buried wood provide material for understanding deep-time plant–climate relationships [34]. Integrated $\delta^{18}O$ studies at the Asian scale show that long-term changes in the monsoon and westerly systems can be cross-validated through isotope networks [28].

7. Existing Problems and Prospects

7.1. Mechanisms and Experiments

Current understanding remains concentrated on fractionation at the leaf level; fractionation during the transfer of photosynthate to cellulose, the storage and reallocation of sucrose and starch, and the time lag in earlywood and latewood formation remain unclear. Systematic observations of differences in isotopic composition among tree species, azimuths and site conditions are also lacking. Future work should strengthen investment in controlled experiments, isotope labelling and high-frequency sampling and monitoring, so as to connect the chain "leaf–phloem–cambium–cellulose".

7.2. Spatial and Temporal Coverage

The distribution of sampling sites is highly uneven. The Tibetan Plateau and the arid Northwest contain most of the series, whereas Northeast China, South China, the karst regions of Southwest China and tropical areas remain sparse; long series exceeding a millennium are few, and most series are shorter than 300 years. Regional network construction and the use of buried wood and wood from ancient buildings should be used to fill gaps in key regions and key periods.

7.3. Non-stationary Signals

The relationship between tree-ring isotopes and climatic factors is not constant. Studies have found that the relationship between $\delta^{18}O$ and climate variables in Southwest China changes over time, possibly related to rising central Pacific sea surface temperatures [35]. If regression relationships established over the modern observational period are extrapolated directly into the past, reconstruction results may be distorted. Therefore, assessment of signal stability, segment-wise modelling and cross-validation among multiple series should become routine steps.

7.4. Data Sharing and Standardization

Domestic isotope data are mostly scattered among individuals and research groups, lacking unified metadata standards and public databases, which limits networked analysis and model calibration. Testing standards, pretreatment procedures and data formats should be harmonized, and a sharing platform including site locations, tree species, replication, series length and quality indicators should be established and linked with international tree-ring databases.

8. Conclusion

Tree-ring stable isotope research in China has undergone a transition from the single indicator $\delta^{13}C$ to the dominance of $\delta^{18}O$, from scattered sites to regional networks, and from centennial reconstructions to millennial and late Holocene series. $\delta^{13}C$ has formed a relatively mature methodological system in the reconstruction of temperature, relative humidity and atmospheric CO_2 concentration and in the assessment of water-use efficiency; $\delta^{18}O$, relying on well-defined fractionation mechanisms and its ability to preserve low-frequency signals, has become the principal indicator for hydroclimatic reconstruction on the plateau and in arid regions; δD and multi-isotope combinations provide a means of separating source-water and physiological signals.

Constraints remain evident: post-photosynthetic fractionation mechanisms are insufficiently explained, site coverage is uneven, signals are non-stationary through time, and data sharing and standardization lag behind. The next stage should focus on multi-isotope coupling and intra-annual high-resolution measurements, the calibration and application of isotope process models, and the construction of cross-regional data platforms.

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