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# 生态学报

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# 生态学报

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**封面图说:** 在树上嬉戏的大熊猫——大熊猫是中国的国宝, 自然分布狭窄, 数量极少, 世界上仅分布在中国的四川、陕西、甘肃三省的部分地区, 属第四纪冰川孑遗物种, 异常珍贵。被列为中国国家一级重点保护野生动物名录, 濒危野生动植物种国际贸易公约绝对保护的 CITES 附录一物种名录。瞧, 够得上“功夫熊猫”吧。

彩图提供: 陈建伟教授 国家林业局 E-mail: cites.chenjw@163.com

商志远,王建,崔明星,陈振举,王志军,刘丰,钱君龙.樟子松树轮不同组分的稳定碳同位素分析.生态学报,2011,31(18):5148-5158.  
Shang Z Y, Wang J, Cui M X, Chen Z J, Wang Z J, Liu F, Qian J L. Analysis of stable carbon isotopes in different components of tree rings of *Pinus sylvestris* var. *mongolica*. Acta Ecologica Sinica, 2011, 31(18):5148-5158.

## 樟子松树轮不同组分的稳定碳同位素分析

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**摘要:**对大兴安岭北部樟子松树轮中的全木、综纤维素和 $\alpha$ 纤维素3种组分按早晚材分别测定稳定碳同位素( $\delta^{13}\text{C}$ )值,分析比较早晚材两种材质的3种组分 $\delta^{13}\text{C}$ 值差异,探讨其对气候环境变化的响应。结果表明:从组分来看,樟子松树轮综纤维素的 $\delta^{13}\text{C}$ 指标更接近于 $\alpha$ 纤维素;从材质来看,樟子松树轮晚材不同组分的稳定碳同位素信号对气候环境变化响应的一致性和敏感程度要大于早材。樟子松树轮晚材的综纤维素 $\delta^{13}\text{C}$ 指标是研究过去气候或环境变化的理想载体,而 $\alpha$ 纤维素在提取过程中很可能丢失了部分气候信息。

**关键词:**树轮;碳同位素;气候变化;纤维素;材质;樟子松

## Analysis of stable carbon isotopes in different components of tree rings of *Pinus sylvestris* var. *mongolica*

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**Abstract:** Analysis of stable isotopes in tree rings is an important tool for global change research. There are two major advantages of using tree ring stable isotope data; they can be used for paleoclimate reconstructions with perfect annual resolution, and the confidence limits can be statistically defined. In addition, trees grow worldwide, and so it is possible to examine geographical climatic variations that have occurred in the past. Another advantage of analyses based on isotope ratios in tree rings is that the physiological mechanisms controlling their variations are reasonably well understood, and are relatively simple compared with the numerous factors that control the annual growth increment. Most research on stable isotopes in tree rings has focused on the stable isotopes of carbon, because they are the easiest to measure and show the most rapid development. However, to date, there is no consensus on which component of tree rings best reflects the climatic and environmental changes in terms of the carbon isotope ratio ( $\delta^{13}\text{C}$ ). In this study, we investigated the differences in  $\delta^{13}\text{C}$  among different tissue components of tree rings. Two tree disks of *Pinus sylvestris* var. *mongolica* (SZX01-08 and BZ4-10-1.2) were sampled from forest on the north slope of Yilehuli Mountain, Greater Khingan (approx.  $51^{\circ}57' - 52^{\circ}00'N$ ,  $124^{\circ}13' - 124^{\circ}36'E$ ). This site is located in the exclusive cool temperature zone of China that is dominated by coniferous forest

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vegetation. Tree-ring samples of earlywood (EW) and latewood (LW) were obtained with different sculpturing and pooling programs to avoid interference from non-uniform aspect distributions, i. e. both samples were sculptured for no less than two aspects (E+S+W for SZX01-08 and ENE+W for BZ4-10-1.2). Based on measurement of ring widths and cross-dating, the periods analyzed were the maximum growth periods; AD1904—1908/1924—1928/1944—1948 for SZX01-08 and AD1930—1944 for BZ4-10-1.2, according to polynomial fitting of ring-width sequences. The holocellulose and  $\alpha$ -cellulose fractions were extracted using the Soxhlet method, and the purity of the fractions was confirmed using a NEXUS670 Fourier transform infrared spectrometer. Stable carbon isotope ratios in different components ( $\alpha$ -cellulose, holocellulose and wholewood) of samples were measured using a ThermoFinnigan-Delta<sup>plus</sup> XP mass spectrometer and expressed as  $\delta^{13}\text{C}$  relative to the Vienna Pee Dee Belemnite (VPDB) standard. On the basis of relative analyses, the following results were obtained: (1) The  $\delta^{13}\text{C}$  values were highest for  $\alpha$ -cellulose followed by holocellulose, and lowest for wholewood. In general, the differences in  $\delta^{13}\text{C}$  values among the different components were greater in LW than in EW, as demonstrated by the standard deviations. All differences were statistically significant at the 0.001 level as determined by ANOVA tests. (2) The scatter plots of  $\alpha$ -cellulose vs. holocellulose and  $\alpha$ -cellulose vs. wholewood showed that holocellulose was more similar than wholewood to  $\alpha$ -cellulose, in terms of  $\delta^{13}\text{C}$  values. There were no significant correlations between  $\alpha$ -cellulose and holocellulose or between holocellulose and wholewood for EW. In contrast, correlations between the  $\delta^{13}\text{C}$  values of the three components were all statistically significant at the 0.01 level for LW. This indicated that the isotope signals of LW in tree rings are more coherent and more sensitive to changes in the local climate and environment than EW. (3) To some extent, the climate or environment signals reflected by the  $\delta^{13}\text{C}$  ratios are more significant for holocellulose than for  $\alpha$ -cellulose. This probably implies that the climate signals were impaired during extraction of  $\alpha$ -cellulose. The relationship between  $\delta^{13}\text{C}$  of wholewood and climate or environment factors was statistically insignificant. The extraction of  $\alpha$ -cellulose is time consuming and results in decreased accuracy; therefore, it is preferable to base palaeoclimatic or palaeoenvironmental reconstructions on data obtained from holocellulose in LW.

**Key Words:** tree rings; stable carbon isotopes; dendroclimatology; environmental change; cellulose; conifers

植物中的稳定碳同位素已经被广泛应用于过去环境和气候<sup>[1-5]</sup>等方面的研究。在过去的一百多年中,人们了解到树木是复杂的聚合物如纤维素、半纤维素和木质素等不同组分的混合体。由于光合作用过程中各种组分形成的生物化学反应不同,各组分的同位素组成也存在差异<sup>[6]</sup>,从而显示出不同的同位素值;反过来,又由于各自在树木中相对含量的不同而影响原木的  $\delta^{13}\text{C}$  值<sup>[7-9]</sup>。起初,人们对树轮同位素研究是从全木着手的<sup>[10-11]</sup>,为保证样品准备过程中尽量减少同位素分馏的影响,早期的研究通常对树轮全木的同位素值进行测定<sup>[12-15]</sup>。然而自 Wilson 和 Grinsted<sup>[16]</sup>阐述了木材不同化学成分之间的同位素差异后,绝大多数研究开始转向利用纤维素或者综纤维素(即纤维素和半纤维素的组合)。已发表的大量文献指出了温带树种中纤维素提取的必要性<sup>[17-18]</sup>,但是对于树轮中具体哪种成分的  $\delta^{13}\text{C}$  序列对环境变化信息的响应最为显著以及响应程度的差异,研究人员持有不同观点<sup>[19-23]</sup>。其中,由于  $\alpha$  纤维素的组成成分相对单一,具备在树轮生长过程中形成后保持稳定不变的特征,因而在多数情况下被优先选取<sup>[7,24-25]</sup>,但直到今天,纤维素提取依然是一项耗时低效的工作。一些学者通过对比研究认为,全木和纤维素能够记录同样的气候信息,仅分析全木也不会丢失气候信息<sup>[19-20,26-27]</sup>。因此认为,采用这类成分进行同位素分析是可以被接受的,而且采用全木或去脂后的成分进行分析可以避免样品量的损失。另外一种增加样品量的途径是在同位素分析之前对样品进行逐年混合,但令人遗憾的是,这种方法存在一个弱点,即难以满足用于气候重建的统计置信限度的要求。

随着树轮年际或多年分辨率的稳定同位素研究的不断发展,许多学者发现,树木单轮之内存在显著的同位素比率变化,即季节性变化<sup>[2,28-36]</sup>。为研究树轮  $\delta^{13}\text{C}$  序列的年内变化特征及其对气候和环境变化的响应关系,有关学者已经针对不同地域的不同树种做过若干研究<sup>[37-41]</sup>,目前较为普遍且可行的方法是将年轮细分为

早材和晚材两部分。针对上述问题,考虑到年轮的木质部含量存在季节性差异,而其反过来也会影响不同组分的 $\delta^{13}\text{C}$ 季节性差异,本文在前人研究的基础上,以大兴安岭北部的典型针叶树种——樟子松(*Pinus sylvestris* var. *mongolica* Litv)为研究对象,对其树轮中全木、综纤维素和 $\alpha$ 纤维素3种不同组分按早晚材分别进行 $\delta^{13}\text{C}$ 值测定,并在此基础上对比早晚材上述3种组分的 $\delta^{13}\text{C}$ 序列相互关系,以进一步探讨树轮不同组分的 $\delta^{13}\text{C}$ 差异以及它们对气候或环境变化的响应程度。

## 1 材料与方法

### 1.1 研究区概况

采样点位于黑龙江省大兴安岭地区新林林业局碧洲林场境内,地处大兴安岭伊勒呼里山北坡(图1),地势为西南高东北低,系大兴安岭古老褶皱断块山,海拔高度一般在300—800 m,山岭起伏不大,坡缓谷宽,境内丘陵连绵起伏,河流纵横密布,具有明显的山地气候特点。

本区属寒温带大陆性季风气候区:年平均气温 $-2.54\text{ }^{\circ}\text{C}$ ,年均积温( $\geq 10\text{ }^{\circ}\text{C}$ )约 $1430\text{ }^{\circ}\text{C}$ ,无霜期约90 d;全年日照2357 h,年日照率为51%—56%;年均降水519.4 mm,年蒸发量952.7 mm,主要降水多集中在7—8月份;年平均风速2—3 m/s<sup>①</sup>。主要土壤为山地棕色针叶林土,其次是沼泽土。本区森林植物属于寒温带明亮夏绿针叶林,树种组成有兴安落叶松(*Larix gmelinii*)、樟子松、云杉(*Picea*)和桦树(*Betula*)等,其中樟子松一般分布在海拔600 m以下低山上部,为零星散生或是面积不大的小块纯林,其中有少量落叶松混生<sup>[42-44]</sup>。

### 1.2 样品采集与室内处理

选取林场下辖大青山十支线樟子松树盘(编号SZX01-08)和林场后山樟子松树盘(编号BZ4-10-1.2)作为研究对象(表1):其中SZX01-08样品所在地势开阔,为孤立木,生长受人类活动影响较小,而BZ4-10-1.2样品所在地势也相对较为平坦,但郁闭度较大,生长受到一定的人为干扰。样本采集前做好方位标识,运回实验室后置于阴凉通风处风干,用200—600目的干砂纸打磨表面至早晚材界限清晰可见,利用AeuRite年轮宽度仪的MeasureJ2X量测系统对两样品分不同方位测量早晚材宽度,测量精度0.001 mm,并利用COFECHA程序进行交叉定年检验。判断两树盘各方位生长特征,用钢锯沿5—10°的弧度范围由正北方向顺时针分8个方位小心锯开,为了满足综纤维素和 $\alpha$ 纤维素提取对样本量的要求,对两个盘轮宽数据进行高次多项式拟合,并对趋势线求极值来确定生长量最大段所在年份(图2):其中SZX01-08生长高值区较长,为1904—1948年,选取其中等间隔的3段,每段各5 a(分别为1904—1908年,1924—1928年,1944—1948年);BZ4-10-1.2选取了连续的15 a(1930—1944年)。

为避免方位一致带来的干扰,同时考虑纤维素提取时对样本量的要求,参考有关文献<sup>[45]</sup>,对SZX01-08号盘选取相互成直角的东(E)、南(S)和西(W)3个方位样本进行同年份混合,对BZ4-10-1.2号盘选取成钝角的东北东(ENE)和西(W)两个方位样本进行同年份混合,干燥研磨并过60目筛混合均匀,每个样本均留存0.2 g左右作为全木样本,剩余样本进行综纤维素提取,提取完成后再分别留存0.2 g左右作为综纤维素待测样本,其余样本继续进行 $\alpha$ 纤维素提取。

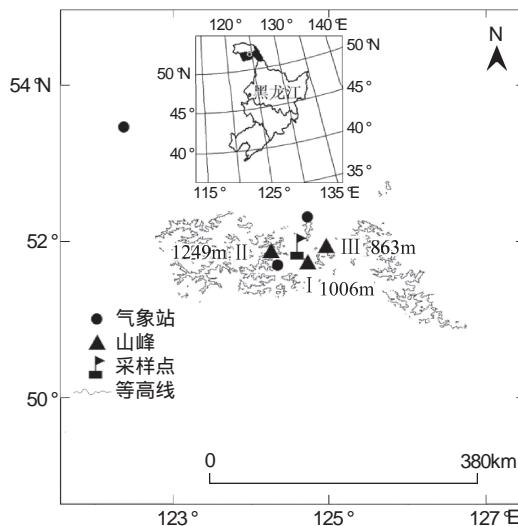


图1 采样点分布图

Fig. 1 Location map of the sampling sites

I: 西雅吉雅勒山, II: 卡尔加山, III: 玻马勒山

<sup>①</sup> 气象指标统计时间均为1972年1月至2009年12月。

表 1 样品信息表

Table 1 Basic information of the tree disk samples

| 树盘编号<br>Samples No. | 地理位置<br>Locations                             | 采样时间<br>Sampling time | 树龄/a<br>Tree-age | 雕刻方案<br>Sculpturing program | 混合方案<br>Pooling program |
|---------------------|---|-----------------------|------------------|-----------------------------|-------------------------|
| SZX01-08            | 51°59'.739'N, 124°13'.203'E,<br>796m a. s. l. | 2005-01               | 231              | 分早晚材,<br>3 段×5a             | E+S+W                   |
| BZ4-10-1.2          | 51°56'.995'N, 124°36'.070'E,<br>494m a. s. l. | 2008-07               | 117              | 分早晚材,<br>连续 15a             | ENE+W                   |

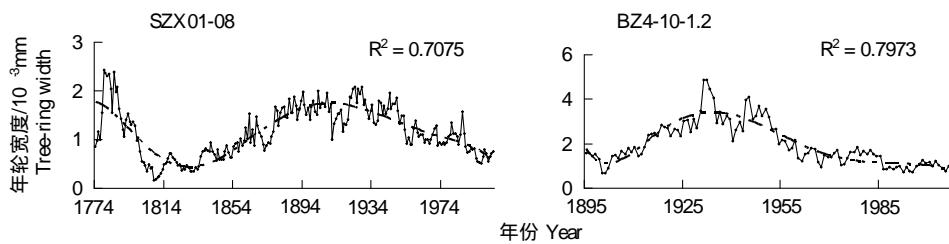


图 2 样品宽度序列原始值

Fig. 2 Original values of samples width

按雕刻方案方向测量平均,虚线均为六次多项式拟合趋势线,  $R^2$  为决定系数

### 1.3 纤维素提取及纯度检验

参考有关文献<sup>[4,46-48]</sup>,采用索氏抽提法对本研究样品的综纤维素和  $\alpha$  纤维素进行提取(图 3)。为保证实验的精度和准确性,选取提取的综纤维素样品和  $\alpha$  纤维素样品与全木样品一同进行红外光谱扫描分析,并与标准  $\alpha$  纤维素样品红外光谱进行对比,以检验此流程提取的纤维素纯度是否符合标准。本项工作在南京师范大学分析测试中心 FTIR-NEXUS670 型傅里叶变换红外光谱仪上完成。参考相关文献<sup>[49-52]</sup>,对比分析表明此流程提取的综纤维素和  $\alpha$  纤维素样品符合标准,满足研究要求。

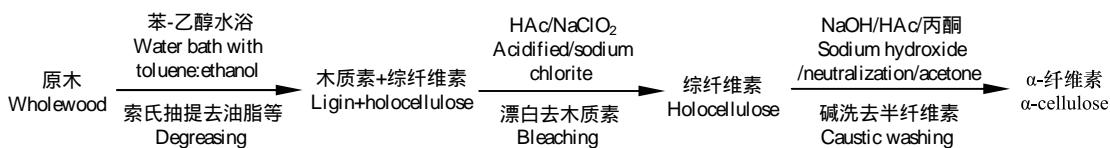


图 3 索氏抽提法简要流程图

Fig. 3 Brief flowchart of Soxhlet extraction

### 1.4 样品 $\delta^{13}\text{C}$ 测定

将提取好的综纤维素样品、 $\alpha$  纤维素样品和全木样品( $(0.20\pm0.05)\text{ mg}$ )送入质谱仪自动进样器,以测定样品的碳同位素 $^{13}\text{C}/^{12}\text{C}$  之比,本项工作在中国科学院沈阳应用生态研究所 ThermoFinnigan-DeltaplusXP 同位素比例质谱仪上完成,整个流程分析误差 $\leq 0.15\text{\%}$ 。采用尿素标准样(UREA,  $\delta^{13}\text{C}=-49.1\text{\%}$ )进行校验,测定结果相对于 PDB 标准表示为  $\delta^{13}\text{C}_{\text{PDB}}$ ,简写为  $\delta^{13}\text{C}$ ,表达式为<sup>[53]</sup>:

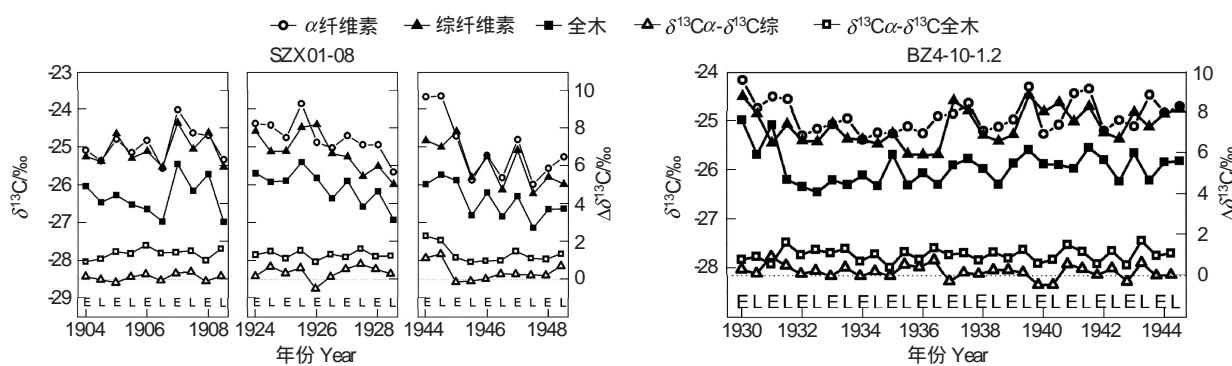
$$\delta^{13}\text{C} = [(\text{C}^{13}/\text{C}^{12})_{\text{样品}} / (\text{C}^{13}/\text{C}^{12})_{\text{标准}} - 1] \times 1000\text{\%}$$

## 2 结果与分析

以上两个树盘合计全木、综纤维素和  $\alpha$  纤维素样本各 60 个,总计 180 个样本进行  $\delta^{13}\text{C}$  测定,测定结果见图 4。

### 2.1 $\alpha$ 纤维素、综纤维素和全木的 $\delta^{13}\text{C}$ 序列对比

表 2 为两样本分早晚材的  $\alpha$  纤维素、综纤维素和全木的  $\delta^{13}\text{C}$  序列统计结果,结合图 4 对比发现,总体来看,两棵树无论是早材还是晚材,基本都是  $\alpha$  纤维素的  $\delta^{13}\text{C}$  值最大,综纤维素的  $\delta^{13}\text{C}$  值次之,全木的  $\delta^{13}\text{C}$  值

图4 树轮不同组分  $\delta^{13}\text{C}$  值序列Fig. 4 Original values of samples  $\delta^{13}\text{C}$  values for different components

E: 早材 Earlywood; L: 晚材 Latewood

最小。从平均值之差来看:早材的综纤维素比 $\alpha$ 纤维素低 $0.121\text{‰}—0.223\text{‰}$ ,全木又比综纤维素低 $0.714\text{‰}—1.086\text{‰}$ ;晚材的综纤维素比 $\alpha$ 纤维素低 $0.3\text{‰}—0.393\text{‰}$ ,全木又比综纤维素低 $0.943\text{‰}—1.002\text{‰}$ 。分早晚材来看,对于同一材质,同个样本不同组分之间的 $\delta^{13}\text{C}$ 值存在不同程度的差异,从标准差指标来看,晚材不同组分之间的 $\delta^{13}\text{C}$ 值差别整体较早材更大一些。

表2 两样本 $\alpha$ 纤维素、综纤维素和全木的 $\delta^{13}\text{C}$ 序列的统计结果Table 2 Statistical indices of the  $\delta^{13}\text{C}$  sequences for different components in samples

| 树盘编号<br>Samples No. | 材质<br>Material | 成分<br>Component                  | 最大值/‰<br>Maximum | 最小值/‰<br>Minimum | 平均值/‰<br>Mean | 标准差<br>Std dev. |
|---------------------|----------------|----------------------------------|------------------|------------------|---------------|-----------------|
| SZX01-08            | 早材 EW          | $\alpha$ 纤维素 $\alpha$ -cellulose | -23.658          | -25.550          | -24.723       | 0.455           |
|                     |                | 综纤维素 holocellulose               | -23.347          | -25.780          | -24.946       | 0.423           |
|                     |                | 全木 wholewood                     | -25.445          | -26.638          | -26.032       | 0.337           |
|                     | 晚材 LW          | $\alpha$ 纤维素 $\alpha$ -cellulose | -23.636          | -25.978          | -25.090       | 0.706           |
|                     |                | 综纤维素 holocellulose               | -24.460          | -26.219          | -25.483       | 0.491           |
|                     |                | 全木 wholewood                     | -25.390          | -27.123          | -26.485       | 0.502           |
| BZ4-10-1.2          | 早材 EW          | $\alpha$ 纤维素 $\alpha$ -cellulose | -24.151          | -25.372          | -24.975       | 0.365           |
|                     |                | 综纤维素 holocellulose               | -24.483          | -25.682          | -25.097       | 0.340           |
|                     |                | 全木 wholewood                     | -24.970          | -26.329          | -25.811       | 0.370           |
|                     | 晚材 LW          | $\alpha$ 纤维素 $\alpha$ -cellulose | -24.288          | -25.231          | -24.807       | 0.310           |
|                     |                | 综纤维素 holocellulose               | -24.46           | -25.675          | -25.107       | 0.397           |
|                     |                | 全木 wholewood                     | -25.536          | -26.439          | -26.050       | 0.307           |

图5为两样本分早晚材的 $\alpha$ 纤维素分别与综纤维素和全木对应的散点图,表3为对应的回归方程及检验结果。由图5可以看出,无论早材还是晚材,两样本均表现出综纤维素相对于全木与同材质的 $\alpha$ 纤维素的 $\delta^{13}\text{C}$ 值更为一致(更靠近等值线),表明在稳定碳同位素指标上,综纤维素的特征更接近于 $\alpha$ 纤维素。结合图5显示结果,由表3可知,两样本早晚材的综纤维素、全木与相应的 $\alpha$ 纤维素的线性回归拟合结果相对都比较理想,且均表现出晚材好于早材。这也意味着晚材的各组分对气候环境要素响应的一致性要好于早材。

## 2.2 樟子松不同组分的 $\delta^{13}\text{C}$ 序列方差分析

对樟子松不同组分的 $\delta^{13}\text{C}$ 序列进行方差分析(表4),结果显示,无论早材还是晚材,两样本的不同组分之间的 $\delta^{13}\text{C}$ 差异是极其显著的,均超过了0.001的显著性水平,而从均方差来看,晚材的各组分之间相互差异更大一些。

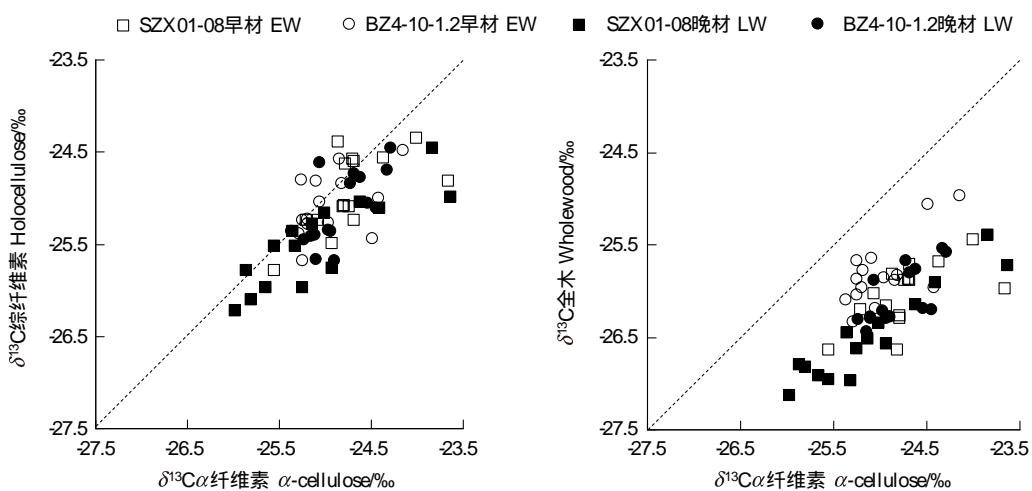
图5 树轮不同组分 $\delta^{13}\text{C}$ 值的变化特征Fig. 5 Variation patterns of the  $\delta^{13}\text{C}$  values for different components in samples表3 两样本早晚材的综纤维素和全木相对于 $\alpha$ 纤维素的回归分析

Table 3 Linear Regression of holocellulose and wholewood for cellulose with different materials

| 树盘编号<br>Samples No. | 材质<br>Material | 回归方程<br>Regression equation  | 校正 $R^2$<br>Correction coefficient | P      |
|---------------------|----------------|--|------------------------------------|--------|
| SZX01-08            | 早材 EW          | $\delta^{13}\text{C}$ 综纤维素 = $0.586 (\pm 0.200) \delta^{13}\text{C} \alpha$ 纤维素 - $10.456 (\pm 4.941)$ | 0.352                              | 0.012  |
|                     |                | $\delta^{13}\text{C}$ 全木 = $0.443 (\pm 0.164) \delta^{13}\text{C} \alpha$ 纤维素 - $15.069 (\pm 4.067)$   | 0.309                              | 0.018  |
|                     | 晚材 LW          | $\delta^{13}\text{C}$ 综纤维素 = $0.591 (\pm 0.102) \delta^{13}\text{C} \alpha$ 纤维素 - $10.645 (\pm 2.552)$ | 0.701                              | <0.001 |
|                     |                | $\delta^{13}\text{C}$ 全木 = $0.668 (\pm 0.068) \delta^{13}\text{C} \alpha$ 纤维素 - $9.723 (\pm 1.703)$    | 0.873                              | <0.001 |
| BZ4-10-1.2          | 早材 EW          | $\delta^{13}\text{C}$ 综纤维素 = $0.451 (\pm 0.226) \delta^{13}\text{C} \alpha$ 纤维素 - $13.822 (\pm 5.652)$ | 0.176                              | 0.067  |
|                     |                | $\delta^{13}\text{C}$ 全木 = $0.707 (\pm 0.202) \delta^{13}\text{C} \alpha$ 纤维素 - $8.156 (\pm 5.045)$    | 0.446                              | 0.004  |
|                     | 晚材 LW          | $\delta^{13}\text{C}$ 综纤维素 = $0.872 (\pm 0.260) \delta^{13}\text{C} \alpha$ 纤维素 - $3.466 (\pm 6.445)$  | 0.423                              | 0.005  |
|                     |                | $\delta^{13}\text{C}$ 全木 = $0.699 (\pm 0.194) \delta^{13}\text{C} \alpha$ 纤维素 - $8.698 (\pm 4.806)$    | 0.462                              | 0.003  |

表4 两样本不同组分的 $\delta^{13}\text{C}$ 序列 ANOVA 分析 \*Table 4 ANOVA analysis of the  $\delta^{13}\text{C}$  sequences for different components in samples

| 树盘编号<br>Samples No. | 变异来源<br>Source of variation | 方差<br>SS | 自由度<br>df | 均方<br>MS | F      |
|---------------------|-----------------------------|----------|-----------|----------|--------|
| SZX01-08            | 早材 EW                       | 14.722   | 2         | 7.361    | 44.213 |
|                     | 晚材 LW                       | 15.517   | 2         | 7.759    | 23.472 |
| BZ4-10-1.2          | 早材 EW                       | 6.118    | 2         | 3.059    | 23.814 |
|                     | 晚材 LW                       | 12.623   | 2         | 6.311    | 54.336 |

\* 显著值均小于 0.001

利用 Student-Newman-Keuls(S-N-K)方法对不同组分的 $\delta^{13}\text{C}$ 序列进行子集归类(表5),可以看出:对于早材而言,两样本的综纤维素与 $\alpha$ 纤维素 $\delta^{13}\text{C}$ 序列之间的差异不显著,可以归为一类,而全木与这两者的差异显著,单独划为另一类。对于晚材而言,SZX01-08样本的综纤维素与 $\alpha$ 纤维素的 $\delta^{13}\text{C}$ 序列之间的差异仍不显著,可以归为一类,而全木与这两者的差异仍然显著,单独划为另一类;BZ4-10-1.2样本的3种组分之间差异均比较显著,即便如此,也可以看出其综纤维素与 $\alpha$ 纤维素的 $\delta^{13}\text{C}$ 序列差异要小于其与全木的 $\delta^{13}\text{C}$ 序列差异。以上分析同样表明在稳定碳同位素指标上,综纤维素的特征更接近于 $\alpha$ 纤维素。

表5 两样本不同组分的 $\delta^{13}\text{C}$ 序列子集Table 5 Subgroups of the  $\delta^{13}\text{C}$  sequences for different components in samples

| 树盘编号<br>Samples No. | 组分<br>Components                 | 早材子集 Subsets of EW |         | 晚材子集 Subsets of LW |         |         |
|---------------------|----------------------------------|--------------------|---------|--------------------|---------|---------|
|                     |                                  | 1                  | 2       | 1                  | 2       | 3       |
| SZX01-08            | 全木 Wholewood                     | -26.032            |         | -26.485            |         |         |
|                     | 综纤维素 Holocellulose               |                    | -24.946 |                    | -25.483 |         |
|                     | $\alpha$ 纤维素 $\alpha$ -cellulose |                    | -24.723 |                    | -25.090 |         |
|                     | 显著值 Significance value           | 1.000              | 0.141   | 1.000              | 0.068   |         |
| BZ4-10-1.2          | 全木 Wholewood                     | -25.811            |         | -26.050            |         |         |
|                     | 综纤维素 Holocellulose               |                    | -25.097 |                    | -25.107 |         |
|                     | $\alpha$ 纤维素 $\alpha$ -cellulose |                    | -24.975 |                    |         | -24.807 |
|                     | 显著值 Significance value           | 1.000              | 0.359   | 1.000              | 1.000   | 1.000   |

### 2.3 檫子松不同组分的 $\delta^{13}\text{C}$ 序列相关分析

此外,各成分的 $\delta^{13}\text{C}$ 值变化虽然不十分一致,但仍有一定的相关性(表6)。其中,早材的 $\alpha$ 纤维素与全木之间的相关性最高,并达到了0.01的显著性水平,而 $\alpha$ 纤维素与综纤维素以及综纤维素与全木之间的相关性较差,都没有达到显著性水平;晚材的各成分之间相关性均达到了0.01的显著性水平,其中综纤维素与全木之间的相关性最高,与早材之间的相关性差别也最明显。

表6 不同组分的 $\delta^{13}\text{C}$ 之间的相关性(BZ4-10-1.2, 1930—1944)Table 6 Correlation coefficients of the  $\delta^{13}\text{C}$  sequences between different components (BZ4-10-1.2, 1930—1944)

|       | $\alpha$ 纤维素-综纤维素<br>$\alpha$ -cellulose-holocellulose | $\alpha$ 纤维素-全木<br>$\alpha$ -cellulose-wholewood | 综纤维素-全木<br>Holocellulose-wholewood |
|-------|--|--|------------------------------------|
| 早材 EW | 0.484  | 0.697 **   | 0.337                              |
| 晚材 LW | 0.682 **   | 0.708 **   | 0.897 **                           |

\* \* 在0.01水平上显著相关

为比较不同成分的早晚材之间 $\delta^{13}\text{C}$ 序列的相关性,将BZ4-10-1.2的不同成分 $\delta^{13}\text{C}$ 序列按早晚材求相关,结果见表7。

表7 不同成分的早晚材之间 $\delta^{13}\text{C}$ 的相关性(BZ4-10-1.2, 1930—1944)Table 7 Correlation coefficients between EW and LW of the  $\delta^{13}\text{C}$  sequences for different components (BZ4-10-1.2, 1930—1944)

| $\alpha$ 纤维素 $\alpha$ -cellulose | 综纤维素 Holocellulose | 全木 Wholewood |
|----------------------------------|--------------------|--------------|
| 0.653 **                         | 0.611 *            | 0.302        |

\* 在0.05水平上显著相关; \* \* 在0.01水平上显著相关

由表7可以看出,不同成分的早晚材之间 $\delta^{13}\text{C}$ 序列相关性也有差别,其中两种材质的 $\alpha$ 纤维素 $\delta^{13}\text{C}$ 序列之间的相关性最显著,达到了0.01的显著性水平,综纤维素的 $\delta^{13}\text{C}$ 序列相关性也比较显著,达到了0.05的显著性水平,而全木的 $\delta^{13}\text{C}$ 序列相关性最差,尚未达到显著相关的程度。这说明,在每年的早材向晚材转化过程中,由于3种成分的合成途径不同,在气候响应的一致性方面, $\alpha$ 纤维素由于组成单一,具有较好的稳定性,导致了其早晚材的 $\delta^{13}\text{C}$ 相关性最为显著;而综纤维素由于去除了油脂类和木质素部分,其稳定性也相对比较理想,因而其早晚材的 $\delta^{13}\text{C}$ 相关性也比较显著;而全木的成分组成过于复杂,故其早晚材对气候和环境变化响应的一致性也远不如前两者明显。

### 2.4 两种材质的不同组分 $\delta^{13}\text{C}$ 与生长量的相关性

植物的生长量大小是指其固碳能力的大小,会直接影响固碳过程中碳同位素的分馏。借鉴前人研究方法<sup>[18]</sup>,将BZ4-10-1.2样本分早晚材的 $\alpha$ 纤维素、综纤维素及全木的 $\delta^{13}\text{C}$ 序列与早晚材年生长量进行相关性分析(表8)。其中,早晚材年生长量用树轮早晚材宽度序列(与雕刻方案相同的各方向宽度数据取平均)及

去趋势序列(对宽度序列采用高次多项式拟合并计算差值序列)代替。分析发现,不论是早材还是晚材,树轮 $\alpha$ 纤维素、综纤维素及全木的 $\delta^{13}\text{C}$ 序列与年生长量之间均呈负相关关系,也就说明树轮宽度就越宽,其树轮的 $\delta^{13}\text{C}$ 值越低。其中,相关系数最高的为综纤维素,且早材的综纤维素 $\delta^{13}\text{C}$ 序列与树轮宽度序列的负相关性达到了0.05的显著性水平。

表8  $\alpha$ 纤维素、综纤维素及全木的 $\delta^{13}\text{C}$ 序列和树轮宽度相关性比较(BZ4-10-1.2, 1930—1944年)

Table 8 Correlation coefficients between the  $\delta^{13}\text{C}$  sequences of three components and tree ring width sequences (BZ4-10-1.2, 1930—1944)

|       | 材质/序列<br>Material/sequences     | $\alpha$ 纤维素<br>$\alpha$ -cellulose | 综纤维素<br>Holocellulose | 全木<br>Wholewood |
|-------|---------------------------------|-------------------------------------|-----------------------|-----------------|
| 早材 EW | 宽度序列 Ring Width Sequences (RWS) | -0.030                              | -0.516 *              | -0.088          |
|       | 去趋势序列 detrended RWS             | -0.008                              | -0.491                | -0.073          |
| 晚材 LW | 宽度序列 Ring Width Sequences (RWS) | -0.098                              | -0.209                | -0.279          |
|       | 去趋势序列 detrended RWS             | -0.066                              | -0.173                | -0.250          |

\* 在0.05水平上显著相关

### 3 讨论

Warren等<sup>[54]</sup>研究发现,针叶树的全木 $\delta^{13}\text{C}$ 值总比纤维素低0.87‰。Helle和Schleser<sup>[39]</sup>发现由于树轮木质素比例的变化,欧洲山毛榉(*Fagus sylvatica L.*)的3a $\delta^{13}\text{C}$ 值由纤维素到全木降低约0.5‰—1.8‰,并指出,其不同成分之间的 $\delta^{13}\text{C}$ 差值在树轮中存在不同程度的连续性,但是在不同年份有所差异。Loader等<sup>[20]</sup>在对英国栎(*Quercus robur L.*)晚材的研究中发现纤维素和木质素成分中的碳同位素分馏值分别比全木高1‰和低2‰,并认为其很可能与木质化和纤维素合成阶段中光合作用产物分解的二次新陈代谢过程有关。从不同材质的 $\delta^{13}\text{C}$ 值差异和幅度来看,本研究的结果与上述研究基本类似。同时还表明,按材质看,早材的各成分 $\delta^{13}\text{C}$ 值之差别不如晚材显著,而按成分看,全木的 $\delta^{13}\text{C}$ 值最低,显著低于 $\alpha$ 纤维素和综纤维素,而 $\alpha$ 纤维素和综纤维素之间的差别并不明显(图4和图5)。从标准差来看,无论早材还是晚材,全木的标准差相对要小于纤维素和综纤维素,这也反映了全木对气候环境变化的敏感性不如纤维素和综纤维素,而分材质来看,两棵树的早晚材标准差各有不同,但各自的综纤维素的标准差都是晚材大于早材,这也在一定程度上反映了对于综纤维素成分而言,晚材对当年气候或环境变化响应的敏感性更强(表2)。

大气 $\text{CO}_2$ 中的 $\delta^{13}\text{C}$ 值一般认为是在-6.41‰(工业化之前)——7.87‰(20世纪80年代)之间<sup>[55]</sup>,而本地区的樟子松树轮 $\alpha$ 纤维素中的 $\delta^{13}\text{C}$ 值多年平均值为-23.65—-24.35‰(1948—2002年)。当外界的气候和环境条件比较适宜时,植物的生理活动较强,其光合作用和固碳能力就越强,相应的就会形成较负的纤维素 $\delta^{13}\text{C}$ 值<sup>[18]</sup>。树轮的宽度在树木的木质部形成之后相对保持稳定,其中包含了影响植物生长的各种外界气候和环境信息<sup>[56]</sup>。早材的综纤维素 $\delta^{13}\text{C}$ 值与树轮的宽度序列关系最为密切(表8),也说明其中包含了树木当年生长时的气候环境信息,进一步表明了树轮纤维素中碳在经历了光合作用的碳同位素分馏后,其性质保持相对稳定。而晚材的各种成分与年生长量之间的相关系数普遍不高,这应与晚材的轮宽较小,相对所占比例较低等原因有关。

部分研究发现 $\alpha$ 纤维素和原木之间的 $\delta^{13}\text{C}$ 存在和木质素之间一样显著的相关性<sup>[1-3,19,24,57]</sup>,使得通过原木 $\delta^{13}\text{C}$ 可以反推出 $\alpha$ 纤维素的 $\delta^{13}\text{C}$ 值,因而一些研究人员对树轮研究中纤维素提取的必要性提出质疑<sup>[9,19]</sup>。此外,在气候代用指标方面,原木可以达到和纤维素或 $\alpha$ 纤维素相同甚至某些情况下更好的效果<sup>[19-20]</sup>,尽管Borella等<sup>[19]</sup>认为这种说法比较适用于橡树(*Quercus palustris*)、桦树和榉树(*Zelkova*)以及其它硬木树种,并不适用于针叶木。而Loader等<sup>[20]</sup>的研究认为,与纤维素或木质素相比,全木的 $\Delta\delta^{13}\text{C}$ 含有更强烈的气候信号,并认为这可能是全木的同位素成分与固定在叶片中的总糖最为类似。本研究中,早晚材两种材质的 $\alpha$ 纤维素和综纤维素的 $\delta^{13}\text{C}$ 序列相关性都比较显著,分别达到了0.01和0.05的显著性水平,而全木的 $\delta^{13}\text{C}$ 序列相关性尚未达到显著相关的程度(表7),表明综纤维素和 $\alpha$ 纤维素 $\delta^{13}\text{C}$ 序列性质更加相近,在反映气候环境变化的能力上更加相似。Cullen和Grierson<sup>[22]</sup>对澳大利亚圆柏松(*C. glauophylla*)的研究认为,究竟采用全木

或纤维素哪种成分进行树轮气候研究,应当视具体研究目标而论。他们认为,研究气候长期变化趋势时采用全木是有效的指标,而当气候的高频变化是主要关注目标时,纤维素才是理想的材料。总之,以上各学者的研究表明,树轮不同成分的 $\delta^{13}\text{C}$ 序列对气候信息的响应程度有所差异。本研究显示的综纤维素 $\delta^{13}\text{C}$ 中的气候信息在某种角度甚至比 $\alpha$ 纤维素 $\delta^{13}\text{C}$ 更显著一些(表8),而全木 $\delta^{13}\text{C}$ 和气候变化的关系不明显。Jäggi等<sup>[58]</sup>研究了欧洲云杉(*Picea abies*)树轮早材和晚材的碳稳定同位素组成,发现早材 $\delta^{13}\text{C}$ 值与冬季降雨呈弱相关,晚材 $\delta^{13}\text{C}$ 值与总辐射、相对湿度和温度有关,越是干热气候,同位素就越富集,因此他们认为早材同位素信号由生化分馏(如淀粉形成)决定,晚材同位素信号主要受气候条件影响,本研究的结果从另一方面支持了这一结论。

在木材的纤维素形态特征方面,相对于早材而言,晚材的纤维素长度较长,宽度较短,即长宽比要大于早材,而壁较厚,腔径较小,即壁腔比大于早材。各种木材的化学组成常因树种、生长区域和生长部位的不同而发生变异,即使同种同株树木也有差别。李阳根等对本区域的樟子松化学成分分析结果表明,综纤维素为主要成分,占78.62%,而综纤维素中的 $\alpha$ 纤维素又具有较大的比例,含量为68.31%,其余为少量的抽提物和灰分等<sup>[59]</sup>。通常认为, $\alpha$ 纤维素的理化性质相对最为稳定,但是在其提取过程中去除了木质素和半纤维素等成分,因而是否同时也不同程度的损失了气候信息至今尚未有一致性的结论。由于本研究立足于分析早晚材两种材质的不同组分性质,考虑样本雕刻及测试时对样本量的需求,选取的雕刻时段无对应的气象站点数据记录,因而未能对树轮分早晚材两种材质的3种不同组分 $\delta^{13}\text{C}$ 与气候因子建立联系。但本研究的结果表明,利用树轮晚材的综纤维素成分进行气候或环境重建方面的分析,应该是一种相对稳妥而又比较简便的办法。

#### 4 结论

(1) 相关分析结果表明早材除 $\alpha$ 纤维素与全木之间的相关性外, $\alpha$ 纤维素与综纤维素以及综纤维素与全木之间的相关性都没有达到显著性水平;而晚材的各成分之间相关性均达到了0.01的显著性水平,且全部相关系数都明显高于早材的各成分之间的相关系数,这一点与前期的多数研究结果类似<sup>[20,22]</sup>,同时也表明晚材的各成分之间同位素信号受气候影响的一致性要比早材更为显著。

(2) 树轮晚材的综纤维素 $\delta^{13}\text{C}$ 序列是研究过去气候环境变化的理想载体。考虑到 $\alpha$ 纤维素提取流程规范对操作的精度要求较高,以及其工作量大而低效等因素,在样本量充裕的情况下利用树轮晚材的综纤维素 $\delta^{13}\text{C}$ 序列进行气候或环境变化研究既能很大程度地保留信息,其实验室提取工作又相对简便易于操作,是一项非常值得考虑的理想选择,在今后的研究中具有广泛且很有价值的应用前景。

(3) 综纤维素 $\delta^{13}\text{C}$ 中的气候信息在某些情况下比 $\alpha$ 纤维素 $\delta^{13}\text{C}$ 更为显著,这很有可能意味着在 $\alpha$ 纤维素的提取过程中丢失了部分气候信息,同时也支持了本文前面提到的部分研究对 $\alpha$ 纤维素提取的必要性的质疑。因为其不仅是单纯增加工作量一方面的因素,很可能会对 $\alpha$ 纤维素在气候或环境重建过程中的作用和影响重新提出疑问,而对这一点的确证以及 $\alpha$ 纤维素究竟在多大程度上丢失信息,需要继续深入研究和探讨。

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