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RADIOCARBON DATING OF HIGHLY DEGRADED AND PROBLEMATIC FOSSIL WOOD: VERIFICATION OF THE EFFECTIVENESS OF VARIOUS PREPARATION METHODS

Maksymilian Jędrzejowski[1] • Danuta J Michczyńska[1] • Marzena Kłusek[1] • Adam Michczyński[1]* • Fatima Pawełczyk[1] • Natalia Piotrowska[1] • Karin Wyss Heeb[2,3] • Irka Hajdas[2]

[1]Institute of Physics – CSE, Silesian University of Technology, Konarskiego 22B, Gliwice 44-100, Poland
[2]Laboratory of Ion Beam Physics, ETHZ, Otto-Stern-Weg 5, 8093 Zürich, Switzerland
[3]Bern University of Applied Sciences, HKB, Bern 3027, Switzerland

ABSTRACT. This paper compares various wood pretreatment methods for highly degraded, and problematic fossil wood extracted from the opencast Szczerców site of the Bełchatów Lignite Mine in Central Poland. The study evaluates the pretreatment methods using both large samples (55–255 g, referred to as series A) and small samples (36–150 mg, referred to as series B). Additionally, all preparation methods were applied to medium-sized samples (approximately 3 g, referred to as series C) with solvent washes in the Soxhlet apparatus. Radiocarbon dating was conducted using the LSC technique (subseries A_1) and the AMS technique (subseries A_2, series B, and C). The effectiveness and utility of each pretreatment protocol were compared based on ^{14}C measurements and FTIR analysis. Through the conducted research and a multi-criteria analysis, the most effective method for preparing old fossil wood was identified. Our experience indicates that an extended, multistage preparation of highly degraded fossil wood samples, with a ^{14}C concentration near the detection limit of the radiocarbon method, may result in a significant increase in ^{14}C content.

KEYWORDS: alpha-cellulose, ^{14}C, fossil wood, FTIR, holocellulose, wood pretreatment methods.

INTRODUCTION

Radiocarbon dating of wood is used in many fields of environmental research. Together with dendrochronology, it helps in developing the calibration curve using annual tree rings (e.g. Pearson et al. 2021; Hua et al. 2022). Ancient wood is also subject to radiocarbon dating, especially subfossil wood from New Zealand kauri trees, which is used for the development of the Southern Hemisphere component of the global calibration curve (e.g. Turney et al. 2010; Hogg et al. 2020). In recent years, many radiocarbon age determinations of wood samples from different regions have been carried out (e.g. Kuitems et al. 2020; Krąpiec et al. 2021). The radiocarbon dating of wood has been used in the analysis of annual ^{14}C concentrations in tree rings, allowing the detection of abrupt increases in radiocarbon concentration in given calendar years related to solar or cosmogenic events (e.g. Miyake et al. 2012; Miyake et al. 2013; Büntgen et al. 2018; Rakowski et al. 2019; Brehm et al. 2022; Panyushkina et al. 2022). Recently, radiocarbon measurements in tree rings have also been used to reconstruct solar cyclic activity (e.g. Land et al. 2020; Usoskin et al. 2021).

The pretreatment of subfossil or fossil wood has been the subject of numerous previous studies (e.g. Southon and Magana 2010; Santos and Ormsby 2013; Staff et al. 2014; Hajdas et al. 2017; Capano et al. 2018; Gillespie 2018; Michczyńska et al. 2018), but in most cases, wood samples were well-preserved. In this study, we examine the effectiveness and problems of radiocarbon dating and chemical pretreatment of a highly degraded fossil wood sample. This article aims to answer several questions. Are all preparation steps necessary for highly degraded samples? Which fractions of such wood are significantly contaminated with exogenous carbon? Is it advisable to use all described reagents and procedures when a large part or even most of the cellulose and hemicelluloses have decomposed?

*Corresponding author: Email: Adam.Michczynski@polsl.pl

MATERIAL

Fossil wood, which comprises wood remains from conifer species, was obtained from the opencast Szczerców of the Bełchatów Lignite Mine. This fossil wood originates from lignite seams formed in the Miocene (23 Ma–5 Ma), thus rendering its age beyond the scope of radiocarbon dating. Therefore, this fossil wood was considered suitable as blank material for radiocarbon measurements. As a result of the large amount of material available (more than 1 kg in a single piece of wood), different pretreatment protocols were tested.

The material was divided into three sets of samples: 7 large samples (55–255 g, referred to as series A), 7 small samples (36–150 mg, referred to as series B), and 7 medium-sized samples (approximately 3 g each, referred to as series C), each representing a different pretreatment protocol. The wood was cut into small pieces using an OLFA® knife and then divided into samples for series A and C, ensuring that each sample contained pieces from different tree-rings of the original 1 kg stem. This allowed for some degree of homogenization of the material in series A and C. For series B, samples were taken from a single fragment of the initial material to ensure comparability of the results.

The unusually large sizes of samples in series A used in this study are due to the fact that some of the procedures and measurements discussed involve Liquid Scintillation Counting (LSC), which benefits from larger sample sizes for improved counting statistics and accuracy.

METHODS

Pretreatment Protocols

Our preparation methods include 7 different pretreatment protocols described in Table 1. Series A includes samples with a relatively high initial weight that were prepared at the Radiocarbon and Mass Spectrometry Laboratory (Gliwice Laboratory) for LSC measurements (subseries A_1). Part of those samples was selected for additional AMS measurements at the Ion Beam Physics Laboratory (ETH Laboratory) forming subseries A_2. Series B consists of samples with a small initial weight prepared and measured with the AMS technique at the ETH Laboratory. Series C consists of medium-sized samples prepared at the Gliwice Laboratory, in which each pretreatment protocol was preceded by Soxhlet extraction. A detailed protocol for each sample can be found in the Supplementary Material.

Measurements were performed using both the LSC and the AMS techniques to investigate the influence of sample size and pretreatment protocol on the dating results in each technique.

Solvent Treatment

The first step in the preparation of wood for radiocarbon dating may involve a removal of resins, which can be carried out using a Soxhlet apparatus (abbreviated as "S" in this article). In our study, the resin extraction was conducted in three steps, after Sheppard and Thompson 2000; Guerrieri et al. 2011; Kłusek and Pawełczyk 2014. First, the samples were treated with a 1:1 mixture of ethanol (C_2H_5OH) and toluene (C_7H_8) at boiling temperature for 4 hours. Second, they were treated with C_2H_5OH alone for 4 hours. Finally, the samples were cleaned with boiling water for 1 hour and then rinsed.

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Table 1 Pretreatment protocols analyzed in the study. A detailed protocol for each sample can be found in the Supplementary Material.

		Mercerizing (base) **B**		Acid-Base-Acid pretreatment **ABA**						Bleaching **Bl**			Alpha-cellulose extraction (base) **B**				
Protocol code	Deionized water, overnight, 75 °C	2-4% NaOH, 12–18 h, 75 °C	RINSE	2-4% HCl, 1 h, 60–85 °C	RINSE	2-4% NaOH, 1 h, 60–85 °C	RINSE	2-4% HCl, 1 h, 60–85 °C	RINSE	5% $NaClO_2$ + 1M HCl, 2 h, repeated, 75 °C	US, RT	RINSE	10% NaOH, 45 min, 75 °C	17% NaOH, 45 min, RT	RINSE	1% HCl, <5 min, RT	RINSE
d. water	✓																
BABA	✓	✓				✓											
ABA	✓					✓											
BABABl	✓	✓				✓					✓						
BABABlB	✓	✓				✓					✓				✓		
Bl	✓										✓						
BlB	✓										✓				✓		

Abbreviations: US – ultrasonic bath, RT — room temperature.

Mercerization

Mercerization, a sodium base (NaOH) pretreatment (abbreviated as "B" in this article), was proposed by Němec et al. (2010b) as a means of enhancing the effectiveness of the ABA (acid-base-acid) pretreatment. The procedure takes advantage of the fact that the alcoholic, phenolic, and carboxylic groups of the main wood components are more dissociated at high pH. During mercerization, the samples were treated with 2–4% NaOH for 12–18 hours at 75ºC, mostly overnight. The samples were then rinsed with deionized water until they reached a neutral pH.

Acid-Base-Acid

The Acid-Base-Acid (ABA) or Acid-Alkali-Acid (AAA) is a standard procedure that is used for radiocarbon dating, and in this study was conducted after Michczyńska et al. 2018. In the first step, the samples were treated with a hydrochloric acid (HCl) solution for 1 hour at 60–85ºC to remove carbonates. The samples were then rinsed to neutral pH. The second step involved treating the samples with NaOH for 1 hour at 60–85ºC to remove humic and fulvic acids, although the alkalization time was reduced to 30 minutes for most samples to prevent the material from dissolving. After rinsing the samples to a neutral pH, the third step was applied. The samples were treated with an HCl solution for 1 hour at 60–85ºC to remove modern carbon incorporated into the sample mainly during the alkali step. After the third step, the samples were rinsed to neutral pH.

Bleaching

Old fossil woods primarily consist of lignin (Obst et al. 1991), a complex polymer of phenolic alcohol derivatives (Pettersen 1984). To remove the lignin while preserving the holocellulose (the collective term for cellulose and hemicelluloses), a process known as bleaching (abbreviated as "Bl" in this article) was used. Bleaching followed the method described by Němec et al. (2010b), which involves a 2-hour treatment at 75ºC using acidified $NaClO_2$. The bleaching process was repeated if necessary to achieve a whitish residue. In this study, HCl was used for acidifying the solution.

Alpha-Cellulose Extraction

Cellulose, which is a glucan polymer with a high degree of polymerization, and specifically its fraction known as alpha-cellulose, is the compound that is the most resistant to carbon exchange with the environment (Stuiver and Quay 1981; Hoper et al. 1997; Helle et al. 2022). Thus, alpha-cellulose is a commonly the preferred material in isotope-ratio mass spectrometry and radiocarbon dating.

Alpha-cellulose is obtained by using a strong NaOH solution after bleaching (see the previous section). NaOH allows the removal of hemicelluloses, also known as beta-cellulose and gamma-cellulose. Hemicelluloses are a group of polysaccharides composed of various sugars (arabinose, galactose, glucose, mannose, rhamnose, and xylose) with a low degree of polymerization.

To obtain alpha-cellulose, the samples in this study were treated after Loader et al. (1997), that is with a 10% NaOH solution at 75ºC for 45 min, followed by a 17% NaOH solution at room temperature for another 45 min, without rinsing in between. The samples were then rinsed to

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neutral pH and treated with 1% HCl at room temperature for less than 5 min, and then rinsed again to neutral pH.

Benzene Synthesis and LSC Measurements

To prepare the samples for radiocarbon dating, they were subjected to carbonization (pyrolysis) in a cylindrical reactor. The carbonization process took place at a temperature of 750ºC for approximately 15 minutes, with limited oxygen availability. Subsequently, lithium was added to create lithium carbide Li_2C_2, which reacted under vacuum conditions at a temperature of 700–750ºC for 30 minutes. After the hydrolysis of lithium carbide to generate ethyne (C_2H_2), trimerization occurred with the assistance of a chromium(III) oxide (Cr_2O_3) catalyst, resulting in the production of benzene (C_6H_6).

The potential contamination of the samples by the radioactive isotope ^{222}Rn (Hood et al. 1989), which with its daughter isotopes can induce additional counts into radiocarbon dating results, was addressed by refrigerating the samples for over a month. This duration allowed for the decay of approximately ten half-lives of radon atoms, reducing their count rate to levels close to background levels.

The samples in subseries A_1 were analyzed by LSC measurements using a Quantulus 1220™ Liquid Scintillation Beta Spectrometer at the Gliwice Laboratory (Pawlyta et al. 1997; Pazdur et al. 2003).

LSC measurements were predominantly performed on a 2 mL geometry for subseries A_1 using the d. water, BABA, ABA, BABABl, and Bl protocols. However, for the Bl sample, the addition of inactive benzene p.a. was necessary to obtain the required 2 mL sample volume. BABABlB and BlB samples from subseries A_1, were dated on a 0.5 mL geometry.

Graphitization and AMS Measurements

After undergoing chemical pretreatment, the samples from subseries A_2, series B and C were graphitized using an AGE-3 system, to which was attached an elemental analyzer VarioMicroCube by Elementar (Němec et al. 2010a; Wacker et al. 2010b). Typically, approximately 3 mg of the prepared sample material were weighed into a tin capsule and combusted in the elemental analyzer. The resulting CO_2 produced during the process was captured by a molecular sieve and transferred to one of the graphitization reactors. Every graphite was formed on 5 mg of pre-conditioned fine iron powder, used as a catalyst. The reaction of CO_2 and H_2 was performed at a temperature of 580ºC.

The graphitization for series A_2 and B was carried out at the ETH Laboratory. Likewise, samples from series C underwent graphitization at the Gliwice Laboratory using the same procedure. In both laboratories, the AMS measurements were performed using the MICADAS spectrometer (Synal et al. 2007; Wacker et al. 2010a), with series A_2 and B at the ETH MICADAS and series C at the Gliwice MICADAS.

RESULTS AND DISCUSION

Pretreatment, Conversion and Overall Yields

The final product obtained from the pretreatment protocols is either degraded wood (using d. water, ABA, and BABA protocols), holocellulose (using BABABl and Bl protocols),

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or alpha-cellulose (using BABABlB and BlB protocols). Microscope photographs of the final products can be found in the Supplementary Material.

Table 2 presents the pretreatment yield (calculated as the ratio of the mass of sample after pretreatment to the mass of the sample before pretreatment), conversion yield (calculated as the ratio of the mass of the sample after benzene synthesis or graphitization to the mass of sample after benzene synthesis or graphitization), and overall yield (the result of the multiplication of pretreatment yield and conversion yield) for each sample. For series C, the pretreatment yield is shown with and without the Soxhlet step to facilitate comparison.

The pretreatment yields vary significantly depending on the protocol used. Obtained low yield values stand in stark contrast to the majority of values reported in the literature. Yields around 75% for ABA, 30% for holocellulose protocols, and 20% for alpha-cellulose protocols, in the case of ancient wood are not uncommon (e.g. Southon and Magana 2010; Capano et al. 2018; Michczyńska et al. 2018; Cercatillo et al. 2021). However, some researchers have reported similar low pretreatment yields (Hajdas et al. 2017; Pawełczyk et al. 2022). These low values, particularly for series C, where some are below 1%, suggest that certain protocols commonly used for dating ancient wood cannot be applied to highly degraded fossil wood. Also, four samples from series B (namely BABABl, BABABlB, Bl, and BlB protocols) weighing 68–72 mg disintegrated during pretreatment and were prepared again with double mass (150 mg).

FTIR Analysis

Fourier Transform Infrared (FTIR) analysis is a valuable tool for assessing the purity of obtained cellulose for radiocarbon dating purposes (e.g. Richard et al. 2014; Hajdas et al. 2017; Michczyńska et al. 2018; Fogtmann-Schulz et al. 2021).

FTIR analysis was performed in ATR (Attenuated Total Reflection) mode using a PerkinElmer Spotlight 200i spectrometer at the ETH Laboratory. The spectral sensitivity was measured for wavenumbers between 4000 cm^{-1} and 550 cm^{-1}, and the full spectra are available in the Supplementary Material. The FTIR spectra were subjected to baseline correction and normalization. Figure 1 shows selected ranges of FTIR spectra for better clarity. Principal assignments are indicated according to Pandey and Theagarajan (1997); Colom et al. (2003); Pandey and Pitman (2003); Drobniak and Mastalerz (2006); Fan et el. (2012); Richard et al. (2014); Stark et al. (2016) to show the components from which they result (lignin, hemicelluloses, or cellulose).

To lignin, typically removed in the bleaching step, four different strong peaks can be assigned: 1595–1610 cm^{-1}, 1505–1510 cm^{-1}, 1265–1275 cm^{-1}, and 1210–1226 cm^{-1}. All samples that undergo bleaching protocols (BABABl, BABABlB, Bl, BlB, S+BABABl, S+BABABlB, S+Bl, S+BlB) do not show these peaks at all, indicating successful removal of lignin in the analyzed old fossil wood sample.

Typically, hemicelluloses are mostly eliminated during alpha-cellulose extraction. However, in our study, a noteworthy peak at around 1735–1740 cm^{-1} associated with hemicellulose is present in most samples and absent only in cellulose products from series C. This indicates that the removal of hemicelluloses was unusual in this particular old fossil wood. Both alpha-cellulose protocols (BABABlB and BlB) for series A and B show a strong signal from this peak, suggesting that the alpha-cellulose extraction protocol applied in this study failed to remove hemicelluloses. In contrast, samples from series C that underwent alpha-cellulose protocols

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Table 2 Pretreatment, conversion and overall yields grouped by pretreatment protocol.

		Pretreatment yield, approx. %		Conversion yield, approx. %		Overall yield, approx. %	
Protocol code	Dated material (final product)	Series A	Series C	Subseries A_1 benzene synthesis	Series C graphitization	Subseries A_1	Series C
d. water	Degraded wood	87	– with S: 65	23	61	20	40
BABA	Degraded wood	47	71 with S: 46	26	64	12	29
ABA	Degraded wood	61	80 with S: 52	29	63	18	33
BABABl	Holocellulose	6.2 [1]	0.5 with S: 0.3	33	34	2.0	0.1
BABABlB	Alpha-cellulose	2.8 [1,2]	– [3]	15	–	0.4	–
Bl	Holocellulose	11 [1]	2.4 with S: 1.6	25	37	2.8	0.6
BlB	Alpha-cellulose	5.3 [1]	0.9 with S: 0.6	13	33	0.7	0.2

[1]These samples were centrifuged.

[2]As it is the longest pretreatment method, during preparation there were some early results. After the BABA step, the material was divided into larger, well-preserved pieces of wood and a small fraction. In these well-preserved, larger pieces of wood, pretreatment yield was approx. 13%.

[3]The sample disintegrated during pretreatment and was prepared again with additional material; however, the pretreatment yield was almost zero.

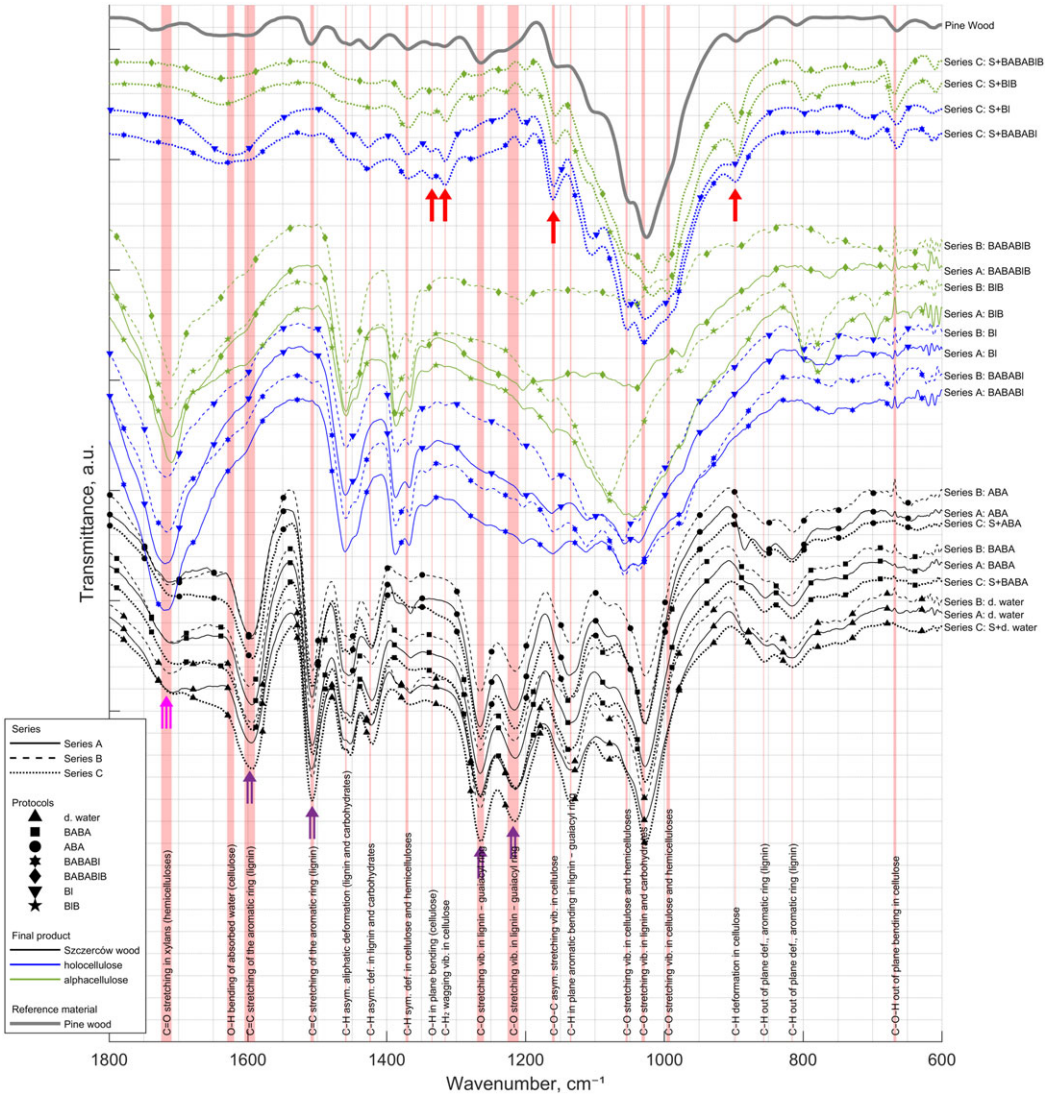

Figure 1 The FTIR spectra of the wood samples subjected to preparation methods used in this study presented against the spectrum for contemporary pine wood. Each line in the FTIR spectra plot is labeled with a protocol code and laboratory name, and is marked with the following convention: series A by a solid line, series B by a dashed line, and series C is represented by a dotted line. In the online version of the plot, samples where the final product is wood are shown in black, samples where the final product is alphacellulose are shown in green, and samples where the final product is holocellulose are shown in blue. Principal assignments are indicated according to Pandey and Theagarajan (1997); Colom et al. (2003); Pandey and Pitman (2003); Drobniak and Mastalerz (2006); Fan et el. (2012); Richard et al. (2014); Stark et al. (2016) to show the components from which they result (lignin, hemicelluloses, or cellulose). The arrows in the figure indicate assignments mentioned in the text, with one, two, or three shafts denoting cellulose, lignin, and hemicelluloses assignments, respectively. Detailed analysis is presented in the Supplementary Material.

(S+BABABlB and S+BlB) and holocellulose protocols (S+BABABl and S+Bl) did not show this peak at all (see Figure 1). After pretreatment in the Soxhlet apparatus, this peak is still present (e.g., in the S+ABA sample). We speculate that for this old fossil wood sample, the pretreatment in the Soxhlet apparatus removed some hemicelluloses compounds, supporting

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the complete removal of hemicelluloses during the bleaching step for samples in series C, which for the series A and B apparently failed.

Most of the strong peaks associated with cellulose are also linked to lignin and/or hemicelluloses, so caution is necessary when interpreting them. However, even weak peaks such as those at 1335 cm^{-1}, 1316 cm^{-1}, 1158–1162 cm^{-1}, or 898 cm^{-1} can provide useful information (Colom et al. 2003). These peaks are characteristic for cellulose and present only in samples S+BABABl, S+BABABlB, S+Bl, and S+BlB, indicating that samples that undergo Soxhlet extraction have resulted in relatively pure cellulose (where lignin and hemicelluloses are successfully removed).

Regarding the above, it can be concluded that the commonly used alpha-cellulose extraction method with 10% NaOH and then 17% NaOH was ineffective to remove hemicelluloses from the highly degraded ancient wood analyzed in this study. Only the combination of Soxhlet extraction and bleaching step were successful in removing hemicelluloses.

^{14}C Measurements Analysis

As anticipated, the concentration of the ^{14}C isotope in the wood sample tested is at background levels. However, the results generally exceeded 0.25 pMC (see Table 3), indicating that the samples were contaminated. In many radiocarbon studies of ancient wood, results below 0.2 pMC are not uncommon (e.g. Santos et al. 2001; Southon and Magana 2010; Martinez De La Torre et al. 2019; Hogg et al. 2020; Turney et al. 2021).

In the case of the LSC technique (subseries A_1), background correction was implemented due to the presence of various sources of external radiation that can impact measurements. These sources include high-energy cosmogenic particles and radionuclides found in the building materials of the surrounding structures. As a result, the GdS-4393 sample should be considered indistinguishable from background levels (see Supplementary Material).

In the case of the AMS technique (subseries A_2, series B, and C), no background correction was applied.

In subseries A_2 and series B (measured at ETH MICADAS), measurements were conducted on four blank samples within the same magazine. Kauri tree wood (ETH-44660.482.1) gave a result of 0.2094 ± 0.0062 pMC, while the blank wood prepared using the ABA protocol (ETH-92290.67.1) exhibited a result of 0.2399 ± 0.0066 pMC. Two other blank samples were Phthalic Anhydride with results of 0.2391 ± 0.0067 pMC (ETH-101798.7.44) and 0.2107 ± 0.0062 pMC (ETH-101798.7.45).

In the case of series C (measured at Gliwice MICADAS), a blank wood sample named OLGA, prepared with ABABl protocol, was analyzed as a reference material, resulting in a value of 0.405 ± 0.011 pMC (GdA-6998.1.1). Additionally, two other background samples, anthracite prepared with the use of the ABA protocol, resulted in values of 0.3484 ± 0.0095 pMC (GdA-6999.1.2) and 0.3392 ± 0.0097 pMC (GdA-6999.1.3).

LSC Technique

As mentioned earlier, samples from series A_1 were dated using the LSC technique. Since the mass of obtained benzene was different for some samples (see Table 3), a background correction was applied to facilitate comparison.

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Table 3 Dating results grouped by pretreatment method. In the case of AMS technique, no background correction has been subtracted. In the case of the LSC technique, necessary corrections (e.g. background subtraction) were applied. NDFB stands for Not Distinguishable From Background.

		Sample label ^{14}C measurements result Final mass (LSC – benzene, AMS – graphite)			
Protocol code	Dated material (final product)	Subseries A_1 Large samples LSC technique	Subseries A_2 Large samples AMS technique	Series B Small samples AMS technique	Series C Medium samples with Soxhlet step AMS technique
d. water	Degraded wood	GdS-4393 **NDFB** 1,775.2 mg	ETH-121498.1.1 0.2996 ± 0.0074 pMC 995 µg	ETH-121499.1.1 0.2601 ± 0.0069 pMC 996 µg	GdA-6754.1.1 1.154 ± 0.017 pMC 991 µg
BABA	Degraded wood	GdS-4397 0.37 ± 0.12 pMC 1,770.6 mg	ETH-121500.1.1 0.2719 ± 0.0071 pMC 994 µg	ETH-121501.1.1 0.2169 ± 0.0066 pMC 999 µg	GdA-6754.2.1 0.434 ± 0.010 pMC 990 µg
ABA	Degraded wood	GdS-4402 0.295 ± 0.077 pMC 1,772.4 mg	ETH-121502.1.1 0.2688 ± 0.0070 pMC 994 µg	ETH-121503.1.1 0.1753 ± 0.0058 pMC 996 µg	GdA-6754.3.1 0.3426 ± 0.0092 pMC 988 µg
BABABl	Holocellulose	GdS-4403 0.525 ± 0.085 pMC 1,747.6 mg	ETH-121504.1.1 0.3791 ± 0.0084 pMC 990 µg	ETH-121505.1.1 0.2027 ± 0.0064 pMC 991 µg	GdA-6754.4.1 1.382 ± 0.018 pMC 980 µg
BABABlB	Alpha-cellulose	GdS-4408 2.96 ± 0.15 pMC 450.5 mg	ETH-121506.1.1 0.3691 ± 0.0083 pMC 671 µg	ETH-121507.1.1 0.4348 ± 0.0094 pMC 989 µg	–
Bl	Holocellulose	GdS-4435 1.69 ± 0.17 pMC 772.5 mg	ETH-121508.1.1 0.2893 ± 0.0074 pMC 1 000 µg	ETH-121509.1.1 0.2391 ± 0.0069 pMC 989 µg	GdA-6754.6.1 0.866 ± 0.015 pMC 985 µg
BlB	Alpha-cellulose	GdS-4452 0.93 ± 0.14 pMC 426.2 mg	ETH-121510.1.1 0.3512 ± 0.0080 pMC 992 µg	ETH-121511.1.1 0.503 ± 0.010 pMC 993 µg	GdA-6754.7.1 0.814 ± 0.015 pMC 986 µg

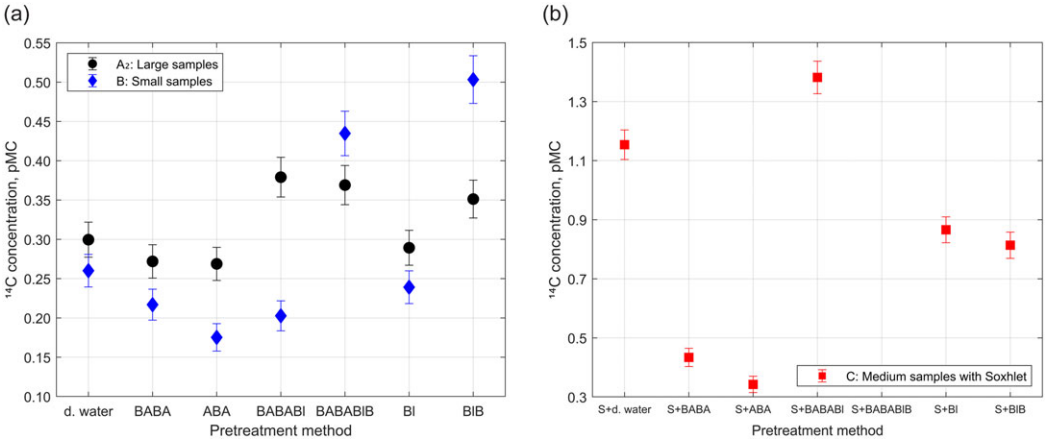

Figure 2 Results of ^{14}C measurements with AMS technique. Terms in labels (small, medium, and large samples) refer to the amount of wood before pretreatment, and not to the final target size (~1 mgC). No background correction has been subtracted. (a) Comparison of large versus small samples using the AMS technique. The results are presented with triple uncertainty. The measurements were conducted in a single magazine at ETH Zurich. (b) Results of Series C, wherein each pretreatment protocol was preceded by extraction in a Soxhlet apparatus. The results are displayed with triple uncertainty. The measurements were performed in a single magazine at the Gliwice laboratory.

The lowest radiocarbon count rate was observed for the d. water protocol. The results obtained using the ABA and BABA protocols were also satisfactory. However, the BABABlB protocol, which had the lowest overall yield, also gave a significantly enriched ^{14}C result due to modern carbon contamination resulting from longer and more severe treatment.

While it is important to note that poor ^{14}C results can be influenced by multiple factors, including sample overhandling, a potential cause for poor results in alpha-cellulose protocol is performing the HCl step too briefly and without applying heat.

A factor to consider is CO_2 reabsorption into NaOH during the extended rinsing required for larger samples. The preparation of larger samples necessitated a significantly extended rinsing duration to achieve a neutral pH, as noted in the Supplementary Material. The mechanism underlying static CO_2 absorption into NaOH solution from the atmosphere has been known in the field of radiocarbon dating for many years and has been studied extensively (e.g. Berger and Libby 1967; Povinec et al. 1968; Awsiuk and Pazdur 1986). In our research, we hypothesize that this mechanism may contribute to the observed phenomena in Gliwice pretreatment and LSC dating, particularly when samples undergo alpha-cellulose extraction, consistently displaying higher ^{14}C count rates (Table 3).

Conversely, for these samples (BABABlB, and BlB protocols), the mass of obtained benzene was insufficient, necessitating the dating of the samples on a secondary detector with a reduced geometry. This setup generally yields less precise results, due to decreased efficiency and lesser factor and figure of merit values (Hogg and Cook 2022).

Large vs. Small Samples with AMS Technique

A comparison of the AMS results for large and small samples (subseries A_2 and series B) presented in Figure 2a indicates, for most pretreatment protocols, higher ^{14}C concentration values for large samples. An exception to the observed trend is the results for alpha-cellulose,

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which raises the possibility that the duration of HCl step applied at the end was too short and performed without heat.

The differences in results with triple uncertainty (Figure 2a) are smallest in single-step protocols, such as d. water and Bl. In contrast, in the ABA, BABA, and BABABl protocols, the differences in ^{14}C count rates are statistically significant, as determined by a t-test. This finding supports the assertion that the extensive and multistage preparation of large samples of highly degraded fossil wood can result in enriched ^{14}C due to modern carbon contamination.

The lowest concentrations of the ^{14}C isotope were obtained for the chemical preparation of small samples using the BABA, and ABA protocols.

Series C Results

The higher radiocarbon concentration observed in the d. water pretreatment in series C (GdA-6754.1.1 sample) exceeds the radiocarbon concentrations observed in series A_2 and B. This finding confirms that pretreatment consisting solely of Soxhlet apparatus extraction and water rinsing is not an adequate treatment for this specific sample. Additional steps may be necessary to ensure proper pretreatment in such cases (Figure 2b). In the ABA and BABA protocols of series C, the lowest ^{14}C concentration was measured. In the protocols involving a bleaching step, the measured ^{14}C concentration was higher than that of the respective protocols in series A_2 and B. FTIR results suggest that series C obtained a holo- or alpha-cellulose fraction of the purest quality compared with series A and B, as hemicelluloses are absent. This indicates that the higher ^{14}C concentration is not associated with the pretreatment in the Soxhlet apparatus but rather with different contamination in this particular fraction of wood.

Almost all samples dated using the AMS technique, except for two (BABABlB protocol in series A_2, S+BABABlB protocol in series C, see Table 3), produced graphite with a standard mass of 1 mg. Protocols that involved the extraction of holocellulose or alpha-cellulose resulted in yields below 2% (indicated as "with S" in Table 2). In such cases, even small modern carbon contamination can result in highly inaccurate results (Santos et al. 2007; Paul et al. 2016).

Multi-Criteria Analysis

A multi-criteria analysis (Table 4) was proposed to select the most suitable pretreatment method. It should be noted that this analysis is only valid for highly degraded fossil wood, and is based on the case study of fossil wood from Szczerców in the Bełchatów Lignite Mine. Therefore, it is not applicable to well-preserved wood. Additionally, this analysis should be interpreted with caution, as pretreatment of wood samples can be case-specific or may give uncommon results (e.g. Patrut et al. 2010; Southon and Magana 2010; Santos and Ormsby 2013), and therefore it occurs that this analysis is applicable to highly degraded ancient wood.

The following criteria were considered in order to select the most suitable pretreatment method:

- Pretreatment cost/efficiency/time: These three factors are interdependent and are listed together. The cost is normalized by efficiency and represents the approximate amount of reagents required to obtain 10 g of the final product (wood, holocellulose, or alpha-cellulose) in the LSC technique, sufficient to yield 2 mL of benzene, or 5 mg of the final product in the AMS technique, sufficient to yield 1 mg of graphite. A table providing detailed information is available in the Supplementary Material. Efficiency refers to the overall yield, which is a combination of pretreatment yield and conversion yield

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Table 4 A multi-criteria analysis of the effectiveness of various preparation methods. The methods were ranked on a scale of 1 to 7, with 1 being the best method and 7 being the worst method. Highlighted rows indicate the identification of the most effective methods for preparing old fossil wood (with a score of up to 2.0).

Criteria Protocol	Cost/Efficiency/Time 25%	Problems 25%	Dating result 50%	Average
Large samples for LSC technique				
d. water	1	1	1	**1.0**
BABA	3	2	3	**2.8**
ABA	2	2	2	**2.0**
BABABl	5	5	4	**4.5**
BABABlB	7	4	7	**6.3**
Bl	4	5	6	**5.3**
BlB	6	5	5	**5.3**
Small samples for AMS technique				
d. water	1	1	5	**3.0**
BABA	3	2	3	**2.8**
ABA	2	2	1	**1.5**
BABABl	6	4	2	**3.5**
BABABlB	7	4	6	**5.8**
Bl	4	4	4	**4.0**
BlB	5	4	7	**5.8**

(see overall yield in Table 2). Time refers to the number of preparation days required to obtain a fully prepared sample ready for measurements, based on the detailed protocol tables provided in the Supplementary Material. It is well-known that the time needed for sample pretreatment can be reduced by preparing samples in batches consisting of several dozen samples (e.g. Gaudinski et al. 2005; Southon and Magana 2010; Staff et al. 2014; Gillespie 2018; Fogtmann-Schulz et al. 2021; Santos et al. 2023).

- Problems: This criterion aims to quantify the challenges and difficulties encountered when dealing with highly degraded, and problematic wood samples. Four main problems were identified: 1) Sample disintegration during pretreatment. 2) Necessity of the changes in planned protocols, including the use of weaker reagents and shortened time. 3) Additional repetitions of bleaching to obtain a white residue, which were not originally planned. 4) The need for centrifugation. Detailed protocol tables providing further information can be found in the Supplementary Material. It should be noted that this criterion is suitable only for highly degraded samples.
- Dating result: This criterion refers to the expected result of dating old fossil wood, which is the lowest possible count rate (LSC technique) or concentration (AMS technique) of isotope ^{14}C (see Table 2).

In the case of the LSC technique, the best results, according to the adopted criteria, for our specific fossil wood were obtained by treating the sample with deionized water. However, it should be noted that these results were specific to the geological situation of the wood and may vary depending on the material tested. Therefore, we do not recommend omitting chemical preparation. After analyzing all results presented in this study and performing a multi-criteria

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analysis, we suggest that for highly degraded old fossil wood dating (samples close to the radiocarbon range or older), minimal pretreatment is sufficient. The classical ABA method gave good results according to the adopted criteria.

Regarding the AMS technique, the classical ABA pretreatment gave the best results, which is in good agreement in the results obtained by some other research (Southon and Magana 2010; Hajdas et al. 2017; Pawełczyk et al. 2022). Deionized water and BABA pretreatments were also satisfactory. Both pretreatment methods that lead to holocellulose extraction, that is, BABABl and Bl, gave very good radiocarbon dating results, especially the former is in good agreement with results obtained by other research (Capano et al. 2018; Lange et al. 2019). However, in both cases, the pretreatment yield was very low, so these methods cannot be recommended if the initial sample mass is small.

Based on our experience with this sample, we do not recommend alpha-cellulose extraction for highly degraded ancient wood dating using either AMS or LSC techniques. This is due to the low overall yield of the process and less precise dating results, which contradicts the general recommendations for the treatment of old wood or wood in general (e.g. Hogg et al. 2006; Fogtmann-Schulz et al. 2021; Santos et al. 2023).

CONCLUSIONS

A large amount of fossil (Miocene) wood from the Bełchatów Lignite Mine, more than 1 kg, was separated into three sets of samples: 7 large samples (55–255 g, series A), 7 small samples (36–150 mg, series B), and 7 medium-sized samples (3 g, series C). Our intention was to find the optimal sample treatment with respect to measured ^{14}C concentration and financial resources used. As described in this study, chemical pretreatment of highly degraded old fossil wood can be challenging. Firstly, the overall yield in protocols that extract cellulose was low or extremely low, even below 1%. Secondly, samples may require centrifugation or disintegrate during cellulose extraction, necessitating restarting the procedure. Thirdly, the rinsing process to achieve a neutral pH can be time-consuming and may increase the likelihood of modern contamination through the absorption of atmospheric CO_2 during the base-step.

Summarizing the sources of contamination in this study, they include pre-existing contamination within the sedimentation environment (such as fulvic and humic acids), different contamination within degraded portions of the wood (lignin and hemicelluloses), contamination stemming from modern carbon introduction during sample pretreatment, as well as challenges arising from the necessity to conduct sub-optimal measurements.

Based on all of the above, we recommend using the classic ABA procedure for both LSC and AMS techniques when dating highly degraded ancient wood. In some specific samples, such as our study sample, protocols involving holocellulose or alpha-cellulose have disadvantages, such as very low yield or less precise dating results, or both.

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SUPPLEMENTARY MATERIAL

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