ABA AND ABOX RADIOCARBON CROSS-DATING ON CHARCOAL FROM MIDDLE PLENIGLACIAL LOESS DEPOSITS IN AUSTRIA, MORAVIA, AND WESTERN UKRAINE

Paul Haesaerts[1,2] • Freddy Damblon[1] • Philip Nigst[3,4] • Jean-Jacques Hublin[3]

ABSTRACT. Four charcoal samples from loess key sites in Austria, Moravia, and western Ukraine were submitted to ABOx (acid-base oxidation) pretreatment to compare results with the classical ABA (acid-base-acid) method. For this purpose, charcoal samples already dated in Groningen laboratory were selected from 3 archaeological sites: Molodova V in western Ukraine (subunit 10-1, ~32.6 ka BP), Willendorf II in Austria (unit C4, ~32.1 ka BP and unit C8, ~38.9 ka BP) and Vedrovice V in Moravia (unit 4, upper part of Bohunice soil, ~39.5 ka BP). Each selected charcoal sample has been homogenized and divided into 3 subsamples, which were submitted to ABA in Groningen and to ABA and ABOx pretreatments in Oxford. The results show that the ABOx dates are older than the ABA dates. Nevertheless, down to ~40 ka BP ABOx and Groningen ABA dates appear in good agreement within a time interval of ~1 millennium at 1σ. However, Groningen ABA pretreatment produces older dates than the Oxford ABA pretreatment. Both Oxford ABOx and Groningen ABA pretreatments provide sets of dates in good agreement with the chronological background of each selected site.

INTRODUCTION

Long series of radiocarbon dates mainly produced in the Groningen laboratory were recovered during the last decades on charcoal remains from Middle and Late Pleniglacial loess deposits in central and eastern Europe (Damblon et al. 1996; Haesaerts et al. 1996, 2009, 2010; Jöris and Street 2008; Nigst and Haesaerts 2012). Recently, the ABOx pretreatment method (Bird et al. 1999) has been implemented on various charcoal materials with the aim to improve the quality of the results, mainly for samples prior to 30 ka uncal BP (Ascough et al. 2010; Higham 2011). This method, for the period 40–30 ka BP, claims to provide around 2 to 4 millennia older ^{14}C ages compared to ABA dates obtained by Oxford laboratory on the same charcoal sample (Brock and Higham 2009; Douka et al. 2010). Consequently, and although most of the previous published Groningen ^{14}C dates on charcoal from loess appeared consistent with their stratigraphical distribution (Haesaerts et al. 2009, 2010), it became necessary to test their reproducibility and precision for the time period 45–30 ka BP by comparing the results after ABA and ABOx pretreatment methods implemented in parallel on identical samples.

METHODS

Selection of the Charcoal Samples

Four conifer samples older than 30 ka BP and already dated in the Groningen laboratory were selected from 3 loess sections related to Paleolithic sites of central and eastern Europe (Figure 1), Molodova V in western Ukraine (subunit 10-1 dated to ~32.6 ka BP; Haesaerts et al. 2003), Willendorf II in Austria (unit C4 dated to ~32.1 ka BP and unit C8, ~38.9 ka BP; Haesaerts et al. 1996; Nigst et al. 2008; Nigst and Haesaerts 2012), and Vedrovice V in Moravia (unit 4, top of the Bohunice soil dated ~39.5 ka BP; Valoch 1993) (Figure 2).

[1]Royal Belgian Institute of Natural Sciences, Brussels, Belgium.
[2]Corresponding author. Email: paul.haesaerts@naturalsciences.be.
[3]Department of Human Evolution, Max-Planck Institute for Evolutionary Anthropology, Leipzig, Germany.
[4]Department of Archaeology and Anthropology, University of Cambridge, United Kingdom.

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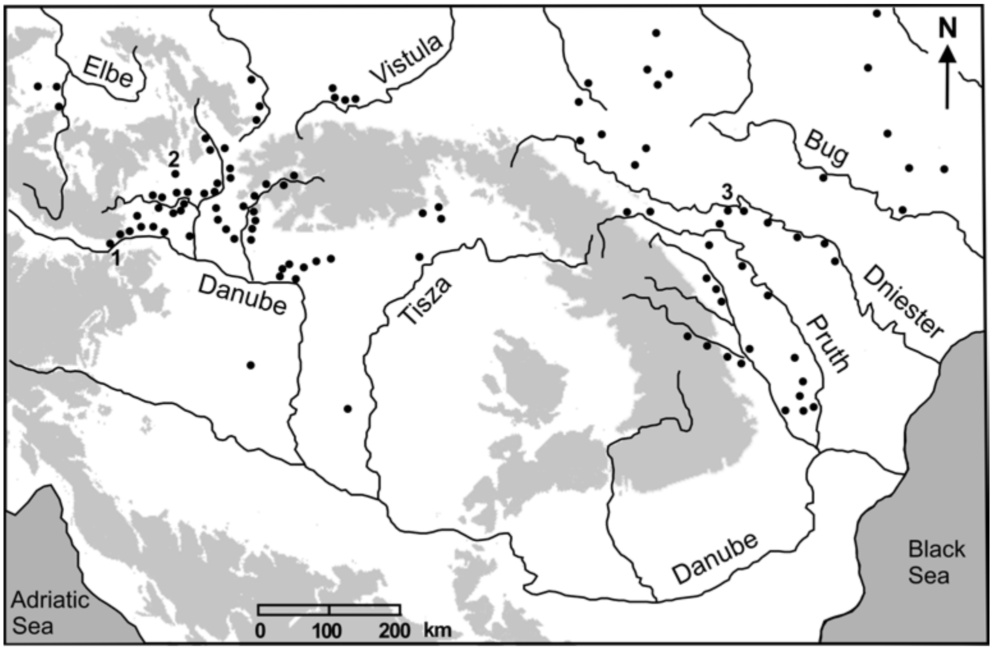

Figure 1 Location of the sites: 1–Willendorf II (Austria); 2–Vedrovice V (Moravia); 3–Molodova V (western Ukraine).

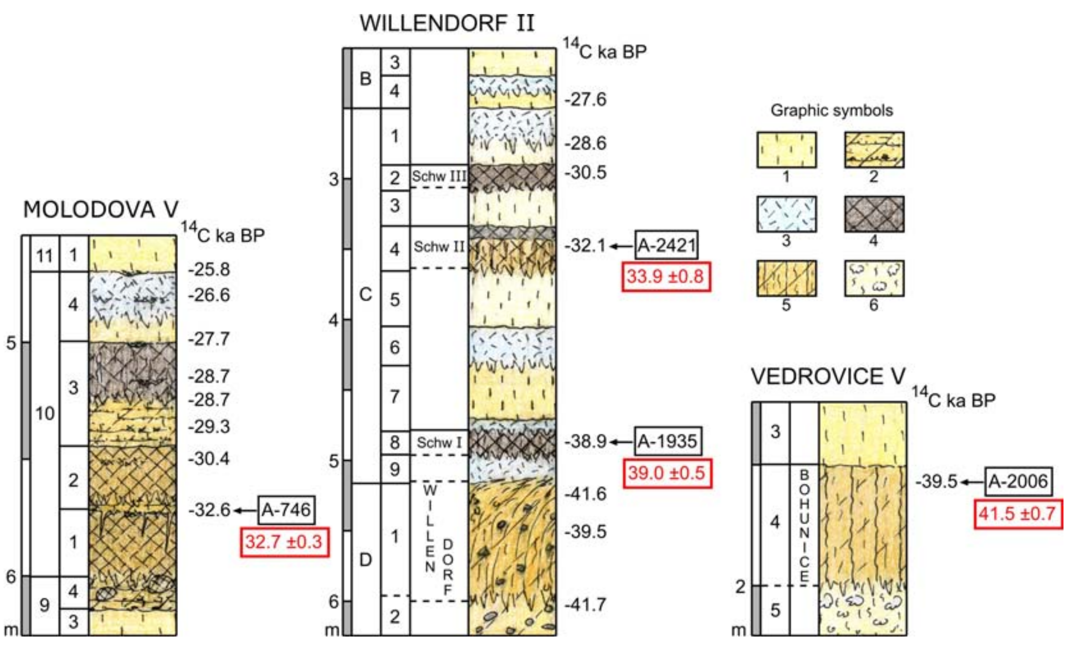

Figure 2 Position of the cross-dated charcoal samples within the local stratigraphic successions. Published previously accepted dates in black; new ABOx dates in red. ^{14}C ages in ka BP. Graphic symbols: 1–loess; 2–loam; 3–tundra gley; 4–humic horizon; 5–bioturbated B horizon; 6–calcic concretions.

Two charcoal samples were collected in direct association with archaeological occurrences. The first sample (A-2421, Willendorf II, unit C4, Aurignacian archaeological horizon 4) is a large piece of charcoal collected by PH on a vertical section during the Willendorf 2007 excavation. The second sample (A-2006, Vedrovice V) comes from a cluster related to a large charcoal accumulation (fireplace?) from the Szeletian layer in squares 11/N and 11/0 (Valoch 1993). Two other samples come from large charcoal clusters without any trace of human activity. Such material has been interpreted as the result of wildfires (Damblon and Haesaerts 2002; Haesaerts et al. 2003). The first sample (A-746, Molodova V, top of subunit 10-1) was collected by PH on a vertical section during the 1998 field campaign. The second sample (A-1935) was collected at Willendorf by PH inside the humic horizon C8 on a vertical section during the 2006 excavation.

Handling in the Brussels Charcoal Laboratory

In order to achieve the best dating possible, handling of loess samples with charcoal in the laboratory followed the procedure below (see also Damblon et al. 1996; Damblon and Haesaerts 2002; Haesaerts et al. 2010). The loess samples were first dried in an oven at 50 °C for 1 day, resulting in hardening of the charcoal. The bulk material was then gently dispersed in water and then sieved (1.0, 0.5, and 0.25 mm) in successive water baths. A first examination of charcoal under binocular magnification enabled discarding pollutant rootlets and allowed a primary selection of charcoal fragments. Given the mineralization of the charcoal material by silicates and carbonates, a sequence of treatment with HF and HCl was necessary. After washing with distilled water, a second selection of charcoal fragments was performed, and the selected cleaned charcoal was oven-dried. This made taxonomic identification and separation of the taxa easier as well as the last careful selection of the best (mid-sized), cleaned charcoal fragments. Any trace of rootlet or other potential pollutant detected in the charcoal fragments led them to being discarded from the selection. Only conifer material (essentially *Picea/Larix*) was selected for dating in order to ensure taxonomic homogeneity of the material. The material was conserved in glass bottles and labeled in our A- sample preparation series.

Strategy of Dating

Our aim being to compare ^{14}C results from 2 laboratories (Groningen and Oxford) and from 2 pretreatment procedures (ABA and ABOx), it was necessary to submit highly homogenized subsamples in order to control the reproducibility of the results. Therefore, 300 mg of cleaned charcoal were selected for each sample. Each charcoal selection was gently crushed and homogenized. Finally, the homogenized charcoal sample was split into 3 subsamples: ~75 mg for ABA pretreatment in Groningen; ~75 mg for ABA in Oxford; and ~150 mg for ABOx in Oxford. For each subsample, the whole homogenized material (75 mg or 150 mg) has been used to dating, following the specific procedure in each ^{14}C laboratory (see van der Plicht et al. 2000; Brock and Higham 2009). No mention of the origin nor estimated age of the submitted samples was made to the Groningen and Oxford laboratories.

RESULTS AND DISCUSSION

All of the ^{14}C dates are presented in Table 1 in ^{14}C yr BP with 1σ measurement uncertainty and in calibrated yr BP with 1σ and 2σ uncertainty, using OxCal v 4.1.4 (Bronk Ramsey 2009) and the IntCal09 data (Reimer et al. 2009) for calibration. For each site, the results of previous dating on non-homogenized charcoal fragments from the same samples (cf. A- number) are given first, most of which are unpublished. The results of cross-dating on homogenized charcoal material are also given.

Table 1 Uncalibrated and calibrated ^{14}C series related to the cross-dating ABA/ABOx.

Date nr	Date uncal BP	Pretreatment	Date cal BP 2σ (1σ)
Molodova V, subunit 10-1, charcoal cluster			
Sample A-746, previous dates on different fragments, non-homogenized			
GrA-24714	32,590 +580/–540	ABA	38,813–36,295 (37,991–36,564)
OxA-18857	32,200 ± 190	ABA	37,199–36,334 (36,835–36,511)
Sample A-746, cross-dating on several fragments, homogenized			
GrA-44957	31,690 +240/–220	ABA	36,701–35,330 (36,578–35,615)
OxA-22291	30,920 ± 230	ABA	36,285–34,903 (36,188–35,025)
OxA-23519	32,720 ± 310	ABOx	38,431–36,622 (37,682–36,719)
Willendorf II, stratigraphic unit C4 (top), 1 single fragment			
Sample A-2421, date on the non-homogenized large fragment			
GrA-45804	32,360 +210/–190	ABA	37,496–36469 (37,015–36,572)
Sample A-2421, cross-dating on the same large fragment, homogenized			
GrA-45011	32,790 +210/–200	ABA	38,383–36706 (37,633–36,835)
OxA-22294	31,750 ± 260	ABA	36,775–35314 (36,620–35,819)
OxA-23562	33,850 ± 800	ABOx	40,770–36820 (39,927–37,583)
Willendorf II, stratigraphic unit C8, charcoal cluster			
Sample A-1935, previous dates on different fragments, non-homogenized			
GrA-44894	37,420 +300/–270	ABA	42,664–41,693 (42,392–41,912)
GrA-35409	37,910 +440/–380	ABA	43,150–41,898 (42,791–42,166)
Sample A-1935, cross-dating on several fragments, homogenized			
GrA-45012	38,790 +400/–350	ABA	43,892–42,430 (43,398–42,707)
OxA-22295	36,500 ± 450	ABA	42,258–40,828 (41,893–41,213)
OxA-23520	39,000 ± 500	ABOx	44,175–42,503 (43,683–42,804)
Vedrovice V, upper part of the Bohunice Soil, charcoal cluster			
Sample A-2006, previous dates on different fragments, non-homogenized			
GrA-44892	40,190 +390/–340	ABA	44,815–43,446 (44,519–43,855)
GrA-35395	40,670 +550/–460	ABA	45,404–43,733 (44,953–44,160)
OxA-17753	37,540 ± 300	ABA	42,739–41,745 (42,471–41,975)
OxA-17735	37,640 ± 300	ABA	42,801–41,807 (42,537–42,037)
Sample A-2006: cross-dating on several fragments, homogenized			
GrA-44961	39,810 ± 550/440	ABA	44,732–43,085 (44,295–43,455)
OxA-22292	38,600 ± 550	ABA	43,983–42,156 (43,375–42,488)
OxA-22293	39,100 ± 650	ABA	44,421–42,405 (43,901–42,835)
OxA-23518	41,500 ± 700	ABOx	46,166–44,130 (45,546–44,551)

Figure 3 shows the distribution of the uncalibrated dates and Figure 4, the calibrated dates. For each site and stratigraphic unit, Figures 3 and 4 show 2 sets of dates: on the left, the dates for the non-homogenized subsamples, and on the right, the dates for the homogenized subsamples.

When considering the distribution through time of the 4 sets of cross-dating, it appears that the Oxford ABOx dates and Groningen ABA dates are systematically older than the ABA dates produced in Oxford (Figure 3). The ABOx dates are most often older than the Groningen ABA dates, with a degree of overlap between both sets of dates in the time window 32–39 ka BP for the 2σ ranges. In particular, the ABOx date 39,000 ± 500 BP (OxA-23520), obtained for the stratigraphic unit C8 at Willendorf II, agrees well with the ABA date 38,790 +400/–350 BP (GrA-45012) and the previous ABA date 38,880 ± 1500 (GrN-17805, Haesaerts et al. 1996). In contrast, for sample A-2006 of Vedrovice V, which is older than 40 ka BP, the ABOx date is at least 1 millennium older than the ABA date of Groningen. On the other hand, the ABA dates previously obtained in Groningen on non-homogenized material show a consistent distribution with regard to the 4 sets of cross-dates,

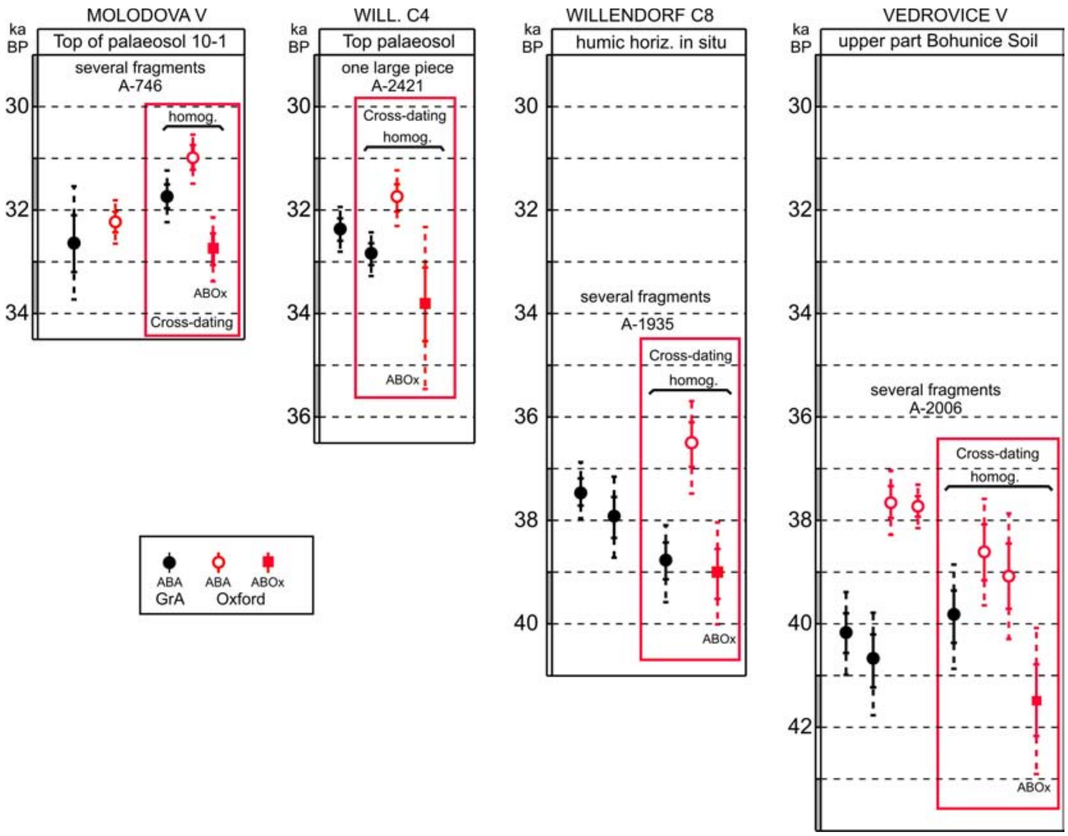

Figure 3 Chronological distribution of the uncalibrated ^{14}C ages (ka BP) obtained for Molodova V, Willendorf II, and Vedrovice V.

within a time window of about 1 millennium. The distribution of the ages when calibrated (Figure 4) leads to the same conclusion, although the overlapping of the ages appears to be somehow more pronounced. This reinforces the degree of accuracy of these dates.

The reliability of the dates is evaluated by regarding the position of the dates in the general chronology of each stratigraphic sequence, notably of Molodova V and Willendorf II (Figure 2). Considering that ABOx pretreatment leads to cleaner charcoal samples and that the ABOx dates appear in good agreement with the general chronology of the sequences, we conclude that ABOx pretreatment provides the most coherent and reliable results. However, this does not rule out accurate results for ABA pretreatment on good charcoal material as exemplified by the Groningen laboratory for ^{14}C ages younger than 39 ka BP.

Finally, crushing and homogenizing charcoal samples is the best method to produce comparable ^{14}C results from different types of pretreatments and laboratories. In the present study, cross-dating of 2 homogenized charcoal subsamples combining Groningen ABA and Oxford ABOx methods seems to be the most efficient way to ensure the accuracy of the obtained ages.

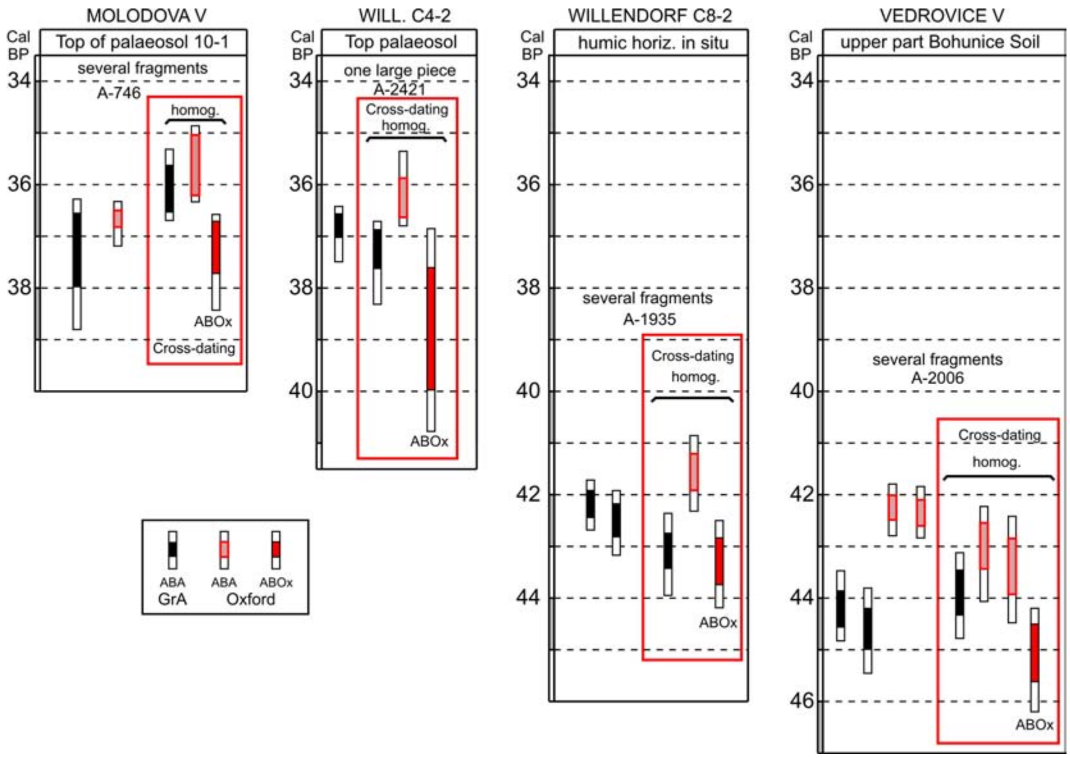

Figure 4 Chronological distribution of the calibrated ^{14}C ages (OxCal v 4.1.4 and the calibration curve IntCal09) obtained for Molodova V, Willendorf II, and Vedrovice V.

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