

## LATE GLACIAL ATMOSPHERIC RADIOCARBON VARIATIONS RECORDED IN SCOTS PINE (*PINUS SYLVESTRIS* L.) WOOD FROM KWIATKÓW, CENTRAL POLAND

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**ABSTRACT.** Our project aimed to construct a Scots Pine (*Pinus sylvestris* L.) chronology for part of the Late Glacial and reconstruct changes in the <sup>14</sup>C concentrations during this period. Kwiatków (Kolska Basin, central Poland) proved to be very prospective site, in which wood from the end of Allerød was recognized. A level of organic deposits with so-called fossil forest was encountered within the late-Vistulian terrace of the low valley of the Warta river. Dendrochronological analysis of over 267 samples complying to the requirements of the method allowed, at the present stage of the research, to construct a chronology spanning 265 yr. Fifty-two samples (5 consecutive rings each) were subjected to  $\alpha$ -cellulose extraction and <sup>14</sup>C measurements. Ninety-six results and the wiggle-matching technique anchor the chronology to the period 13,821–13,561 cal BP ( $A_{\text{comb}} = 141.6\%$ ) according to the D\_Sequence procedure and the IntCal13 calibration curve or to 13,800–13,540 cal BP according to the wiggle-matching technique using the  $\chi^2$  test and raw data, i.e. the Heidelberg tree-ring sequence.

**KEYWORDS:** Allerød, pine wood, radiocarbon AMS dating, tree rings.

### INTRODUCTION

The transition from the last glaciation to the Holocene in the Northern Hemisphere is characterized by consecutive cooler and warmer periods. These abrupt climate shifts were registered in ice cores (Johnsen et al. 1992; Alley et al. 1997; Rasmussen et al. 2006), lacustrine sediments (Goslar et al. 1993, 2000; Hajdas 1993, 1995; Brauer et al. 1999; Schwander et al. 2000; Nakagawa et al. 2003), marine varves (Kitagawa and van der Plicht 1998; Hughen et al. 2000), as well as speleothems (Wang et al. 2001).

Dendrochronological research on subfossil wood ongoing in recent years allowed for construction of chronologies covering the Late Glacial period. Numerous sites with postglacial subfossil wood were found in the Alps. Wood from the sites in Switzerland allowed for construction of the Swiss Lateglacial Master Chronology (SWILM), 1606-yr in length, dated to ca. 14,300–12,700 cal BP (Kaiser et al. 2012). This chronology was correlated with dendrochronological curves based on pinewood from gravel pits of the river Danube and its tributaries spanning the periods: ca. 14,000–13,300 cal BP and ca. 13,280–12,950 cal BP (Spurk et al. 1998a, 1998b; Friedrich et al. 2004).

Chronologies based on subfossil pine trees from sites situated in lowland areas form another group, located several hundred kilometers to the north from the aforementioned ones, e.g. Warendorf (Westphalen), covering the period 13,720–13,260 cal BP, and Reichwalde near Cottbus (Lausitz), spanning 14,020–13,570 cal BP (Friedrich et al. 2001, 2004; Kaiser et al. 2012). Another area in which numerous trunks of subfossil pine trees were encountered is Late-Vistulian terrace in the Warta river valley, in the region of Koźmin and Kwiatków (central Poland) (Dzieduszyńska et al. 2014).

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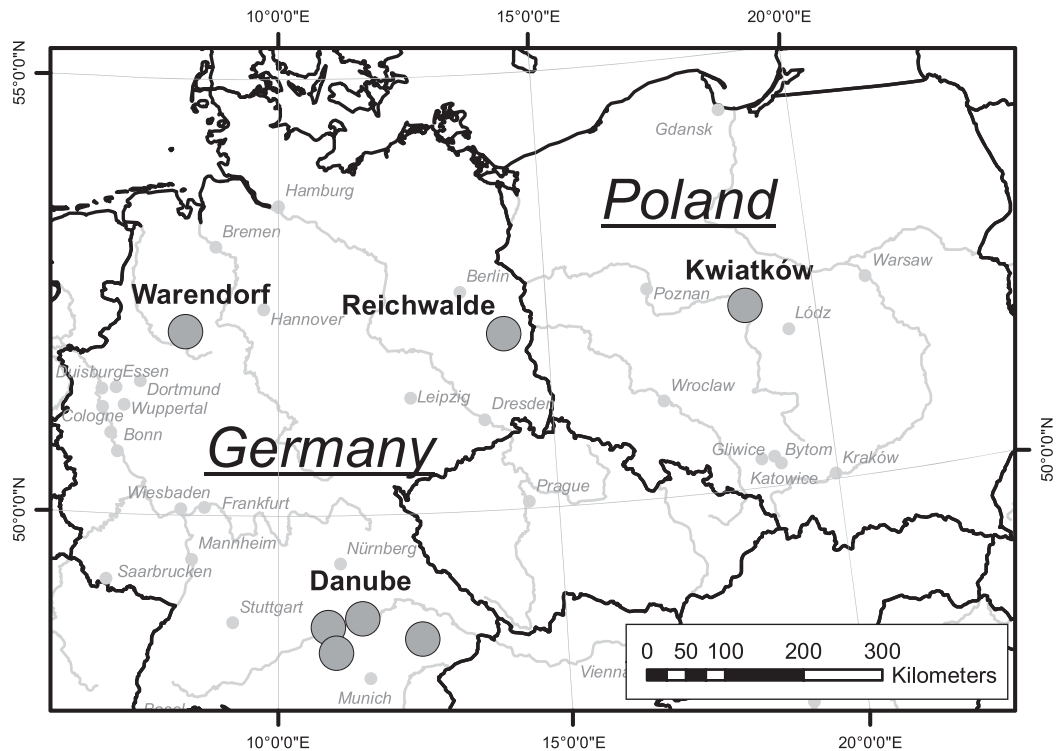


Figure 1 Location of the original study site Kwiatków and German sites with subfossil pine wood from Allerød.

The Kwiatków site lies in the southern stretch of the Warta river valley, which is at this point about 8 km wide. It is located about 12 km south of Koło, at  $18^{\circ}40'48,34''\text{E}$ ,  $52^{\circ}5'58,876''\text{N}$  (Figure 1). The site was discovered during archaeological excavations of a vast settlement complex from the pre-Roman and Roman periods (2nd century BC to 3rd century AD). During the exploration of deep archaeological features, the organic mud horizon with subfossil trees has been recorded, similar to that known from the Koźmin Las site (Dzieduszyńska et al. 2014). The investments aimed at opening up a new exploitation field in the brown coal mine *Adamów*, enabled to unveil the organic level with Late Glacial trunks of pine trees and sampling them.

## MATERIAL AND METHODS

### Dendrochronology

Samples were collected in three large trenches of approximately  $800\text{ m}^2$  each. In total, over 300 wood fragments of collapsed trunks and stumps were collected for dendrochronological analysis and species identification. Most of the samples represented pine (*Pinus sylvestris* L.), but some birch (*Betula* sp.) trees were recognized as well. Dendrochronological analysis was made for 267 selected samples of wood coming from subfossil pine trunks and branches with more than 40 tree rings. Among the pine trees examined, young specimens prevailed. The trees older than 150 yr appeared only occasionally, while the oldest specimen grew 234 yr.

Among the samples analyzed dendrochronologically, the ones cut from pine trunks predominated. On account of the sequence lengths as well as the lowest anatomical perturbations,

they were used for construction of the local chronology. The average curve (2KWI\_A3C), produced from the 46 tree-ring sequences best correlating mutually, spanned 265 yr. The intercorrelation of samples is 0.490 ( $P < 0.01$ ) and the expressed population signal (EPS) equal to 0.9. The EPS indicates how close a dendrochronological mean curve is to a hypothetical chronology of the total population (Cook and Kairiukstis 1990). The approximate age of the pine chronology 2KWI\_A3C was determined on the basis of the AMS radiocarbon ( $^{14}\text{C}$ ) dating of samples containing selected annual growth rings and then teleconnected with Reichwalde chronology to 13,821–13,557 cal BP (M. Friedrich and F. Reinig, personal communication). This dating is supported by high statistical agreement between the chronologies:  $t = 5.5$  and  $G/ = 61$  (Gleichlaufigkeit-% [ $G/$ ] and the  $t$ -value [ $t$ ]; see Baillie and Pilcher 1973; Rinn 2005 for details).

### Material

Two trunks, laboratory coded K\_XX1 and K\_XX6, which did not contain extremely narrow annual increments, were selected for the  $^{14}\text{C}$  analysis. The prepared samples consisted of 5 consecutive annual increments each: 44 samples from the trunk K\_XX1 and 13 from K\_XX6. Five samples encompassing the youngest increments from the trunk K\_XX1 overlapped with 5 samples containing the contemporaneous rings from K\_XX6 (cf. Figure 2). Samples selected for dating cover period of 260 yr.

### Wood Pretreatment for AMS Measurements

The methods of chemical pretreatment of wood for  $^{14}\text{C}$  dating, including high accuracy dating, were examined and described by numerous authors (e.g. Hoper et al. 1998; Bird et al. 1999; Santos et al. 2001; Anchukaitis et al. 2008; Nemeč et al. 2010; Southon and Magana 2010; Santos and Ormsby 2013; Staff et al. 2014; Wacker et al. 2014; Hajdas et al. 2016; Sookdeo et al. 2016). Also, the authors of this article had decided to conduct their own tests, carried out in three Polish laboratories (Gliwice, Kraków, and Poznań). The tests included 3 methods of  $\alpha$ -cellulose preparation, 2 methods of holo-cellulose preparation, FTIR spectroscopy,  $\delta^{13}\text{C}$  measurements and interlaboratory comparisons. The detailed description of methodology and results were subject of a separate paper (Michczyńska et al. 2018). The outcome indicated the  $\alpha$ -cellulose production as the most suitable preparation method. The  $\alpha$ -cellulose extraction was preceded by the mercerization step and the standard ABA treatment. Then, in the bleaching process (with  $\text{NaClO}_2 + \text{HCl}$ ), the production of holo-cellulose followed (see BABAB method described by Nemeč et al. 2010). Finally, strong sodium bases (10% and 17%) and weak (1%) hydrochloric acid were used. In order to avoid the influence of possible interlaboratory shifts,

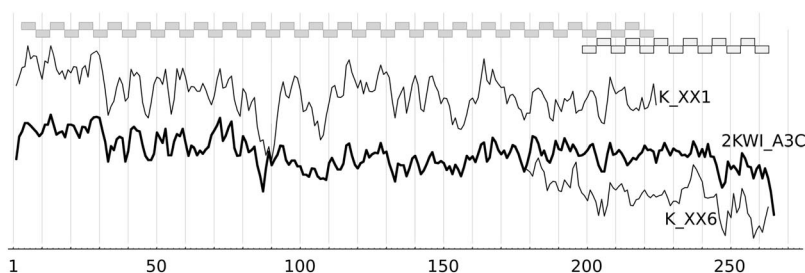


Figure 2 Dendrochronological curves of pinewood samples K\_XX1 and K\_XX6, and mean ring-width curve of the chronology 2KWI\_A3C. 44 samples, each containing 5 consecutive annual increments, were prepared from the trunk K\_XX1, and 13 similar samples from the trunk K\_XX6. Their time intervals are presented above the dendrochronological curves.

the chemical preparation and graphitization of samples was carried out in one laboratory, the Gliwice Radiocarbon Laboratory. The one exception reported here was sample 206-210, which was used for interlaboratory comparison and for assessment of differences between  $^{14}\text{C}$  age for holo- and  $\alpha$ -cellulose.

### Graphitization

Samples of  $\alpha$ -cellulose have been converted to graphite for AMS  $^{14}\text{C}$  measurements. The process was performed in automated graphitization system AGE, manufactured by IonPlus<sup>TM</sup> (Wacker et al. 2010). Subsamples of ca. 3 mg of  $\alpha$ -cellulose were weighted to tin capsules and combusted in elemental analyzer vario MICRO cube (Elementar<sup>TM</sup>). The  $\text{CO}_2$  from sample was transferred to graphitization unit and reduced with hydrogen at 580°C. The graphite was deposited on 2 mg of Fe powder.

Two blank materials were used, coal and subfossil wood (called OLGA). The wood was subjected to the same chemical procedure as unknown samples, while coal was prepared with standard ABA treatment. The blank samples and reference material, Oxalic Acid II (NIST SRM4990C) were combusted and graphitized as described above.

### AMS Measurements

AMS measurements were performed in AMS Laboratory in Poznań, which is equipped with two 1.5 SDH-Pelletron Model “Compact Carbon AMS”, ser. no. 003 (Goslar et al. 2004) and ser. no. 012, produced in 2001 and 2012 by the National Electrostatics Corporation, Middleton, WI, USA. Conventional  $^{14}\text{C}$  ages of the analyzed samples were calculated using fractionation-corrected (Stuiver and Polach 1977)  $^{14}\text{C}/^{12}\text{C}$  ratios (basing on simultaneously measured  $^{13}\text{C}/^{12}\text{C}$ ), after their normalization based on  $^{14}\text{C}/^{12}\text{C}$  measured on modern standard (OxII) and blank samples. All the samples have been analyzed in 3 AMS runs, with 4 OxII and 3–4 background samples measured in a run. To control stability of the spectrometer during the run, each sample underwent 6–7 partial measurements. 1-sigma uncertainty of calculated  $^{14}\text{C}$  age was determined using uncertainty implied from counting statistics and standard deviation of mean of partial  $^{14}\text{C}/^{12}\text{C}$  results, whichever was bigger. Scatter of  $^{14}\text{C}$  results obtained on individual modern standards (SDOM better than 16 yr), and standard deviation of blanks measured one long-term period (SD not worse than 0.11 pMC) were included in the uncertainty of calculated  $^{14}\text{C}$  ages.

### RESULTS

Results of AMS dating are presented in Table 1. Most samples have two lab codes: a GdA- code indicates the graphite production in the Gliwice Radiocarbon Laboratory, while a Poz- code indicates the AMS measurement performed in Poznań Radiocarbon Laboratory. The tests described in another publication (see Michczyńska et al. 2018) proved no significant differences between  $^{14}\text{C}$  ages obtained for holo- or  $\alpha$ -cellulose prepared from the same sample. Therefore, the results for holo-cellulose (for sample 206-210) are also reported in the Table 1. If several measurements were performed for one sample, the  $\chi^2$  test value is given. In case of 2 measurements, the *t*-test value is additionally added. *t*-test and  $\chi^2$  test values indicated, in most cases, good reproducibility of the results and allowed the weighted average to be used as a final  $^{14}\text{C}$  age.

In two cases (samples covering tree-rings 51–55, 61–65) statistical tests indicated poor agreement and a simple average was calculated as a final age value. For these samples uncertainty

Table 1 Results of AMS measurements for the Kwiatków sequence. If several measurements were performed for one sample, the  $\chi^2$  test results are given as a  $\chi^2$  value per degrees of freedom. In the case of 2 measurements, the  $t$ -test value is additionally added. The last column presents the final age values.

No.	Position in chronology	Sample name: Lab codes; $^{14}\text{C}$ age $\pm$ uncertainty (BP)	$t$ -value	$\chi^2/\text{df}$	Final $^{14}\text{C}$ age value (BP)
1	1-5	K1S/1-5: GdA-5136A; Poz-90562; 11958 $\pm$ 54 GdA-5136B; Poz-94323; 12081 $\pm$ 59	1.54	2.4	12014 $\pm$ 40
2	6-10	K1S/6-10: GdA-5137A; Poz-90563; 12022 $\pm$ 55			12022 $\pm$ 55
3	11-15	K1S/11-15: GdA-5138A; Poz-90564; 12011 $\pm$ 54			12011 $\pm$ 54
4	16-20	K1S/16-20: GdA-5139A; Poz-90565; 11932 $\pm$ 52 GdA-5139B; Poz-94324; 12071 $\pm$ 58	1.78	3.2	11994 $\pm$ 39
5	21-26	K1S/21-25: GdA-5140A; Poz-90566; 12041 $\pm$ 54 GdA-5140B; Poz-94325; 11948 $\pm$ 58	1.17	1.4	11998 $\pm$ 40
6	26-30	K1S/26-30: GdA-5141A; Poz-90568; 12002 $\pm$ 54			12002 $\pm$ 54
7	31-35	K1S/31-35: GdA-5142A; Poz-90569; 11981 $\pm$ 55			11981 $\pm$ 55
8	36-40	K1S/36-40: GdA-5143A; Poz-90570; 11995 $\pm$ 55			11995 $\pm$ 55
9	41-45	K1S/41-45: GdA-5144A; Poz-90572; 12077 $\pm$ 55 GdA-5144B; Poz-94327; 11923 $\pm$ 55	1.98	3.9	12000 $\pm$ 39
10	46-50	K1S/46-50: GdA-5145A; Poz-90573; 11943 $\pm$ 54			11943 $\pm$ 54
11	51-55	K1S/51-55: GdA-5146A; Poz-90574; 11834 $\pm$ 54 GdA-5146B; Poz-94328; 12058 $\pm$ 59	2.80	7.9	11946 $\pm$ 206*
12	56-60	K1S/56-60: GdA-5147A; Poz-90575; 11879 $\pm$ 53			11879 $\pm$ 53
13	61-65	K1S/61-65: GdA-5148A; Poz-90576; 12000 $\pm$ 54 GdA-5148B; Poz-94329; 11828 $\pm$ 57	2.19	4.8	11914 $\pm$ 158*
14	66-70	K1S/66-70: GdA-5149A; Poz-90577; 11935 $\pm$ 52			11935 $\pm$ 52
15	71-75	K1S/71-75: GdA-5150A; Poz-90578; 11910 $\pm$ 53			11910 $\pm$ 53
16	76-80	K1S/76-80: GdA-5151A; Poz-90579; 11879 $\pm$ 55			11879 $\pm$ 55
17	81-85	K1S/81-85: GdA-5152A; Poz-90580; 11920 $\pm$ 50			11920 $\pm$ 50
18	86-90	K1S/86-90: GdA-5153A; Poz-90582; 11949 $\pm$ 52 GdA-5153B; Poz-94331; 11925 $\pm$ 55	0.32	0.1	11938 $\pm$ 38

Table 1 (Continued)

No.	Position in chronology	Sample name: Lab codes; <sup>14</sup> C age ± uncertainty (BP)	<i>t</i> -value	$\chi^2/df$	Final <sup>14</sup> C age value (BP)
19	91-95	K1S/91-95: GdA-5154A; Poz-90583; 11868 ± 54			11868 ± 54
20	96-100	K1S/96-100: GdA-5155A; Poz-90584; 11855 ± 53 GdA-5155B; Poz-94332; 11930 ± 58	0.95	0.9	11889 ± 39
21	101-105	K1S101-105: GdA-5156A; Poz-90585; 11891 ± 55			11891 ± 55
22	106-110	K1S/106-110: GdA-5157A; Poz-90586; 11910 ± 56 GdA-5157B; Poz-94333; 11920 ± 57	0.13	0.0	11915 ± 40
23	111-115	K1S/111-115: GdA-5158A; Poz-90587; 11882 ± 55 GdA-5158B; Poz-94334; 11895 ± 52	0.17	0.0	11889 ± 38
24	116-120	K1S/116-120: GdA-5159A; Poz-90588; 11881 ± 53 GdA-5159B; Poz-94335; 11960 ± 58	1.00	1.0	11917 ± 39
25	121-125	K1S/121-125: GdA-5160A; Poz-90589; 11771 ± 54 GdA-5160B; Poz-94336; 11828 ± 52	0.76	0.6	11801 ± 37
26	126-130	K1S/126-130: GdA-5161A; Poz-90590; 11888 ± 55 GdA-5161B; Poz-94337; 11968 ± 58	1.00	1.0	11926 ± 40
27	131-135	K1S/131-135: GdA-5162A; Poz-90592; 11819 ± 53			11913 ± 52
28	136-140	K1S/136-140: GdA-5163A; Poz-90593; 11913 ± 52 GdA-5163B; Poz-94338; 11887 ± 54	0.35	0.1	11900 ± 37
29	141-145	K1S/141-145: GdA-5164A; Poz-90594; 11876 ± 54			11876 ± 54
30	146-150	K1S/146-150: GdA-5165A; Poz-90595; 11858 ± 53			11858 ± 53
31	151-155	K1S/151-155: GdA-5166A; Poz-90596; 11848 ± 53			11848 ± 53
32	156-160	K1S/156-160: GdA-5167A; Poz-90597; 11962 ± 53 GdA-5167B; Poz-94339; 11827 ± 57	1.73	3.0	11899 ± 39
33	161-165	K1S/161-165: GdA-5168A; Poz-90484; 11855 ± 55			11855 ± 55
34	166-170	K1S/166-170: GdA-5169A; Poz-90485; 11927 ± 52 GdA-5169B; Poz-94341; 11859 ± 56	0.89	0.8	11896 ± 38
35	171-175	K1S/171-175: GdA-5170A; Poz-90486; 11877 ± 54			11877 ± 54
36	176-180	K1S/176-180: GdA-5171A; Poz-90487; 11804 ± 56 GdA-5171B; Poz-94342; 11842 ± 58	0.47	0.2	11822 ± 40

Table 1 (Continued)

No.	Position in chronology	Sample name: Lab codes; <sup>14</sup> C age ± uncertainty (BP)	<i>t</i> -value	$\chi^2$ /df	Final <sup>14</sup> C age value (BP)
37	181-185	K1S/181-185: GdA-5172A; Poz-90488; 11820 ± 56			11820 ± 56
38	186-190	K1S/186-190: GdA-5173A; Poz-90490; 11834 ± 55			11834 ± 55
39	191-195	K1S/191-195: GdA-5174A; Poz-90491; 11876 ± 56 GdA-5174B; Poz-94343; 11786 ± 55	1.15	0.65	11830 ± 39
40	196-200	K1S/196-200: GdA-5175A; Poz-90492; 11886 ± 50 K6/ 19-23: GdA-5175A; Poz-90492; 11886 ± 60	1.16	1.4	11849 ± 38
41	201-205	K1S/201-205: GdA-5176A; Poz-90494; 11748 ± 51 K6/ 24-28: GdA-5176A; Poz-90494; 11748 ± 59	0.77	0.6	11774 ± 39
42	206-210	K1S/206-210: GdA-5177A; Poz-90495; 11890 ± 57 GdA-4814; Poz-84118; 11740 ± 56 GdA-4815; Poz-84120; 11890 ± 60 GdA-4817; Poz-84122; 11800 ± 70 K6/ 29-33: GdA-5182A; Poz-90500; 11721 ± 58 Graphites produced in Poznań: K1S/206-210: Poz-84213; 11691 ± 55 Poz-84270; 11767 ± 58 Poz-84214; 11790 ± 57 Poz-84271; 11752 ± 57 Poz-84215; 11868 ± 57 Poz-84272; 11741 ± 92 <u>Holo-celulose:</u> Poz-84216; 11769 ± 56 Poz-84273; 11799 ± 57 Poz-84217; 11861 ± 57 Poz-84274; 11680 ± 57 Poz-84218; 11805 ± 56 Poz-84276; 11751 ± 57		1.2	11784 ± 14
43	211-215	K1S/211-215: GdA-5178A; Poz-90496; 11744 ± 54 GdA-5178B; Poz-94344; 11840 ± 55 K6/ 34-38: GdA-5178A; Poz-90496; 11744 ± 64		1.2	11772 ± 33
44	216-220	K1S/216-220: GdA-5179A; Poz-90497; 11987 ± 53* GdA-5179B; Poz-94345; 11892 ± 55 GdA-5179C; Poz-95215; 11849 ± 52 K6/ 39-43:	2.7 1.1 (without marked date)		11824 ± 27 (without marked date)

Table 1 (Continued)

No.	Position in chronology	Sample name: Lab codes; <sup>14</sup> C age ± uncertainty (BP)	<i>t</i> -value	$\chi^2/df$	Final <sup>14</sup> C age value (BP)
45	221-225	GdA-5184A; Poz-90502; 11778 ± 53			11802 ± 57
		GdA-5184C; Poz-95216; 11780 ± 54			
46	226-230	K6/ 44-48:			11831 ± 56
		GdA-5185A; Poz-90504; 11802 ± 57			
47	231-235	K6/ 49-53			11792 ± 56
		GdA-5186A; Poz-90505; 11831 ± 56			
48	236-240	K6/ 54-58	0.82	0.7	11792 ± 39
		GdA-5187A; Poz-90506; 11792 ± 56			
49	241-245	K6/ 59-63:	0.83	0.7	11720 ± 40
		GdA-5188A; Poz-90507; 11757 ± 55			
50	246-250	GdA-5188B; Poz-94321; 11693 ± 56			11770 ± 50
		K6/ 64-68:			
51	251-255	GdA-5189A; Poz-90508; 11685 ± 58			11736 ± 58
		GdA-5190A; Poz-90509; 11770 ± 50			
52	256-260	K6/ 74-78:			11633 ± 58
		GdA-5191A; Poz-90510; 11736 ± 58			
		K6/ 79-83:			
		GdA-5192A; Poz-90511; 11633 ± 58			

\*Date excluded from modeling.

was calculated as standard deviation of mean, multiplied by a Student-Fisher coefficient. These dates were excluded from further analysis. A similar situation was observed for the sample 216-220, but repeated measurements (marked by letter “C” in GdA- code) allowed to indicate the outlier (GdA-5179A; Poz-90497; 11987 ± 53) and exclude it from further analysis.

## DISCUSSION

The Kwiatków floating chronology presented above was anchored using the IntCal13 calibration curve. For this purpose the authors used the D\_Sequence procedure in the OxCal program (Bronk Ramsey et al. 2001). As a result, the Kwiatków floating chronology was affixed to the IntCal13 calibration curve at 13,561 cal BP. The uncertainty of this anchoring resulting solely from D\_Sequence algorithm is ±8 yr (1-sigma). The goodness of fit, specified by a combination agreement index was very good ( $n = 50$ ,  $A_{\text{comb}} = 141.6\%$ ,  $A_n = 10.0\%$ ). The results of the measurements for the Kwiatków chronology anchored to the IntCal13 calibration curve are shown in Figure 3.

Independently, the Kwiatków floating chronology was anchored to the raw data (the Heidelberg tree-ring sequence) using the classical wiggle-matching method based on the  $\chi^2$  test (Bronk Ramsey et al. 2001). For this purpose:

- in some cases it was necessary to calculate a weighted average of the two <sup>14</sup>C dates for the same calendar date,



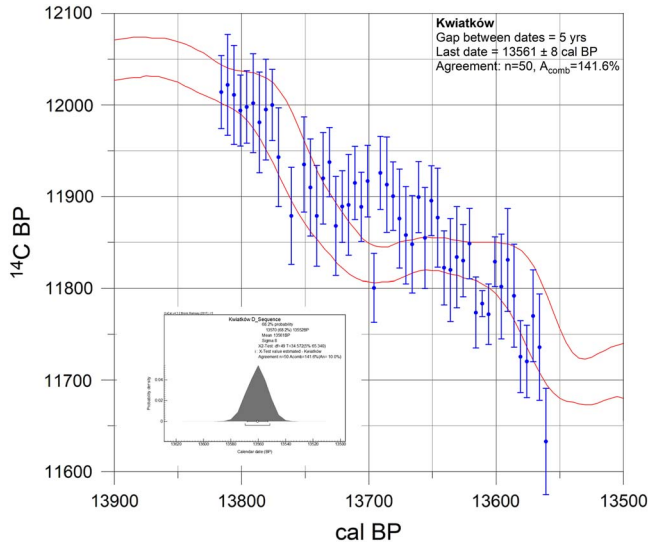


Figure 3 The Kwiatków floating chronology anchored using the IntCal13 calibration curve and D\_Sequence procedure in OxCal programme (Bronk Ramsey et al. 2001). As a result, the Kwiatków floating chronology was affixed to the IntCal13 calibration curve at 13,561 cal BP with the uncertainty of 8 yr.

- both sets of data have been replaced by polygonal chains. Because in the case of data from Heidelberg there is no constant distance between particular points (distance from 0.5 to 21 yr), it was decided to present both series with a resolution of 1 year,
- the Kwiatków sequence has been shifted relative the Heidelberg sequence every 1 year and for each position the sum of squares of deviations between the polygonal chains divided by the sum of squares of uncertainty was calculated:

$$\chi^2 = \sum \frac{(y_{iK} - y_{iH})^2}{u^2(y_{iK}) + u^2(y_{iH})}$$

- the position of the Kwiatków sequence for which the  $\chi^2$  test value has the minimum is selected as the best fit of the waveforms.

The Kwiatków floating chronology anchored to the Heidelberg tree-ring sequence data is presented in Figure 4.  $\chi^2$  values around the minimum are presented in the inset. Although the  $\chi^2$  function has a minimum for 13,540 cal BP, the graph of the value of this function clearly shows that the lowest, similar test values occur for a range of about 20 yr. In fact, there are two minima—one global, anchoring the Kwiatków sequence about 20 yr younger than according to D\_Sequence (13,540 cal BP), and the other local one giving anchorage close to D\_Sequence (13,554 cal BP).

The length of the plateau in the minimum (20 yr) can be a measure of the uncertainty of the anchorage. The values of the test function in the minimum (370.7 and 376.2) indicate that both sequences are not fully compatible with each other. The expected value in the case of full compliance is 257, and the critical value at the confidence level of 5% is 295. Differences

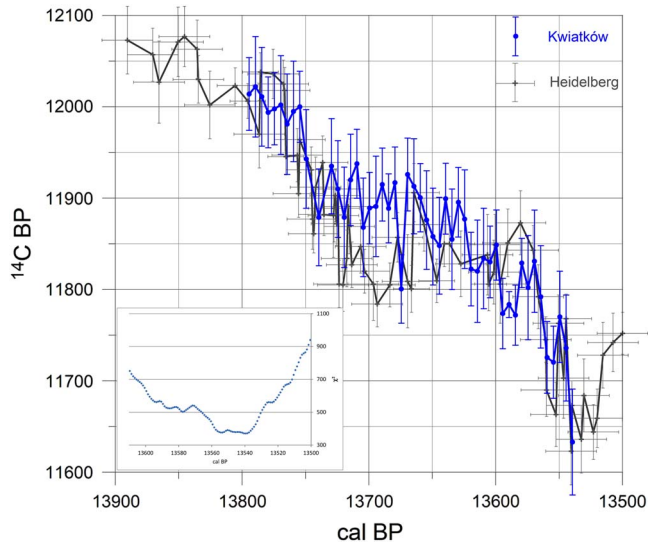


Figure 4 The best correlation between the Kwiatków floating chronology and the Heidelberg tree-ring sequence data. The  $\chi^2$  test results around minimum are presented in the inset. The Kwiatków floating chronology was affixed to the Heidelberg data at 13,540 cal BP.

between the sequences Kwiatków and Heidelberg are revealed for two periods—about 13,580–13,600 cal BP and 13,680–13,700 cal BP. Small wiggles of both sequences are very similar for the rest of the time period.

Observed differences between chronologies can result from several reasons:

- local effects,
- $^{14}\text{C}$  dates for Kwiatków chronology were produced for 5 consecutive tree rings, and for Heidelberg data for 10 consecutive tree rings,
- different intervals between individual dates. For data from Kwiatków it was a fixed interval of 5 yr (except for 2 dates excluded from modeling; see Table 1), and for data from Heidelberg intervals were variable—from 0.5 yr to 21 yr.

## CONCLUSIONS

The constructed Kwiatków chronology was based on a pine tree sequence, 260 yr in length, which covers the period ca. 13,821–13,561 cal BP as fitted to the IntCal13 calibration curve or 13,800–13,540 cal BP as fitted to the Heidelberg data. Dendrochronologically dated wood samples were used to reconstruct changes in the concentration of the  $^{14}\text{C}$  isotope in the atmosphere in this part of the Allerød.

The  $^{14}\text{C}$  concentration measurements performed by the authors proved that the constructed dendrochronological scale Kwiatków is related to the time interval, when the only record of  $^{14}\text{C}$  changes in the atmosphere from terrestrial archives is the series of data for the two floating pine chronologies from southern Germany and Switzerland. The IntCal 13 calibration curve in the time range of 12–14 ka cal BP is based exclusively on the Heidelberg floating tree-ring series (Reimer et al. 2013, see IntCal13 Supplemental Data, Figures S1–S25). Each new, high-

precision  $^{14}\text{C}$  concentration change data in the cited time interval, may thus contribute to the refinement of the calibration curve. The presented data show more complex changes of atmospheric  $^{14}\text{C}$  concentration compared to the smoothed IntCal13 calibration curve.

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## REFERENCES

- Alley RB, Shuman CA, Meese DA, Gow AJ, Taylor KC, Cuffey KM, Fitzpatrick JJ, Grootes PM, Zielinski GA, Ram M, Spinelli G, Elder BC. 1997. Visual-stratigraphic dating of the GISP2 ice core: basis, reproducibility, and application. *Journal of Geophysical Research* 102:26367–81.
- Anchukaitis KJ, Evans MN, Lange T, Smith DR, Leavitt SW, Schrag DP. 2008. Consequences of a rapid cellulose extraction technique for oxygen isotope and radiocarbon analyses. *Analytical Chemistry* 80:2035–41. doi: 10.1021/ac7020272.
- Baillie MGL, Pilcher JR. 1973. A simple cross-dating program for tree-ring research. *Tree-Ring Bulletin* 33:7–14.
- Bird M, Ayliffe LK, Fifield LK, Turney CSM, Cresswell RG, Barrows T, David B. 1999. Radiocarbon dating of “old” charcoal using a wet oxidation, stepped-combustion procedure. *Radiocarbon* 41(1):127–40.
- Brauer A, Endres C, Günther C, Litt T, Stebich M, Negendanka JFW. 1999. High resolution sediment and vegetation responses to Younger Dryas climate change in varved lake sediments from Meerfelder Maar, Germany. *Quaternary Science Reviews* 18(3):321–9.
- Bronk Ramsey C, van der Plicht J, Weninger B. 2001. “Wiggle matching” radiocarbon dates. *Radiocarbon* 43(2A):381–9.
- Cook ER, Kairiukstis LA, editors. 1990. *Methods of Dendrochronology*. Dordrecht: Kluwer Academic Publishers.
- Dzieduszyńska DA, Kittel P, Petera-Zganiacz J, Brooks SJ, Korzeń K, Krapiec M, Pawłowski D, Plaza DK, Płóciennik M, Stachowicz-Rybka R, Twardy J. 2014. Environmental influence on forest development and decline in the Warta River valley (Central Poland) during the Late Weichselian. *Quaternary International* 324:99–114.
- Friedrich M, Knipping M, von der Kroft P, Renno A, Ullrich O, Vollbrecht J. 2001. Ein Wald am Ende der letzten Eiszeit. Untersuchungen zur Besiedlungs-, Landschafts- und Vegetationsentwicklung an einem verlandeten See im Tagebau Reichwalde, Niederschlesischer Oberlausitzkreis. *Arbeits- und Forschungsberichte zur sächsischen Bodendenkmalpflege* 43:21–94.
- Friedrich M, Remmele S, Kromer B, Hofmann J, Spurk M, Kaiser KF, Orcel C, Küppers M. 2004. The 12,460 year Hohenheim oak and pine tree-ring chronology from Central Europe e a unique annual record for radiocarbon calibration and paleo-environment reconstructions. *Radiocarbon* 46(3):1111–22.
- Goslar T, Kuc T, Ralska-Jasiewiczowa M, Różanski K, Arnold M, Bard E, Van Geel B, Pazdur MF, Szeroczyńska K, Wicik B, Więckowski K, Walanus A. 1993. High-resolution lacustrine record of the Lateglacial/Holocene transition in Central Europe. *Quaternary Science Reviews* 12:287–94.
- Goslar T, Arnold M, Tisnerat-Laborde N, Czernik J, Ralska-Jasiewiczowa M. 2000. Variations of Younger Dryas atmospheric radiocarbon explicable without ocean circulation changes. *Nature* 403:877–80.
- Goslar T, Czernik J, Goslar E. 2004. Low-energy  $^{14}\text{C}$  AMS in Poznan radiocarbon Laboratory, Poland. *Nuclear Instruments and Methods in Physics Research B* 223-224:5–11.
- Hajdas I, Hendriks L, Fontana A, Monegato G. 2016. Evaluation of preparation methods in radiocarbon dating of old wood. *Radiocarbon* 58(1):1–11. doi: 10.1017/RDC.2016.98.
- Hajdas I, Ivy-Ochs SD, Beer J, Bonani G, Imboden D, Lotter AF, Sturm M, Suter M. 1993. AMS radiocarbon dating and varve chronology of Lake Soppensee: 6,000 to 12,000  $^{14}\text{C}$  years BP. *Climate Dynamics* 9:107–16.
- Hajdas I, Ivy-Ochs SD, Bonani G, Lotter AF, Zolitschka B, Schlüchter C. 1995. Radiocarbon age of the Laacher See tephra: 11,230  $\pm$  40 BP. *Radiocarbon* 37(2):149–54.
- Hoper ST, McCormac FG, Hogg AG, Higham TFG, Head MJ. 1998. Evaluation of wood pretreatments on oak and cedar. *Radiocarbon* 40(1):45–50.
- Hughen KA, Southon JR, Lehman SJ, Overpeck JT. 2000. Synchronous radiocarbon and climate shifts during the last deglaciation. *Science* 290:1951–4.
- Johnsen SJ, Clausen HB, Dansgaard W, Fuhrer K, Gundestrup N, Hammer CU, Iversen P, Jouzel J, Stauffer B, Steffensen JP. 1992. Irregular glacial interstadials recorded in a new Greenland ice core. *Nature* 359:311–3.
- Kaiser KF, Friedrich M, Miramont C, Kromer B, Sgier M, Schaub M, Boeren I, Talamo S, Guibal F,

- Sivan O. 2012. Challenging process to make the Lateglacial tree-ring chronologies from Europe absolute—an inventory. *Quaternary Science Reviews* 36:78–90.
- Kitagawa H, van der Plicht J. 1998. A 40,000 years varve chronology from Lake Suigetsu, Japan: extension of the  $^{14}\text{C}$  calibrations curve. *Radiocarbon* 40(3):505–15.
- Micheczyńska DJ, Krapiec M, Micheczyński A, Pawlyta J, Barniak J, Goslar T, Nawrocka N, Piotrowska N, Szychowska-Krapiec E, Waliszewska B, Zborowska M. 2018. Different pretreatment method for  $^{14}\text{C}$  dating of Younger Dryas and Allerød pine wood (*Pinus sylvestris* L.). *Quaternary Geochronology*. doi: 10.1016/j.quageo.2018.07.013
- Nakagawa T, Kitagawa H, Yasuda Y, Tarasov PE, Nishida K, Gotonda K, Sawai Y. 2003. Asynchronous climate changes in the North Atlantic and Japan during the last termination. *Science* 299:688–91.
- Nemec M, Wacker L, Hajdas I, Gäggeler H. 2010. Alternative Methods for Cellulose Preparation for Ams Measurement. *Radiocarbon* 52(3):1358–70.
- Rasmussen SO, Andersen KK, Svensson AM, Steffensen JP, Vinther BM, Clausen HB, Siggaard-Andersen M-L, Johnsen SJ, Larsen LB, Bigler M, Röthlisberger R, Fischer H, Goto-Azuma K, Hansson ME, Ruth U. 2006. A new Greenland ice core chronology for the last glacial termination. *Journal of Geophysical Research* 111:D06102. doi: 10.1029/2005JD006079.
- Reimer PJ, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck CE, Cheng H, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hafflidason H, Hajdas I, Hatté C, Heaton TJ, Hoffmann DL, Hogg AG, Hughen KA, Kaiser KF, Kromer B, Manning SW, Niu M, Reimer RW, Richards DA, Scott EM, Southon JR, Staff RA, Turney CSM, van der Plicht J. 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55(4):1869–87. doi: 10.2458/azu\_js\_rc.55.16947.
- Rinn F. 2005. TSAP-win. Time Series Analysis and Presentation for Dendrochronology and Related Applications. User Reference. Heidelberg.
- Santos GM, Ormsby K. 2013. Behavioral variability in ABA chemical pretreatment close to the  $^{14}\text{C}$  age limit. *Radiocarbon* 55(3):534–44. doi: 10.2458/azu\_js\_rc.55.16102.
- Santos GM, Bird MI, Pillans B, Fifield LK, Alloway BV, Chappell J, Hausladen PA, Arneith A. 2001. Radiocarbon dating of wood using different pretreatment procedures: Application to the chronology of Rotoehu Ash, New Zealand. *Radiocarbon* 143(1):239–48.
- Schwander J, Eicher U, Ammann B. 2000. Oxygen isotopes of lake marl at Gerzensee and Leysin (Switzerland), covering the Younger Dryas and two minor oscillations, and their correlation to the GRIP ice core. *Palaeogeography, Palaeoclimatology, Palaeoecology* 159(3–4):203–14. doi: 10.1016/S0031-0182(00)00085-7.
- Sookdeo A, Wacker L, Fahrni S, McIntyre CP, Friedrich M, Reinig F, Nievergelt D, Tegel W, Kromer B, Büntgen U. 2016. Speed dating: a rapid way to determine the radiocarbon age of wood By EA-AMS. *Radiocarbon* 58(1):1–7. doi: 10.1017/RDC.2016.76.
- Southon JR, Magana AL. 2010. A comparison of cellulose extraction and ABA pretreatment methods for AMS  $^{14}\text{C}$  dating of ancient wood. *Radiocarbon* 52(3):1371–9.
- Spurk M, Friedrich M, Hofmann J, Remmele S, Frenzel B, Leuschner HH, Kromer B. 1998a. Paleo-environment and radiocarbon calibration as derived from Lateglacial/Early Holocene tree-ring chronologies. *Quaternary International* 61:27–39.
- Spurk M, Friedrich M, Hofmann J, Remmele S, Frenzel B, Leuschner HH, Kromer B. 1998b. Revisions and extension of the Hohenheim oak and pine chronologies: New evidence about the timing of the Younger Dryas/Preboreal transition. *Radiocarbon* 40(3):1107–16.
- Staff R, Reynard L, Brock F, Bronk Ramsey C. 2014. Wood pretreatment protocols and measurement of tree-ring standards at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 56:709–15. doi: 10.2458/56.17449.
- Stuiver M, Polach HA. 1977. Discussion: reporting of  $^{14}\text{C}$  data. *Radiocarbon* 19(3):355–63.
- Wacker L, Nemec M, Bourquin J. 2010. A revolutionary graphitisation system: Fully automated, compact and simple. *Nuclear Instruments and Methods in Physics Research B* 268(7-8):931–4.
- Wacker L, Güttler D, Goll J, Hurmi JP, Synal H-A, Walti N. 2014. Radiocarbon dating to a single year by means of rapid atmospheric  $^{14}\text{C}$  changes. *Radiocarbon* 56:573–9. doi: 10.2458/56.17634.
- Wang YJ, Cheng H, Edwards RL, An ZS, Wu JY, Shen C-C, Dorale JA. 2001. A high-resolution absolute-dated Late Pleistocene monsoon record from Hulu Cave, China. *Science* 294:2345–8.