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INTERVALIDATION OF DENDROCHRONOLOGY AND ^{14}C DATING ON A 700-YR TREE-RING SEQUENCE ORIGINATING FROM THE EASTERN CARPATHIANS

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ABSTRACT. We present a comparative study on a 700-yr sequence of dendrochronologically ordered tree-rings of *Pinus cembra* originating from Eastern Carpathians for the period AD 1009–1709. This period covers the solar minima of the Little Ice Age. The aim of this study was to assess the accuracy of our radiocarbon (^{14}C) determinations interpreted on the IntCal13 calibration data and to observe any apparent offsets. The ^{14}C measurements on single and double tree-rings were "wiggle-matched" to secure the dendrochronology cross-matching of all the *Pinus cembra* wood pieces. The results showed a very good agreement between the age datasets for four out of five wood trunks. However, for one of them a new cross-matching was performed after a quality assurance test, establishing an earlier 48-yr position, recommended by wiggle-matching Bayesian statistics and dendrochronological analysis. Following this adjustment, the quantification of the ^{14}C level variability with respect to the IntCal13 calibration curve was obtained by calculating Δ^{14}C for all tree-ring samples. As a final conclusion, an insignificant ^{14}C concentration offset of $-0.63 \pm 3.76‰$ was found for the Romanian samples.

KEYWORDS: dendrochronology, Eastern Carpathians, radiocarbon wiggle-matching, RoAMS.

INTRODUCTION

Radiocarbon (^{14}C) dating and dendrochronology are recognized partner methods. It is well known that the ^{14}C dating method is based on calibration via an independent dating method. For this purpose, dendrochronology offers the absolute dating information with annual resolution, which is necessary to reconstruct the atmospheric ^{14}C levels from the past. While dendrochronology carries the particularities of the region where the sample grows, ^{14}C dating can be applied globally due to the fast mixing of CO_2 in the atmosphere. However, the ^{14}C production and distribution among carbon reservoirs may show specific levels of atmospheric ^{14}C in different regions of the globe due to climatic conditions. (i.e. Hong et al. 2013; Manning et al. 2018). These levels are influenced by a mixing of natural activities such as climate changes, volcanic eruptions, and ocean proximity with anthropogenic factors including nuclear bomb tests and the burning of fossil fuels. The basis of the IntCal calibration curves for the last 12 kyr are the chronologies established on Irish oaks, German oaks, and European pine trees, as well as bristlecone pine trees from the North American continent (Washington, Oregon, California, and Alaska) after careful intercomparisons (Reimer et al. 2013).

Since 2015, the year of its official foundation, the RoAMS laboratory in Bucharest has begun a series of ^{14}C determinations on samples from archaeological sites spread all over the Romanian territory (R.A.N. 2018). In this regard, archaeologists often raised questions about the observation and analysis of any particular regional signature of the ^{14}C atmospheric levels. Some of these questions are the result of the observed dendrochronology differences in the tree-ring patterns growing in the southern and central-north parts of the European

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continent, which were observed in the oak chronologies (Ważny 2009; Ważny et al. 2014). To reveal and interpret these differences new attempts were taken to bridge the oak chronologies from wider Mediterranean region to the Northern regions (Pearson et al. 2014). In the Moldova region of Romania, floating chronologies of oak and elm subfossils collected along the course of Suceava River (Rădoane et al. 2015, 2018) have been studied by Kern and Popa (2016). However, there are certain cases where dendrochronology cannot deliver calendar dates as discussed in Bayliss et al. (2017) and which can originate in (1) different tree species between the sample and the available reference chronology; (2) reduced number of tree rings in the sample, usually 50 tree rings are normally required for a reliable dendrochronology; and (3) mismatch between tree-ring sequence and the dendrochronology master-curve. In the following we will provide an example from this last case, where the alternative method of ^{14}C "wiggle-matching" was employed to validate and secure a suspiciously misplaced dendrochronology cross-matching.

SAMPLE COLLECTION AND DENDROCHRONOLOGY

The test was performed on five subfossil wood trunks of cembra pine (*Pinus cembra*) collected from Călimani Mountains, Eastern Carpathians (47°06′30″N, 25°15′10″E and 1750 m asl), Figure 1. Wood samples, namely CAL25 (*t*-value 18.2, Glk 69, CDI 86), CAL39 (*t*-value 1.6, Glk 65, CDI 34), CAL57 (*t*-value 7.3, Glk 63, CDI 84), CAL143 (*t*-value 23.8, Glk 63, CDI 76) and CAL152 (*t*-value 7.2, Glk 52, CDI 20) are from a larger millennial-scale dendrochronological dataset, based on living and dead wood samples, established for paleoclimate reconstruction (Popa and Kern 2009). All the samples were prepared in accordance to the standard dendrochronological methodology (Cook and Kairiukstis 1990), using *t*-value, coefficient of coincidence Gleichläufigkeit (Glk), correlation coefficient (c_{coeff}), and cross-date index (CDI) as cross-dating parameters (Rinn 2010). The 41 single and double tree-rings were split from these trunks at a chosen interval of around 25–30 yr, which represents the routine standard deviation of our ^{14}C determinations. The time period covered by these samples spread from the year 1009 AD to 1709 AD. TSAP-Win$^{\mathrm{TM}}$ 4.81 software package was used for dendrochronology.

^{14}C MEASUREMENT AND DATING METHODOLOGY

The AMS ^{14}C dating method of wood samples requires cellulose extraction and purification for reliable and reproducible results. The chemical pretreatment followed the standard (base-acid-base-acid-bleaching) BABAB laboratory protocol (Sava et al. 2018), while for the graphitization stage we used an AGE III automated system, manufactured by Ionplus AG, (Wacker et al. 2010a). All the samples were normalized against NIST 4990C—Oxalic Acid II (NIST 1983) modern reference standard and background corrected using SIRI Sample L ($\mathrm{pMC_{avg}} = 0.28 \pm 0.06$; Scott et al. 2017). The ^{14}C/^{12}C isotopic ratios were δ^{13}C corrected for natural and induced fractionation by simultaneously measuring the ^{13}C/^{12}C ratio. The measurement was performed on our 1 MV AMS system. The measurement time was divided in 12 sections, each section of 300 sec, thus totalizing 60 min measurement time for each sample. The AMS analysis was taken on the +2 charge state at typical currents of ~ 25µA of ^{12}C, while the terminal voltage was set at 1MV. The resulting data was analyzed using BATS software (Wacker et al. 2010b) in accordance with Stuiver and Polach (1977).

The resulted ^{14}C ages were wiggle-matched using OxCal v4 3.2 (Ramsey 1995) D-Sequence function and IntCal13 (Reimer et al. 2013) calibration data. This technique basically fits

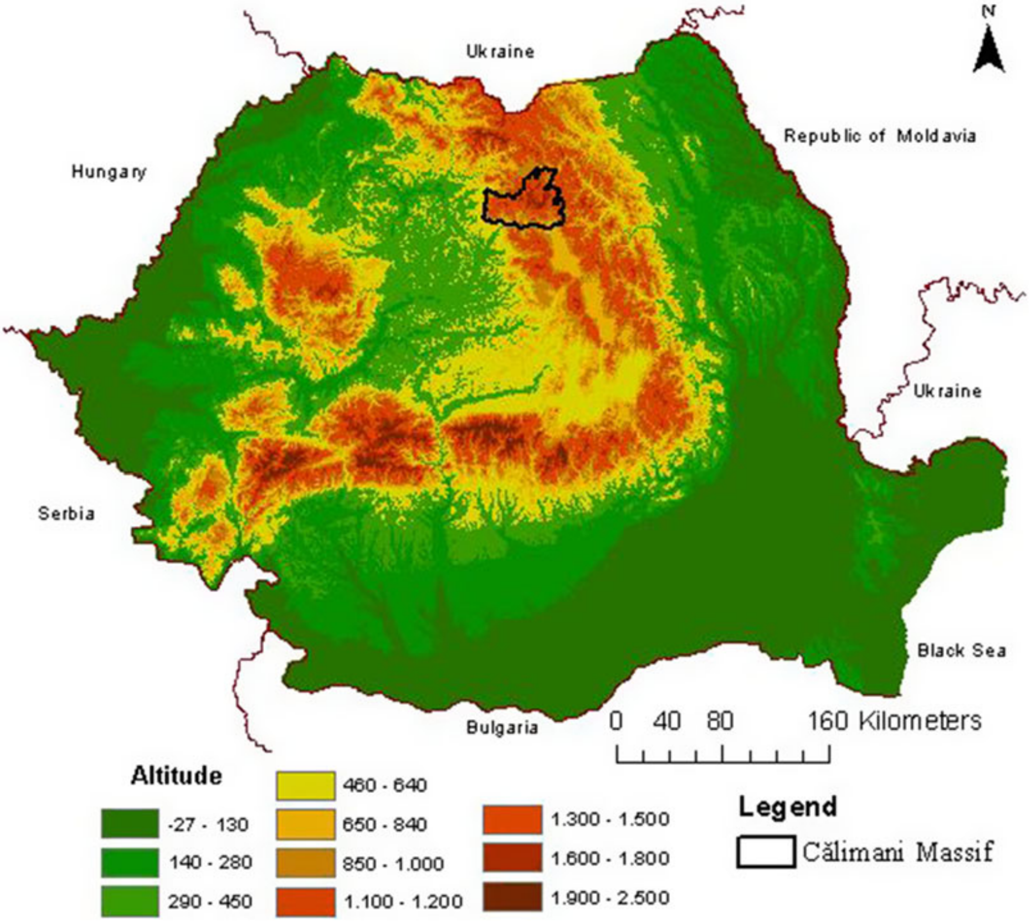

Figure 1 Călimani Mountains in the Eastern Carpathians, where the samples were collected.

the obtained data to the shape of the calibration curve. As described in Ramsey et al. (2001), for the generation of the agreement factors for individual rings, which are essentially an estimate of the goodness of the fit, a Bayesian probabilistic approach is employed to relate the posterior probability distribution to the likelihood distribution using an overlap integral. Subsequently, the overall agreement is defined as a product of all the individual agreement factors in the wiggle-match to the power $1/\sqrt{n}$. Various dependencies of the method precision upon parameters like the number of analyzed samples (tree rings), ^{14}C determination uncertainty, and general profile of the calibration curve are quantized in Galimberti et al. (2004).

RESULTS AND DISCUSSIONS

Table 1 lists the obtained ^{14}C ages modeled by wiggle-matching according to agreement and combined agreement indices, as well as Δ^{14}C for each sample.

All the determined ^{14}C ages were found to be in good agreement, at 95.4% confidence, with the dendrochronology ages (Table 1). However, the initial dendrochronology cross-matching established for trunk CAL57 was indicating a 48-yr younger position with respect to the

Table 1 Results of ^{14}C determinations in 41 tree-ring samples (1009–1709 AD) correlated via wiggle-matching and grouped in 5 distinct wood trunks. Age (AD) was determined by dendrochronology. The uncertainties represent 1σ.

Sample code	^{14}C age (yr BP)	Δ^{14}C (‰)	Posterior density estimate (cal AD, 95.4%)	Agreement index (%)	Combined agreement index (%)	Age (AD) of single and double tree rings	Trunk
RoAMS G1646	1030 ± 28	−14.26 ± 3.45	1000–1020	126.1	79.4	1009	CAL143
RoAMS G1647	1008 ± 28	−11.70 ± 3.46	1001–1021	110.6		1010	
RoAMS G1648	962 ± 28	−8.42 ± 3.47	1021–1041	125.6		1029–1030	
RoAMS G1649	929 ± 27	−6.71 ± 3.38	1041–1061	108.2		1049–1050	
RoAMS G1650	922 ± 28	−8.18 ± 3.47	1061–1081	114.5		1069–1070	
RoAMS G1651	980 ± 29	−17.86 ± 3.53	1082–1102	68.8		1090–1091	
RoAMS G1652	1004 ± 27	−23.09 ± 3.21	1103–1123	31.7		1109–1110	
RoAMS G1653	932 ± 31	−16.80 ± 3.74	1124–1144	112.8		1130–1131	
RoAMS G1654	914 ± 30	−16.77 ± 3.74	1145–1165	112.3		1149–1150	
RoAMS G1655	882 ± 29	−15.27 ± 3.54	1164–1184	140.5		1169–1170	
RoAMS G1656	848 ± 29	−13.55 ± 3.55	1184–1204	132.8		1190–1191	
RoAMS G1657	814 ± 29	−11.81 ± 3.56	1204–1224	92		1210–1211	
RoAMS G1658	819 ± 32	−14.74 ± 4.92	1223–1243	130		1229–1230	
RoAMS G1659	824 ± 30	−17.66 ± 3.63	1243–1263	99.8		1249–1250	
RoAMS G1660	819 ± 40	−19.51 ± 4.90	1263–1283	28.9		1269–1270	
RoAMS G1661	660 ± 32	−2.32 ±3.99	1284–1304	130.7		1290–1291	
RoAMS G1662	591 ± 33	3.95 ± 4.11	1303–1323	96.8		1309–1310	
RoAMS G1663	539 ± 29	7.87 ± 3.73	1324–1344	77		1330–1331	
RoAMS G511	959 ± 32	−7.53 ± 3.97	1018–1058	104	108.4	1026	CAL39
RoAMS G1665	909 ± 30	−4.76 ± 3.38	1046–1186	100.6		1054	
RoAMS G1664	870 ± 30	−2.88 ± 3.98	1070–1210	110		1078	
RoAMS G533	603 ± 31	0.68 ± 3.80	1310–1332	117.5	68.5	1324	CAL57
RoAMS G519	566 ± 29	2.28 ± 3.71	1335–1357	89		1349	
RoAMS G531	707 ± 31	−18.46 ± 3.73	1362–1384	31.4		1376	
RoAMS G534	587 ± 31	−6.68 ± 3.77	1387–1409	112.2		1401	
RoAMS G535	490 ± 30	2.24 ± 3.71	1413–1435	116.3		1427	
RoAMS G506	335 ± 30	13.19 ± 3.75	1482–1510	101.0	87.2	1497	CAL25
RoAMS G514	330 ± 29	10.91 ± 3.74	1506–1534	107.0		1521	
RoAMS G507	268 ± 30	15.62 ± 3.76	1531–1559	81.6		1546	
RoAMS G509	336 ± 30	3.85 ± 3.71	1557–1585	117.6		1572	
RoAMS G508	361 ± 30	−2.19 ± 3.79	1582–1610	115.7		1597	
RoAMS G527	385 ± 31	−8.24 ± 3.77	1607–1635	47.1		1622	
RoAMS G515	241 ± 30	6.81 ± 3.72	1632–1660	122.9		1646	
RoAMS G530	327 ± 30	10.62 ± 3.74	1505–1528	107.0	92.2	1526	CAL152
RoAMS G518	293 ± 30	11.26 ± 3.74	1535–1558	132.8		1556	
RoAMS G536	345 ± 31	1.73 ± 3.81	1560–1583	108.1		1581	
RoAMS G529	412 ± 30	−9.76 ± 3.76	1586–1609	29.3		1607	
RoAMS G517	346 ± 30	−5.00 ± 3.68	1614–1637	102.5		1635	
RoAMS G537	258 ± 32	2.97 ± 3.91	1639–1662	172.2		1660	
RoAMS G532	208 ± 31	6.37 ± 3.82	1663–1686	87.7		1684	
RoAMS G538	102 ± 30	16.61 ± 3.76	1688–1711	113.9		1709	

present moment, which was further considered to be inconsistent. This position was susceptible for correction due to its mismatch with the ^{14}C posterior density estimates delivered by wiggle-matching. Given the discrepancies between the two age sets obtained for the same wood sample we decided to check the accuracy of our ^{14}C determinations modeled by

OxCal wiggle-matching and IntCal13 dataset on a second dendrochronology sequence covering the same age period, 1300–1450 AD, but built on old wood beams of oak (*Quercus* sp.) from Transylvanian medieval churches (Botár et al. 2015). The ages obtained during this quality assurance test showed an excellent agreement, confirming the reliability of our measurements and dating methodology.

Hence, the previous and most probable CAL57 cross-matching described by a *t*-value of 14.9 and an age interval of [1349–1796 AD] was changed to a new position characterized by a lower *t*-value of 7.3 and a corresponding age interval of [1301–1748 AD]. This new position, which agrees the ^{14}C ages, was also indicated as the next maximum of the probability density function in the dendrochronology analysis.

By applying the Bayesian wiggle-matching technique, the calibrated age intervals have been considerably reduced, thus allowing precise and reproducible calendric ages to be obtained. The combined agreement indices A_{comb} for all the samples stemming from single trunks showed very good agreement: A_{comb_CAL143}=79.4%, A_{comb_CAL39}=108.4%, A_{comb_CAL57}= 68.5%, A_{comb_CAL25}=87.2% and A_{comb_CAL152}=92.2%. The precision of the wiggle-matching varied with the number of the analyzed samples, achieving 40 yr. uncertainty for CAL39 (three samples) down to 20 yr. uncertainty for CAL143 (18 samples). However, an excellent value of 22 yr was obtained for CAL57 with only five analyzed samples, as previously demonstrated in Galimberti et al. (2004).

The deviations of the ^{14}C concentration of all the tree-rings with respect to their year of growing were estimated by calculating the Δ^{14}C using the relation:

$$\Delta^{14}C = \left\{pMC \cdot exp\left[\frac{(1950 - y)}{\lambda}\right] - 1\right\} \times 1000$$

Where y is the year (AD) when the ring was grown and $1/\lambda = t_{1/2}/\ln(2) = 8267$ is the mean life-time for the real ^{14}C half-life, 5730 years. The pMC was measured and corrected as discussed in the previous paragraph on ^{14}C AMS measurement. The Δ^{14}C results are plotted in Figure 2 with the IntCal13 data for comparison. The average deviation for the measured points was found –0.63 ± 3.76‰, which is a much smaller value compared to the statistical error. Therefore, this deviation can be ignored when using IntCal data for calibration of ^{14}C ages of Romanian samples.

The values obtained for the Δ^{14}C closely replicate the solar activity events recorded in tree-rings ^{14}C concentration variations for the Northern Hemisphere (Stuiver 1980), overlapping the Little Ice Age period for 1350–1709 AD.

CONCLUSIONS

A number of 41 single and double tree-ring samples spanning AD 1009–1709 were measured to verify the consistency of the IntCal data with the local samples. The ^{14}C concentration offset relative to IntCal was found to be remarkably reduced, showing a Δ^{14}C of –0.63 ± 3.76‰, thus highlighting the validity of using the data included in Intcal13 calibration curve for the Romanian samples.

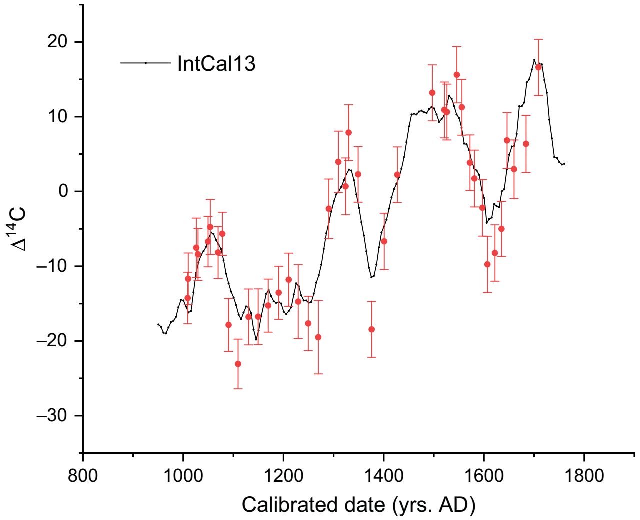

Figure 2 $\Delta^{14}C$ of the 41 cembra pine single and double tree-ring samples collected from Eastern Carpathians. The continuous line represents the IntCal13 data.

The ^{14}C wiggle-matching was used to support the dendrochronology analysis for the cembra pine wood samples. These results proved the maturity of RoAMS ^{14}C determinations as well as the well-established IntCal data and weight of the OxCal mathematical construct.

Pinus cembra can be used as a proxy for determination of the ^{14}C variability, but extra information is recommended to be employed for the validation of the cross-matching. In this regard, the ^{14}C wiggle-matching can offer reliable age information even with a reduced number (5–7) of measured and modeled tree-rings.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2019.56

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