STABLE CARBON ISOTOPIC COMPOSITION IN ANNUAL RINGS OF A PINE TREE (*PINUS DENSIFLORA*) FROM YEONGWOL, KOREA: POSSIBLE APPLICATION TO CLIMATE STUDY

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ABSTRACT. Stable carbon isotope ratios were measured on the alpha-cellulose in tree rings of a pine tree (*Pinus densiflora*) from Yeongwol, Korea. We developed an annual-resolution $\delta^{13}C$ series (1835–1905) by correcting the measured data for changes in $\delta^{13}C$ of air to minimize non-climatic influences. To investigate the climatic signal in the $\delta^{13}C$ series, we performed correlation analysis between $\delta^{13}C$ and the Cheugugi climate data. The Cheugugi precipitation data were first recorded by King Sejong (1397–1450) of the Joseon Dynasty. However, the longest set of precipitation data available is the one collected in Seoul (1776–1907). Although many studies support the reliability of the Cheugugi data, no previous studies have investigated the potential of the $\delta^{13}C$ signal in tree rings as paleoclimate proxy using the Cheugugi data. Recent precipitation trends in Yeongwol are quite similar to that of Seoul, and we found significant correlations between the Cheugugi data and the $\delta^{13}C$ series. We suggest further studies to replicate these results and confirm whether comparing $\delta^{13}C$ variations in tree rings and Cheugugi data is a useful method of investigating the potential of the $\delta^{13}C$ signal as a paleoclimate proxy in or near the Korean peninsula.

KEYWORDS: tree ring, carbon isotope, Cheugugi data, correlation.

INTRODUCTION

Climate change is currently an issue of scientific and political importance. To understand climate change, reconstructions of past climate variations are essential. Natural archives (such as tree rings, ice cores, and corals) are useful for reconstructing past climatic conditions and compensate for the lack of meteorological measurements (McCarroll and Loader 2004; Sano et al. 2009). In particular, the variation of carbon isotope composition in annual tree rings, with their high time resolution, can play an important role in climate reconstructions. The concentrations of radiocarbon ($^{14}C$) and light stable isotopes ($^2H$, $^{13}C$, $^{18}O$, etc.) in annual rings are sensitive indicators of climate variables (such as temperature, precipitation, and insolation), but also reflect anthropogenic influences (McCarroll and Loader 2004; Pazdur et al. 2007).

On the other hand, historical climate data are also useful for reconstructing past climatic conditions. Cheugugi (meaning “rain-measuring device”) data are one such set of historical climate data for the Korean peninsula. They were first recorded by King Sejong (1397–1450) of the Joseon Dynasty. However, the longest set of precipitation data available is the one collected in Seoul AD 1777–1907. The main structure of the Cheugugi data is unique, containing the start time, end time, and total amount of rain during each event (Yoo et al. 2015). Therefore, the duration and total amount of rain during each rainfall event are available. Many studies have found long-term correlations between the Cheugugi data and climate-related data, such as the Southern Oscillation Index, and have claimed that such correlations are evidence of the reliability of the Cheugugi data (Hwang et al. 2009; Kim et al. 2010). Recently, Jung et al. (2001) found statistical similarities between the Cheugugi data and modern precipitation data, and suggested the Cheugugi data are reliable for short-term (diurnal) precipitation study.

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However, although many studies support the reliability of the Cheugugi data, studies have not investigated the potential of the δ¹³C signal in tree rings as paleoclimate proxy using the Cheugugi data. To perform such studies, tree rings that are expected to contain the precipitation information of the Cheugugi data should be identified and analyzed. For example, tree rings should be selected that formed in the period of the precipitation record and also in the region near the measurement station. However, such tree-ring samples are not easy to obtain in Korea for several reasons (such as city or residents’ approval).

We recently obtained tree-ring samples from a pine tree stump (Pinus densiflora) located at Yeongwol, Korea, approximately 100 km east from Seoul, Korea, where the longest Cheugugi data were recorded. Recent 21-yr precipitation trends in Yeongwol are quite similar to Seoul, so we expected precipitation variations from the Cheugugi data would be reflected in δ¹³C in the tree rings, and found significant correlations between the Cheugugi data and δ¹³C data. We suggest further studies to replicate these results and confirm whether comparing δ¹³C variations in tree rings and Cheugugi data is a useful method of investigating the potential of the δ¹³C signal as a paleoclimate proxy in or near the Korean peninsula.

THE YEONGWOL PINE TREE AND ITS GROWING AREA

The pine tree (Pinus densiflora) was located in Seoun Old Pine Tree Park (37°22′19″N, 128°11′19″E), Suju-myeon, Yeongwol-gun, Gangwon-do in South Korea, as shown in Figure 1a. The tree itself, shown in Figure 1b, was listed as a protected tree by Yeongwol County Government, was 20 m high with 3.7 m circumference, and was considered a “protector” of the village. However, the tree was knocked down by wind in March 2010. Now, only the stump of the tree remains, as shown in Figure 1c.

Meteorological data from the Yeongwol station (37°10′52.421″N, 128°27′26.930″E, records started 1995), which is located approximately 30 km from the sample site, were used to assess the climate at the sample site. Over the 1995–2015 period, mean annual temperature was 11°C, mean number of annual days with precipitation was 113, and mean annual precipitation was 1231 mm (with ca. 71% occurring during June–September) (KMA 2016). To investigate the climate similarity between Yeongwol and Seoul (where the Cheugugi data used in this study were recorded), we compared meteorological data from the Seoul station (37°34′17″N, 126°57′56″E, modern records started 1907) and that from the Yeongwol station over years with overlapping records (1995–2015). As shown in Figure 2, the average monthly (annual) precipitation and temperature patterns of the two stations are quite similar. Correlations between the data of the two stations are 0.644, 0.604, and 0.777 for annual temperature, precipitation, and number of precipitation days, respectively (p < 0.01 in all cases). Therefore, we may assume that climate changes (particularly precipitation) at Seoul were similar to that at Yeongwol during the Cheugugi data recording period. Based on this assumption, we used the Cheugugi data recorded at Seoul to investigate the potential of δ¹³C in tree-ring samples from Yeongwol as a paleoclimate proxy.

SAMPLE COLLECTION AND DENDROCHRONOLOGICAL DATING

A radial slice (ca. 12 cm) was cut from the upper part of the stump, about 1.0 m above ground level. Based on radiocarbon (¹⁴C) dating using the wiggle-matching method, the age of the pine tree was estimated to be at least 211 yr (Kim et al. 2015). However, at the time of sampling (2014), many parts of the stump were decayed, so we could not collect all tree rings in the stump, as shown in Figure 1c.

Tree-ring samples were dated at the Tree-Ring Material Bank of Chungbuk National University using the dendrochronological method (Rinn 1996). Ring-width plots (0.01 mm
precision) of the tree-ring samples were crossdated by matching their patterns with master chronologies that had been absolutely dated through matches with living trees. The master chronologies used were GRAND PI (1657–1999) and HGGPD (1906–2011). The calculated

Figure 1 Yeongwol pine tree: (a) location image adapted from Google Earth (2014); (b) before (YTN 2010) and (c) after the wind event in March 2010 (indicated by arrow); (d) remaining stump (2014); and (e) tree-ring width plot and examples of dendrochronologically dated tree-ring samples.
$t$-values were 4.7 and 3.3 for GRAND PI and HGGPD, respectively. The tree rings dated to AD 1807 to AD 2009.

**SAMPLE PREPARATION AND EXPERIMENT**

As shown in Figure 1e, although dendrochronological dating was accomplished, some rings in the period 1900–2009 were rotten and it was not feasible to attempt to separate annual rings. Therefore, tree rings after 1905 were excluded from this study. More detailed and systematic work using modern precipitation data will be left for future studies. Since tree rings near the center of the stump were estimated older than 1802, we also excluded tree rings before 1835, to avoid possible juvenile effects (Leavitt 2010). Ultimately, we selected tree rings from the 1835–1905 interval, which is within the period of recorded Cheugugi data, and focused on comparing the Cheugugi data and $\delta^{13}$C series.

Samples with known ages were cut into annual rings and treated by the alpha cellulose extraction method described in Park et al. (2010). Each wood sample was immersed in 0.5 M of HCl at 80–85°C for 30 min then washed to neutral pH. The samples were then subjected to 0.1 M of NaOH at 80–85°C for 1 hr and then washed to a neutral pH. They were treated by applying 4% NaClO$_2$ at 55–60°C for 1 hr to extract $\alpha$-cellulose then washed to neutral pH. They were again

Figure 2 (a) Monthly average precipitation (number of precipitation days, temperature) for 1995–2015 at Yeongwol and Seoul; (b) annual variation of precipitation (number of precipitation days, temperature) 1995–2015 at Yeongwol and at Seoul.
immersed in 0.5 M of HCl at 80–85°C for 30 min to remove any CO₂ absorbed during the second and third steps, and then washed to neutral pH. Residues were dried at 120°C for 8 h.

The dried samples (0.7–1 mg) were loaded into tin capsules and placed in the elemental analyzer (vario PYRD cube, Elementar, Germany) auto-sampler. Stable carbon isotope content was determined using continuous flow isotope ratio mass spectrometry (Vision, Isoprime, Manchester, UK) attached to the elemental analyzer. IAEA-CH-6 was used as a reference material. IAEA-C6 was measured after every 10 experimental samples to monitor mass-spectrometer stability. The average precision on replicate results was ca. 0.27‰, which reflects sample preparation and measurement errors. The value of the carbon isotope ratios was obtained as an average of the duplicate analyses on an annual tree-ring cellulose sample. In the end, we developed an annual-resolution δ¹³C (PDB standard) series of 1835–1905 by using the measured data.

DATA ANALYSIS
Several studies have reported that the tree-ring δ¹³C series generally shows a downward trend starting around AD 1800–1850, resulting from ¹³C-depleted CO₂ emissions from fossil fuel combustion changing the isotopic composition of the atmosphere. In addition to this effect, there are changes in plant response as a consequence of increasing atmospheric CO₂ concentrations (McCarrall and Loader 2004; McCarrall et al. 2009). Hence, δ¹³C values were corrected for changes in air δ¹³C to minimize non-climatic influences. δ¹³C values were corrected first to remove the atmospheric decline in the δ¹³C values of atmospheric CO₂, by simple addition using the values provided by McCarrall and Loader (2004), and then for changes in the response to the rising CO₂ content of the atmosphere using the pre-industrial (PIN) correction proposed by McCarrall et al. (2009). Then, we investigated the correlation between corrected δ¹³C and Cheugugi rainfall data. We used monthly precipitation data and number of rainy days obtained from the Cheugugi data (Wada 1917; KMA 2011) for correlation analysis. We used ‘PIN’ R package (ver. 0.6, Swansea University) for δ¹³C correction and SPSS (ver. 22) for statistical analysis.

EXPERIMENTAL RESULTS
Figure 3a shows the raw and corrected δ¹³C series (δ¹³Craw and δ¹³Cpin, respectively) of our tree-ring samples. Both δ¹³C profiles are within the range –26.3 to –23.4‰, which is comparable with the results of other studies of Pinus densiflora (Park et al. 2002; Choi et al. 2005; Hong et al. 2013). Climatic records used for comparison were monthly total precipitation and number of precipitation days obtained from the Cheugugi data. The precipitation trends recorded in the Cheugugi data over the period overlapping with the period of our δ¹³C chronologies (1835–1905) are illustrated in Figures 3b and 3c. The mean number of annual precipitation days was 64 days and the mean annual precipitation was 1132 mm (with ca. 74% occurring during June–September) during the observation period. It should be mentioned that the Cheugugi data do not include frozen precipitation (ca. 40 mm/yr) and precipitation events below ca. 2 mm (ca. 35–40 mm/yr). The sum of these is ca. 75–80 mm/yr (Jung et al. 2001).

The growing season of conifer tree species in Korea is typically from April to September (Kim and Park 2011). Therefore, we investigated correlations with monthly precipitation during AD 1835–1905 from October of the previous year to September of the year of ring formation. Since the Cheugugi data do not contain precipitation as snow, we excluded the data recorded during the winter season (December–February) for analysis.

Figure 4a shows the correlation coefficients between the δ¹³C series and monthly precipitation. There are no significant correlations with monthly precipitation for δ¹³Craw. However, when
combined, a significant negative correlation was found for July–September \((-0.292; p < 0.05)\). For \(\delta^{13}C_{\text{pin}}\), significant negative correlation was found with July \((-0.251, p < 0.05)\) and, when combined, the highest correlation was found for July–September \((-0.332; p < 0.01)\). Figure 4a shows that the simple linear regression of \(\delta^{13}C_{\text{pin}}\) with precipitation July–September gives, \(R^2 = 0.110\) and slope = \(-6.44 \times 10^{-4} \, \%/\text{mm}\).

Figure 4b shows the correlation coefficients between the \(\delta^{13}C\) series and the monthly number of precipitation days. There are significant negative correlations for \(\delta^{13}C_{\text{raw}}\) with July \((-0.324, p < 0.01)\) and August \((-0.290, p < 0.05)\). When combined, the highest correlation was found for July–September \((-0.422; p < 0.01)\). There are significant negative correlations for \(\delta^{13}C_{\text{pin}}\) with July \((-0.386, p < 0.01)\), August \((-0.346, p < 0.01)\), and September \((-0.263, p < 0.05)\). When combined, the highest correlation found was for July–September \((-0.501; p < 0.01)\). Figure 4b shows that the simple linear regression of \(\delta^{13}C_{\text{pin}}\) with the number of precipitation days July–September gives, \(R^2 = 0.255\) and slope = \(-0.036 \, \%/\text{num}\).

**DISCUSSION AND CONCLUSION**

There are well-known mechanisms for \(\delta^{13}C\) variation in C3 plants (Francey and Farquhar 1982; Farquhar et al. 1989; Marshall and Monserud 1996), which may explain the correlations.
Carbon stored in tree-ring cellulose is produced using CO₂ taken up by the leaves and the C₃ photosynthetic pathway preferentially uses ¹²C, leading to isotopically depleted tree-ring cellulose. Therefore, CO₂ concentration decrease in stomatal chambers can increase the ¹³C/¹²C ratio of tree-ring cellulose. The balance between the rate at which CO₂ enters, by stomatal conductance, and the rate at which it is removed, by photosynthesis, can explain the variation of CO₂ concentration in stomatal chambers. For example, the increased δ¹³C reflects decreased CO₂ concentration in stomatal chambers, which may be due to either decreased stomatal conductance or increased photosynthetic rate, or some combination of the two. Hence, the observed negative correlations of δ¹³C with precipitation or the number of precipitation days may be explained by stomatal conductance, which can be negatively affected by moisture stress, or by photosynthesis, which can be positively affected by photon flux (sunlight) or temperature. On the other hand, in arid regions, where trees suffer from moisture stress, stomatal conductance may play a more important role in ¹³C fractionation, leading to statistically significant relationships with antecedent or growing-season moisture supply. Where water stress is low, the photosynthetic rate should dominate, and annual δ¹³C is likely to correlate with measured climate variables such as sunshine, cloud cover, and temperature (McCarroll and Loader 2001). Hence, sufficient precipitation during the growing season in Yeongwol (Figure 2), may be one of the reasons why δ¹³C was more negatively correlated with the number of precipitation days than the precipitation amounts. Accuracy of precipitation measurement, may be another reason for reduced correlations between δ¹³C and precipitation.
Whatever the actual mechanism of the observed response, it is clear that some correlations (Figure 4) are large enough to be taken as meaningful. Although it is tempting to state that the climate signal of δ13C in tree rings was successfully demonstrated using the Cheugugi data, replication of initial results in this study is required to confirm our initial results. This may be necessary because results from an individual tree may not be fully representative of a site, and hence results from several trees should be combined to better extract reliable climate signals. On the other hand, some studies have reported examples of δ13C series from single cores that had remarkably strong correlations to climate, which is promising for studies involving rare and limited samples from archaeological or geological contexts (Liu et al. 2010). Consequently, we suggest further studies to replicate our initial results and confirm whether comparing δ13C variations in tree rings and Cheugugi data is a useful method for investigating the potential of the δ13C signal as a paleoclimate proxy in or near the Korean peninsula.

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