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A laboratory inter-comparison of AMS ^{14}C dating of bones of the Miesenheim IV elk (Rhineland, Germany) and its implications for the date of the Laacher See eruption

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ABSTRACT

We conducted inter-laboratory AMS ^{14}C dating of bones of the Miesenheim IV elk (Rhineland, Germany), buried under Laacher See tephra dated to ca. 11,060 BP (13,000 cal BP). The weighted mean of the new dates, which range from 10,920 to 11,270 BP, is 11,092 ± 19 BP. The consistent results from five AMS laboratories are important in two respects. First, they demonstrate that collagen processed by traditional methods can yield accurate ages; the newly obtained ^{14}C dates are in accord with previous hydroxyproline ^{14}C value generated at the Oxford AMS laboratory within the first round of inter-comparison (Fiedel et al., 2013). The results of the first inter-comparison are clearly flawed, except for hydroxyproline ^{14}C date (see Fiedel et al., 2013), and must be affected by the waxy/dark, presumably humic/organic-based contaminant. Second, they provide a new suite of radiocarbon dates for the Laacher See volcanic eruption, a crucial anchor point for Late Glacial chronology in central Europe.

1. Introduction

In radiocarbon (^{14}C) research, dating of split samples by multiple laboratories is performed regularly at both large (e.g. Scott et al., 2018) and smaller scales (e.g., Huels et al., 2017). Among the materials used in these tests is collagen extracted from animal or human bones. In many exercises, parallel ^{14}C dating of bones in different laboratories has produced essentially the same results (e.g., Ovodov et al., 2011; Major et al., 2013). Nevertheless, in some cases the outcome has been unsatisfactory, with relatively large disparities. Recent examples include dating of the Sungir human burials (Nalawade-Chavan et al., 2014; Kuzmin et al., 2014); Kennewick Man (Taylor et al., 2001); and the horse and camel skeletons from Wally's Beach (Kooyman et al., 2006; Waters et al., 2015). In these and many other cases, it is difficult or even impossible to judge which of the disparate ^{14}C dates are reliable because the true age of the sample (i.e., established by an independent dating method) is unknown.

However, in some very rare situations the true age of the sampled bone (or at least one of the age limits, maximal [*terminus post quem*] or minimal [*terminus ante quem*]) is securely known. Fiedel and Kuzmin (2010) suggested a test using bones of an elk (*Alces alces*), or moose in American terms, from the Miesenheim IV site in the Rhineland-Palatinate Province of Germany (Fig. 1), which were originally ^{14}C-dated at the Oxford Radiocarbon Accelerator Unit (ORAU) (Hedges et al., 1993).

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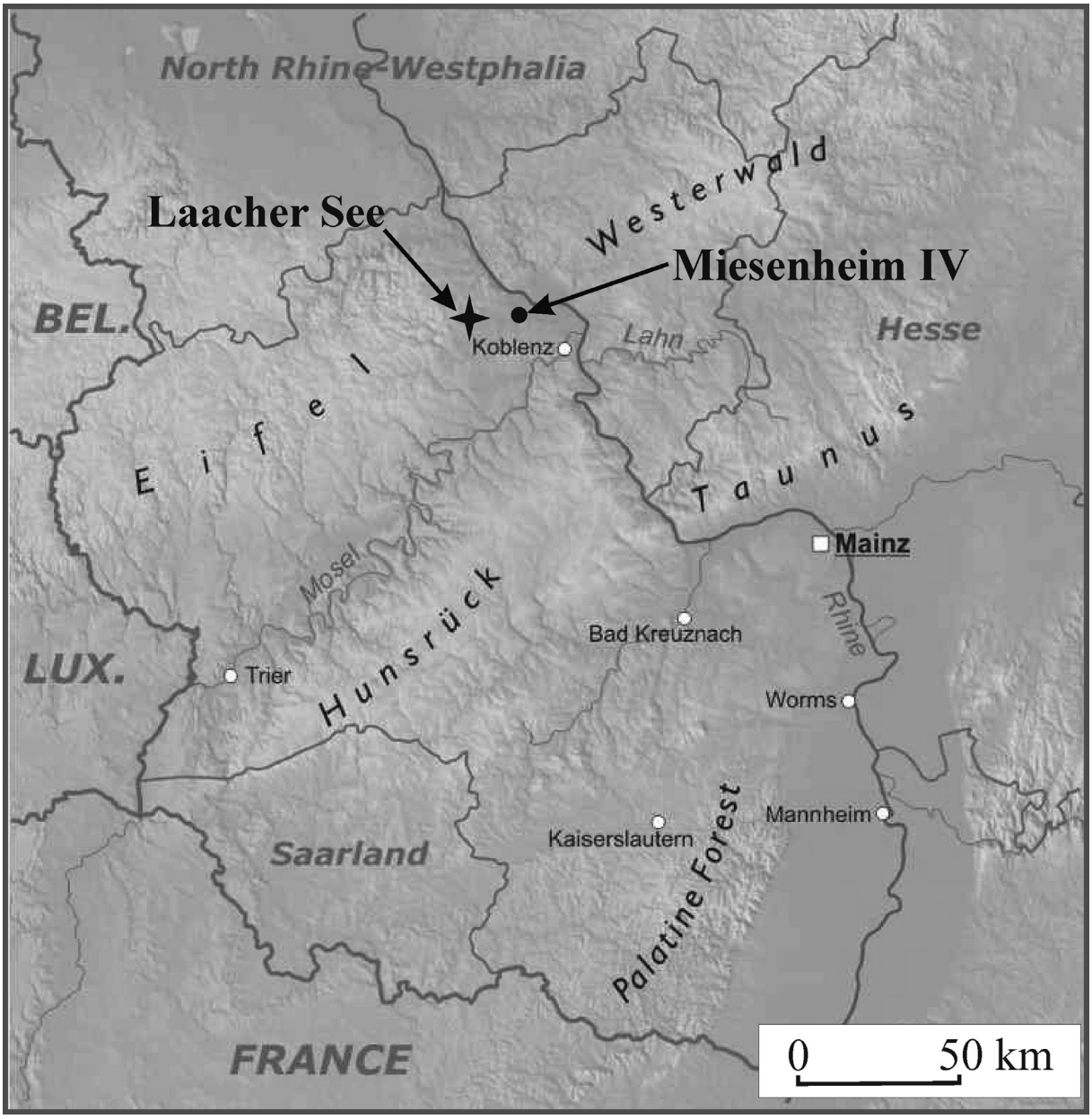

Fig. 1. The positions of the Miesenheim IV locality and Laacher See eruption center in Rhineland-Palatinate (Germany) (after Fiedel et al., 2013; modified).

The elk's skeleton had been covered, soon after the animal's death, by Laacher See tephra (LST) that originated from the eruption of a nearby volcano, now a caldera in the Eifel region. The ^{14}C age of the eruption is well established as ca. 11,060 BP (Baales et al., 2002; Kromer et al., 2004), which after calibration using the IntCal13 dataset (Reimer et al., 2013) corresponds to 12,850–13,050 cal BP. Given this precise *terminus ante quem*, the elk bones are ideal for an inter-laboratory test of the utility of various pretreatment methods for accurate ^{14}C dating of bone collagen.

The first cross-dating was arranged by M. Street (the site's excavator), Y.V. Kuzmin and T.F.G. Higham in 2012 using the original Miesenheim IV elk bone samples stored at ORAU; the results obtained by the Groningen, Kiel, University of California–Irvine, and Oxford laboratories were published the following year (Fiedel et al., 2013). Despite our expectations, the results were not straightforward, and ambiguities remained concerning the integrity of the sub-samples dated and possible contamination of the elk bones prior to dating (for details, see Fiedel et al., 2013:1450–2). This is why we decided to conduct a new inter-comparison test among ^{14}C laboratories, this time with strict recording of C:N ratios, collagen yields, and the stable isotope (δ^{13}C and δ^{15}N) values of the extracted collagen. For this study, we took new samples of exactly the same Miesenheim IV elk bone elements which had been previously dated (see Hedges et al., 1993). We were aware that, in the interim, these remaining specimens had been treated with a conservant (see below).

The Miesenheim IV elk was buried under a thick deposit of tephra from the eruption of the Laacher See volcano. Based upon both varved lake sediments and tree rings in northern Europe, the eruption is dated to about 200 years before the onset of the Younger Dryas cold period. Calendric dating of the eruption has been elusive, with credible estimates ranging from 12,840 to 13,050 cal BP. ^{14}C dating also has been problematic. Trees killed by the ashfall dated the eruption to 11,310 ± 50 BP (Zolitschka, 1990). Dating of plant macrofossils and wood associated with the ash in varved sediments from three lakes yielded an age estimate of 11,230 ± 40 BP (Hajdas et al., 1995). Subsequent dating of the outermost growth rings of killed trees yielded

a date of ca. 11,060 BP (Baales et al., 2002; Kromer et al., 2004), although distinct clusters of both older (ca. 11,200 BP) and younger (ca. 10,800 BP) ages for short-lived samples were recognized. The same age is shown by a ^{14}C date of 11,040 ± 60 BP on vegetation that lay just below the tephra at Miesenheim IV (Bittmann, 2007).

After the elk was excavated in 1991, M. Street submitted bone samples in 1992 to the ORAU Laboratory in Oxford, which AMS ^{14}C-dated them to ca. 11,200 BP (the average of three ^{14}C dates of 11,190 ± 90 (OxA-3584), 11,190 ± 100 (OxA-3586), and 11,310 ± 95 BP (OxA-3585) (Hedges et al., 1993:149–150). Green moss attached to the antler was dated to 11,170 ± 100 BP (OxA-3587). As Street clearly recalls, no preservatives were applied to the bones before submission.

The remnants have been stored at Oxford since 1993, and they were used for the first Miesenheim IV elk inter-comparison (Fiedel et al., 2013). The ^{14}C dates obtained by the Groningen, Kiel, Oxford (ultra-filtered collagen; see Bronk Ramsey et al., 2004), and University of California–Irvine (mostly ultra-filtered collagen) laboratories were all too young, in the range of ca. 10,010–10,975 BP. Only Oxford's date of 11,100 ± 45 BP, based on the hydroxyproline fraction, came within one standard deviation of the expected age of ca. 11,060 BP, or ca. 12,970 cal BP according to the IntCal13 data set (Reimer et al., 2013).

To explain why so many dates (in total, 29) were undoubtedly too young, we concluded that it was most likely that the bone had been affected *in situ* by pervasive post-depositional contamination by more recent humic substances (Fiedel et al., 2013). Although very little water has percolated through the dense tephra at the Miesenheim site cluster, lateral movement of groundwater below the tephra has been observed. At the Miesenheim II locality, pumice removal revealed water running downslope, which immediately formed active erosion channels. The Miesenheim IV locale was waterlogged below the tephra, which accounts for the excellent preservation of bone and vegetal remains. This water is certainly not a closed system and might be the source of younger humic contaminants. When excavated, the bones were very dark and stained. The skeleton lay in a black peaty mud that may have contained humic acids. This could also account for the waxy, shiny appearance of the bone.

These 2013 results appeared to validate the ORAU laboratory's recent use of the isolated hydroxyproline fraction of collagen for ^{14}C dating of late Pleistocene bone samples (McCullagh et al., 2010; Marom et al., 2012; Nalawade-Chavan et al., 2014; Devièse et al., 2017). However, the research question remained: could collagen processed by conventional gelatinization methods also yield accurate ages? To address this issue, we undertook another round of ^{14}C dating of the same bone.

2. Material and methods

2.1. General information on the Miesenheim IV elk sample

In June 2015, M. Street and Y.V. Kuzmin took new samples from the two pieces of elk rib designated as 91/110–1 and 91/111–3 (Fig. 2), which have been stored at the MONREPOS Archaeological Research Center and Museum for Human Behavioral Evolution since the end of excavations at Miesenheim in 1991. These are fragments of the same specimens originally submitted to the ORAU laboratory (Hedges et al., 1993) but they have since been consolidated with polyvinyl acetate (PVA)-ethanol. Completely new samples from the identical elements of the skeleton, each of which was processed separately, could potentially indicate if suspected organic contaminants were uniformly distributed or, instead, concentrated unevenly within the bone. The newly sampled bones are light brown in color, with scattered small black spots (Fig. 2, c) which most probably are remains of newly formed iron and/or manganese aggregates, and less likely of organic matter (humic acids and other compounds). No traces of waxy matter are visible on the surface of either sample (cf., Fiedel et al., 2013: 1448, Fig. 4).

The Miesenheim IV elk (moose) was a young bull carrying antlers. Its death must have occurred at some time between late November and the end of March, by which time most elk have shed their antlers. Seasonal indicators place the timing of the Laacher See eruption at the end of May (Baales et al., 2002). Therefore, at least two months probably elapsed between the elk's death and the eruption. The distribution of the excavated bones suggests that the elk had been killed or scavenged by wolves during the winter, the remains afterwards lying upon ice and sinking into the underlying pond with the spring thaw (Street, 1995). The bones lay in the pond for some indeterminate period, during which they were overgrown by water plants. It is therefore possible that several years might have intervened between the deposition of the carcass and of the overlying tephra.

As we cannot determine exactly how long the bones and antlers lay submerged after the elk's death, there is no exact *terminus post quem*, but we do have a precise *terminus ante quem* (ca. 11,060 BP) for the dated bones – a rare situation in the late Pleistocene. This allows us to judge the accuracy of the results of diverse bone-dating procedures. It has long been recognized that ^{14}C dates on collagen may underestimate the true age (e.g., Higham, 2011). This is generally attributed to the persistence of younger humic contaminants, which several laboratories now regularly attempt to remove by ultrafiltration, an additional purification step in the extraction of collagen. In the case of the elk, we know that any date younger than 11,060 BP must be too low.

The new dates presented here for the Miesenheim IV elk were obtained from five AMS ^{14}C dating laboratories: the Royal Institute for Cultural Heritage (laboratory code RICH), Brussels, Belgium; University of Groningen (GrA), Groningen, the Netherlands; University of Arizona (AA), Tucson, Arizona, USA; Queen's University Belfast (UBA), Belfast, UK; and the Center of Cenozoic Geochronology (NSK/UGAMS), Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia. The NSK laboratory prepared the bone collagen, and AMS dating was performed at the University of Georgia, Athens, Georgia, USA.

2.2. Collagen extraction protocols

2.2.1. Royal institute for cultural heritage

Collagen extraction was performed following Longin's (1971) method. A 1% NaOH-wash was introduced for 15 min between the demineralization and hydrolization steps. First, 1 g of bone (in pieces) was demineralized in 10 ml 8% HCl for 20 min, and rinsed with MilliQ^{TM}-water. After that, it was immersed for 15 min in 1% NaOH, and again rinsed with MilliQ^{TM}-water. Adding 1% HCl for neutralization, it was washed with MilliQ^{TM}-water. For all the steps mentioned above, Ezee-filters were used. Gelatinization of the extract was done in water (pH 3), at 90 °C for 12 h. The resulting gelatin was filtered with a Millipore 7 μm glass filter, and freeze-dried. All collagen samples were combusted, transformed into graphite (Van Strydonck and van der Borg, 1990–1), and AMS ^{14}C-dated (Boudin et al., 2015). Each subsample, 91/110–1 and 91/111–3, was processed and measured twice (Table 1). The bone background value is 0.5 ± 0.02 pMC (percent of modern carbon).

2.2.2. University of Groningen

As in the previous study (see Fiedel et al., 2013), the sample underwent standard chemical cleaning (ABA; Mook and Streurman, 1983) and collagen extraction procedure as originally established by Longin (1971). The steps include applying a 4% HCl solution for a 1 day at room temperature, a 1% NaOH solution for 1 h, and finally 1% HCl for 30 min. Between steps the material was rinsed with decarbonized water. Boiled decarbonized water was added to the soft sample material with a few drops of 37% HCl solution. The sample was put in an oven for 1 night at 85 °C, dissolving the collagen. The solution was filtered with a 50 μm filter, to remove contaminants not removed by the previous steps. The collagen solution was dried in an oven at 85 °C for one

Fig. 2. A view of the Miesenheim IV samples chosen for cross-dating in 2015: a – 91/110–1; b – 91/11–3; c – enlarged photo of the tip of 91/11-3 sample. Scale for "a–b" is in centimeters; and for "c" in millimeters.

night. The collagen was combusted by an Elemental Analyzer (Isocube) coupled to a Stable Isotope Mass Spectrometer (Isoprime). The latter provides $\delta^{13}C$ and $\delta^{15}N$ values for the gases CO_2 and N_2, respectively, as well as the C:N ratio. A fraction of the CO_2 was trapped cryogenically and subsequently reduced to graphite using H_2 gas and Fe powder as catalyst (Aerts-Bijma et al., 2001). The $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios in the graphite were measured by AMS (a 2.5 MV tandetron; van der Plicht et al., 2000). The measured data were converted to conventional ^{14}C ages in BP, which were corrected for isotopic fractionation using the stable isotope ratio ($\delta^{13}C$) of the AMS (Mook and van der Plicht, 1999). The bone background is better than 45,000 BP (< 0.3 pMC).

2.2.3. University of Arizona

Collagen was extracted using an automated flow cell apparatus, following a modified Longin's (1971) method. Sub-samples were mechanically cleaned of surface contaminants, and afterwards ground using a mortar and pestle. The next step was demineralization in 0.5 M HCl; after that, the resulting matter was rinsed with water and treated with 0.1 M NaOH to remove humics and base-soluble contaminants. After rinsing with 0.1 M HCl and water, it was solubilized in 10^{-3} M HCl at 75 °C for 20 h, and freeze-dried. Acid-Base-Acid (ABA) collagen was prepared from each bone sample; ultrafiltered (UF) collagen was produced by rehydrating a sub-sample of ABA collagen and carrying out the additional ultrafiltration step to produce UF collagen. The Sartorius Vivaspin 20 ml devices were used for UF, with 30 kD cutoff. The devices were pre-washed: 3 X centrifugation with 20 ml deionized water, with subsequent 1 h sonication in water at room temperature, followed by another 3 X centrifugation with 20 ml of water, just before use. The resulting collagen was combusted with CuO at > 800 °C, reduced to graphite, and AMS ^{14}C-dated (see Ovodov et al., 2011: 3; Zazula et al., 2014).

The calculations for our bone blank are based upon periodic preparation of ABA collagen from two ^{14}C-dead bone standards used at the Arizona Laboratory: the Lemon Mine *Bos primigenius* bone from a permafrost context near Fairbanks, Alaska; and a mastodon bone from Snowmass, Colorado. One ABA collagen from each of these bones is prepared for approximately every 30 unknown bones processed at the laboratory. The ABA collagen bone blank is recalculated periodically from an average of the previous three years' bone blank measurements. The current blank value is 1.0 ± 0.3 pMC, or 37,000 ± 2400 BP, for

Table 1
Results of second inter-comparison dating of the Miesenheim IV elk bones.

Laboratory	Sample	Collagen yield, %	C:N ratio	$\delta^{13}C$, ‰	$\delta^{15}N$, ‰	^{14}C age, BP	Lab Code	Calendar age, cal BP (± 1 sigma)	Calendar age, cal BP (± 2 sigma)
Brussels	91/110-1	5.8	3.2	−20.1	2.4	11,025 ± 48	RICH-22120.1.1	12,820–12,970	12,750–13,030
		5.8	3.3	−19.9	2.5	11,060 ± 40	RICH-22120.2.1	12,850–13,000	12,800–13,050
	91/111-3	7.9	3.2	−20.1	2.4	11,050 ± 49	RICH-22121.1.1	12,840–12,990	12,780–13,060
		7.9	3.3	−20.5	2.4	11,100 ± 45	RICH-22121.2.1	12,920–13,060	12,830–13,080
Groningen	91/110-1	6.0	3.3	−20.2	2.5	11,030 ± 50	GrA-64379	12,820–12,980	12,750–13,030
	91/111-3	6.0	3.3	−20.2	2.7	11,190 ± 50	GrA-64380	13,020–13,110	12,930–13,160
Arizona	91/110-1	9.9	3.4	−20.0	2.7	11,265 ± 67	AA-106555	13,070–13,190	13,030–13,270
		n.d.[a]	3.4	−20.0	3.2	11,145 ± 65	AA-106555-UF[b]	12,940–13,090	12,820–13,120
	91/111-3	5.3	3.3	−20.0	2.7	11,270 ± 69	AA-106554	13,070–13,190	13,030–13,280
		n.d.[a]	3.4	−20.0	3.5	11,140 ± 66	AA-106554-UF[b]	12,930–13,090	12,820–13,120
Belfast	91/110-1	10.1	3.2	−20.1	2.4	11,240 ± 62	UBA-30011[b]	13,060–13,150	13,000–13,250
	91/111-3	11.7	3.2	−20.2	2.4	11,080 ± 63	UBA-30012[b]	12,860–13,040	12,790–13,080
Novosibirsk	91/110-1	8.5	3.2	−20.2	2.6	11,080 ± 33	NSK-1352/UGAMS-23137	12,890–13,030	12,820–13,060
	91/111-3	6.5	3.4	−19.8	2.9	10,920 ± 31	NSK-1618/UGAMS-27119	12,730–12,790	12,710–12,830

[a] n.d. – not determined.
[b] Ultrafiltered collagen.

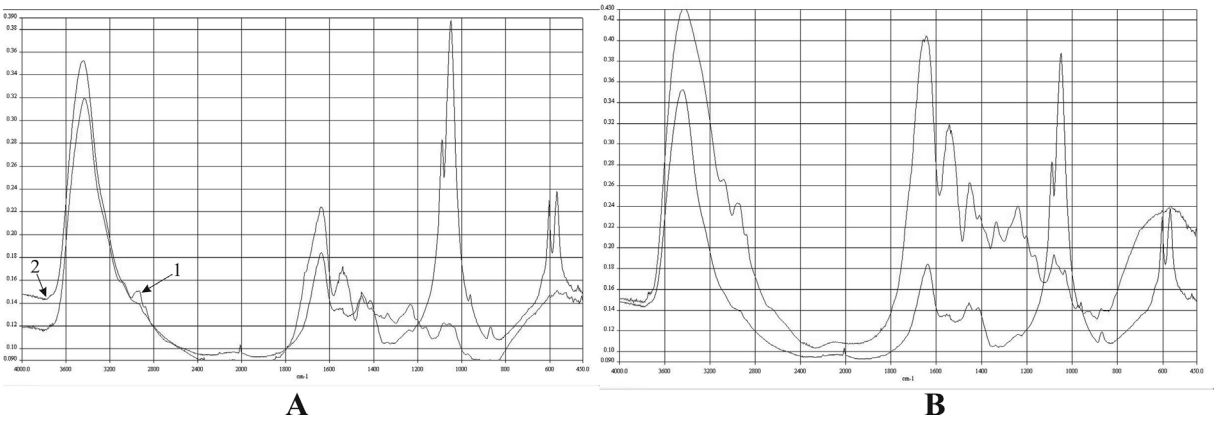

Fig. 3. The FTIR spectra of the UBA-30011 sample. A: collagen (No. 1); bone before pretreatment (No. 2); B: a second aliquot of the same sample with the bone spectra included for comparison.

ABA collagen. The blank for UF collagen is determined separately every time a new lot of ultrafitration devices is purchased by the laboratory. This is accomplished by the preparation of UF collagen from the ^{14}C-dead bone standards. This amounts to approximately one for every 35 unknown UF collagen measurements. Significant variability in UF collagen blank between lots of ultrafilters has been encountered, and so the UF blank value is not time averaged but utilized lot-specifically. At the time of the Miesenheim elk rib dating, the UF collagen blank was the same as the ABA collagen blank, and so no adjustment to the calculations of the respective ^{14}C dates was required.

2.2.4. Queen's University Belfast

To remove PVA or other consolidants, samples were treated with a solvent extraction in a Soxhlet distillation apparatus using a minimum of two cycles of tetrahydrofuran, chloroform, petroleum spirit, acetone, methanol and lastly deionized water, similar to Bruhn et al. (2001). The bone collagen extraction follows the method of Brock et al. (2010), and the Vivaspin™ filter cleaning method introduced by Bronk Ramsey et al. (2004). Bone samples of 1.0–1.1 g were crushed in a stainless steel percussion mortar into small fragments (1–3 mm or smaller). They were then treated sequentially with 2% HCl (three or four rinses over approximately 18 h or until no further reaction was seen), 0.1 M NaOH (15–30 min) and then 2% HCl (15–20 min) with three rinses of MilliQ™ water in between each step. The crude collagen was gelatinized in pH 2–3 solution at 70 °C for 15 h. The resultant gelatin solution was then filtered using "pre-baked" 7 μ and 12 μ glass fibre filters on a ceramic filter holder. The filtrate was transferred into a pre-cleaned ultrafilter (Vivaspin™ Turbo 15–30 kD MWCO) and centrifuged until 0.5–1.0 ml of the > 30 kD gelatin fraction remained. This gelatin was then removed from the ultrafilter with borosilicate Pasteur pipettes and ultrapure water before being freeze-dried. The dried samples were weighed into pre-combusted quartz tubes with an excess of copper oxide (CuO), sealed under vacuum and combusted to obtain carbon dioxide (CO_2) gas. The CO_2 was converted to graphite on an iron catalyst using the zinc reduction method (Slota et al., 1987). The $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios were measured by AMS. The sample $^{14}C/^{12}C$ ratio was background-corrected by subtracting the $^{14}C/^{12}C$ ratio (equivalent to 49,635 BP) measured on collagen extracted from the Latton mammoth bone (Lewis et al., 2006), prepared and analyzed in the same batch and normalized to the HOXII standard (SRM 4990C; National Institute of Standards and Technology). The ^{14}C ages were corrected for isotope fractionation using the AMS-measured $\delta^{13}C$ which accounts for both natural and machine fractionation. The ^{14}C age and standard deviation were calculated using the Libby half-life of 5568 years, following the methods of Stuiver and Polach (1977).

2.2.5. Center of Cenozoic Geochronology

Samples were milled to the size of 200–300 μm, and were treated with chromophore to remove lipids. After that, the material was rinsed with methanol three to four times. The resulting powder was dried, and treated with a 0.5 M solution of HCl overnight. After that, humic acids were removed with 0.1 M solution of NaOH (for 30 min), and then the powder was treated by 0.5 M HCl for 1 h to remove the admixture of atmospheric CO_2. After each treatment, the powder was washed with mQ water 3–4 times. Gelatinization was performed at pH 3 (temperature of 70 °C, 24 h). The gelatin obtained was freeze-dried and converted to graphite. The C:N ratios were measured by a EuroEA 3000 HT elemental analyzer. The bone background value for the UGAMS Lab where the AMS ^{14}C measurements were performed is 41,120 BP, 0.6 ± 0.015 pMC.

2.3. Fourier Transform Infra-Red spectra of the Miesenheim IV elk sample

In view of the ambiguous results of the previous cross-dating experiment with the Miesenheim IV elk (Fiedel et al., 2013), the laboratories undertaking this test were alert to the existence of exogenous contamination. After sending the first bone sample to Oxford in 1992, Street had conserved the skeleton by immersing the bones in PVA *in vacuo*. The PVA treatment introduced old carbon that may not be completely removed from the sample. A recent study indicates the persistence of PVA despite several decontamination procedures (Brock et al., 2017).

At Queen's University Belfast lab, Fourier Transform Infra-Red (FTIR) spectra were determined for the bone and two aliquots of the collagen extracted from each of the two elk bone samples (Figs. 3 and 4). In the figures, the lines labeled with Nos. 1 represent the collagen, and lines with Nos. 2 are the bone before collagen pretreatment. The PVA should show up as a peak around 1730 cm^{-1}, with another smaller peak around 1230 cm^{-1} (cf., Brock et al., 2017). However, pure collagen also has a peak around 1240 cm^{-1}, so only the 1730 cm^{-1} peak is likely to be diagnostic. In fact, there is a small shoulder around 1730 cm^{-1} in one of the two collagen spectra of UBA-30011 but none in the spectra of UBA-30012. Neither of the bone spectra has PVA above the detection limit. Brock et al. (2017) caution that FTIR tests for PVA may not be definitive. In any case, it appears that the effect of exogenous old carbon from the PVA is not significant in UBA-30012. For UBA-30011 there was apparently some PVA that was not removed which showed up in one of the two aliquots. The detection limit and the effect of the PVA on the date of UBA-30011 are discussed below.

At the Royal Institute for Cultural Heritage, FTIR spectra also were determined for the collagen extracted from the two elk bone samples. The sample was pressed between the two diamond windows of a compression cell (SpectraTech®) in order to obtain a thin transparent

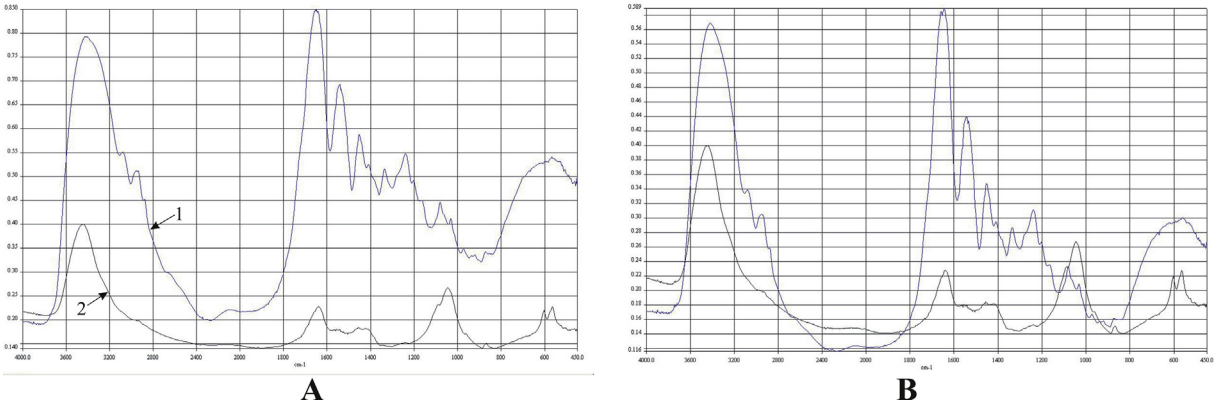

Fig. 4. The FTIR spectra of the UBA-30012 sample. A: collagen (No. 1); bone before pretreatment (No. 2); B: a second aliquot of the same sample with the bone spectra included for comparison.

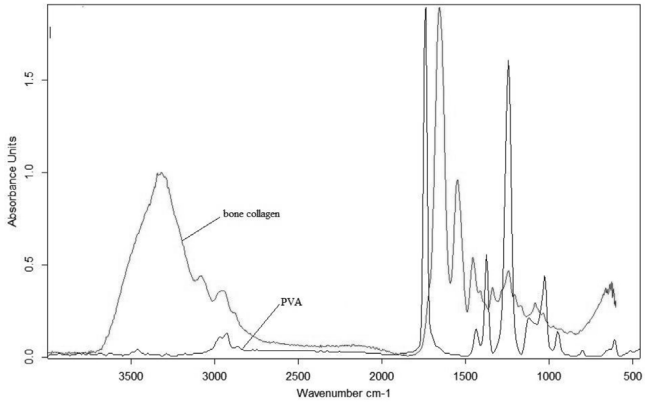

Fig. 5. The FTIR spectra of bone collagen extracted from RICH-22121.1.1 and RICH-22121.1.2 samples and the PVA glue.

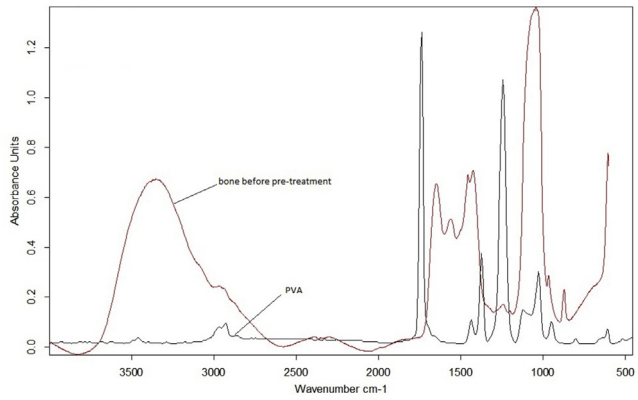

Fig. 6. The FTIR spectra of untreated bone and PVA from RICH-22121.1.1 and RICH-22121.1.2 samples.

layer. The spectra were then recorded in transmission mode using a Vertex 70 spectrometer equipped with a Hyperion 3000 microscope (spectrometer and microscope from Bruker®), by accumulation of 128 scans with a resolution of 4 cm^{-1}. In Figs. 5 and 6, the spectra of the untreated bone, extracted collagen, and PVA are shown. It is clear that no PVA, or perhaps very little (but under the detection limit) is present in the untreated bone and bone collagen. Besides IR, the untreated bones were inspected by microscopy, and no traces of PVA were observed, which is normally the case with PVA-treated objects.

As an example of the detection limit of PVA, we present results on a Coptic linen textile treated with PVA that was ^{14}C-analyzed with and without solvent pre-treatment at the Royal Institute for Cultural Heritage. The solvent pre-treatment in this case was a sequence of hexane/acetone/ethanol, the textile sample being treated for 15 min in each solvent in an ultrasonic bath. The ^{14}C date without solvent pre-treatment is 2487 ± 34 BP (RICH-23674) and the ^{14}C value with solvent pre-treatment is 1815 ± 32 BP (RICH-24872). This means that the textile without solvent pre-treatment contains 8% dead carbon contamination and thus 17% PVA. The PVA-peak is very abundant in the IR spectrum (Fig. 7). The ^{14}C date of the solvent pre-treated linen sample (RICH-24872) is in agreement with two other fragments of the same textile fabric/garment that were not conserved with PVA, according to the restoration archives; ^{14}C dates for the latter sample are 1813 ± 26 BP (RICH-23679) and 1764 ± 32 BP (RICH-23861).

The ^{14}C dates obtained are also in perfect agreement with the stylistic date, and the FTIR spectrum (Fig. 7) shows no presence of PVA after solvent pretreatment. These are two arguments in favor of the conclusion that PVA can be completely removed with solvent pretreatment. Based on the peak at 1730 cm^{-1} on the FTIR before and after solvent pre-treatment of the textile (Fig. 7), we can infer that the detection limit of PVA is 2%. Assuming zero ^{14}C activity for the PVA carbon, and taking into account that PVA contains ca. 55% of carbon, ca. 1% dead carbon weight would add only about 80 years to the measured age. This means that 2% PVA must be present to add 1% dead carbon.

In the case of the Belfast sample UBA-30011, we can estimate a detection limit based on the ^{14}C age of the contaminated sample compared to the date of either the tephra or the hydroxyproline (HYP) amino acid date from Oxford of 11,100 ± 45 BP (OxA-X-2461-1) (Fiedel et al., 2013). For the UBA-30011 sample, the age of 11,240 ± 62 BP is 140 ^{14}C years older than OxA-X-2461-1, which is consistent with around 1.75% PVA being detected by the FTIR (Fig. 3, A) although the limit may be slightly higher as the PVA sample does not appear to be homogeneous (Fig. 3, B). The UBA-30012 value of 11,080 ± 63 BP is in excellent agreement with the Oxford results as well as the known age of the tephra (11,060 BP), which would support the inference that all the PVA was removed for this sample.

3. Results and discussion

3.1. Quality of extracted collagen

The C:N ratio of the bone collagen was used to classify the collagen samples as contaminated or non-contaminated (e.g., DeNiro, 1985; Ambrose, 1990). Any samples providing results outside the 2.9–3.6 range would be defined as contaminated. In our case (see Table 1), all of the sub-samples have C:N ratios within the acceptable range. Also, the δ^{13}C and δ^{15}N values are quite consistent, and within the expected range for a late Pleistocene-aged terrestrial herbivore, although the

Fig. 7. Plot of the PVA peak at 1730 cm^{-1} before and after solvent pre-treatment of the Coptic textile.

former values are notably less negative than $\delta^{13}C$ values for modern moose (Bump et al., 2007; Drucker et al., 2010). The collagen yields for both samples are in the range of 5.3–11.7% (Table 1); these are common values for bone of ca. 11,000 BP. The highest collagen yield, 10.1–11.7%, comes from sub-samples treated at the Queen's University Belfast lab which used ultrafiltration. Therefore, with respect to its quality, the extracted collagen is well-preserved and unaltered, and is suitable for ^{14}C dating.

3.2. Evaluation of the results obtained

The ^{14}C ages resulting from this experiment appear more accurate than the previous dataset (Fiedel et al., 2013) (Table 1; Fig. 8). All but one of the dates are older than 11,000 BP – more than 350 years older than the typical ages from Fiedel et al.'s (2013) study. These dates are in general agreement with the age of ca. 11,200 BP originally obtained by Hedges et al. (1993), and the average age is effectively identical to the age as determined by ORAU on the hydroxyproline fraction – 11,100 ± 45 BP (Fiedel et al., 2013: 1449; see also Fig. 8). There appears to be no difference between the two samples of the rib. The four RICH dates appear to conform most closely to prior expectation; they all overlap at one-sigma and average at ca. 11,060 BP, in agreement with the most precise tree-wood ^{14}C dates for the eruption. The two GrA dates average 11,110 BP. The two NSK/UGAMS values are ostensibly the most precise in terms of standard deviations: 11,080 ± 33 BP and 10,920 ± 31 BP, but they barely overlap at two-sigma (Table 1, Fig. 5). The older NSK/UGAMS date is identical to the UBA-30012 value (for sample 91/111–3) of 11,080 ± 63 BP. This UBA sample was processed by ultrafiltration; the other ultrafiltered specimen was dated to 11,240 ± 62 BP. The average of these two dates is 11,160 BP. Two AA dates were obtained for each sample; one of the dated pieces was processed by ultrafiltration. In each case, the age of the ultrafiltered sample was appreciably younger than the other: 120 ^{14}C years for 91/110–1 (11,145 ± 65 BP vs. 11,265 ± 67 BP) and 130 ^{14}C years for 91/111–3 (11,140 ± 66 BP vs. 11,270 ± 69 BP). This result is contrary to the expectation that ultrafiltration would remove younger contaminants. Nevertheless, these AA date pairs overlap at the one-sigma level (Fig. 8). It is possible that ultra-filtration may have removed contaminant ancient carbon derived from the PVA.

The new dates for the elk confirm our suspicion that the previous dates of ca. 10,650 BP (see Fiedel et al., 2013) were aberrant, although the explanation remains uncertain. We cannot preclude some minor effect of remnant PVA on the dates presented here (perhaps about 120–140 years), but this is very unlikely to account for a difference of ca. 350 ^{14}C years between most of the previous series and the new dates. However, the wide range of the new dates (10,920 ± 31 to 11,270 ± 69 BP) does raise another issue. Two of the AA dates and one UBA date exhibit close agreement at ca. 11,260 BP. This is 200 ^{14}C years older than expected, but it falls within the two-sigma range of several very precise dates for trees in the middle of the LST in the Brohl Valley, including 11,223 ± 22 BP and 11,277 ± 26 BP (Kromer et al., 1998; Baales et al., 2002; see Fiedel et al., 2013, Table 1). According to the IntCal13 calibration curve, a ^{14}C date of 11,260 BP corresponds to ca. 13,100 cal BP, and a ^{14}C value of 11,230 BP to ca. 13,085 cal BP. Given the stated precision of the ca. 11,260 BP and ca. 11,060 BP dates, they do not overlap at two-sigma, and so cannot be easily reconciled. For the moment, several suggestions can be offered to explain this disparity.

One approach is to assess the dates statistically and discard the outliers. If a series of chi-square tests are run and the dates with the largest T' values are removed each time, the majority of the dates pass. However, three samples do not pass: NSK-1618/UGAMS-27119, AA-106554, and AA-106555. The weighted average of the remaining dates is 11,092 ± 19 BP, where the uncertainty is the square root of the variance. Upon calibration, there is a 95.4% (two-sigma) probability that the age is in the range of 12,841 − 13,064 cal BP.

A possibility deserving some consideration is that vegetation in the vicinity of the volcano had absorbed outgassed "dead" CO_2. The existence of such an effect near the Eifel volcanoes, creating apparent ages in modern plants ranging from 90 to 860 ^{14}C years, has been demonstrated by Bruns et al. (1980). This factor, however, is hard to estimate, and currently it is impossible to take it into account. While outgassing might account for the older dates of some trees, it obviously would not explain why most of the previous dates for the elk were too young, not too old.

Another explanation to consider is that both the ca. 11,260 BP and ca. 11,060 BP dates might be correct, with both sets pointing to a date of the LST (and the slightly earlier death of the elk) coinciding with a steep slope in the ^{14}C calibration curve at 13,100 cal BP (see Hogg et al., 2016a, Figure 13). This would require that different subsamples of the bones were inhomogeneous as discussed below. The obvious question

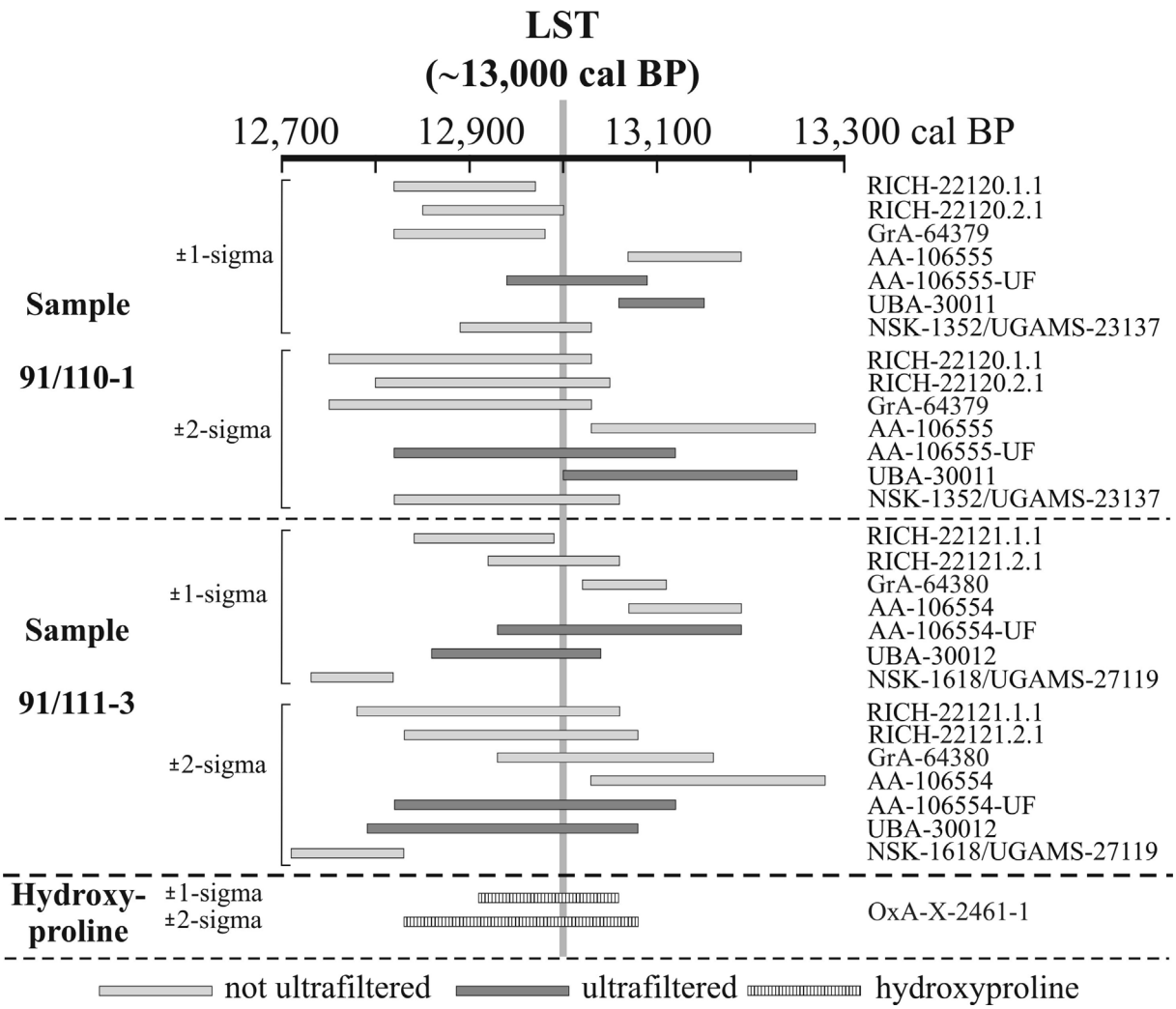

Fig. 8. Calibrated dates for the Miesenheim IV elk and the time of LST: samples 91/110–1 and 91/111–3 (this study); and ^{14}C date on hydroxyproline by ORAU Lab (Fiedel et al., 2013). Lab Nos. are on the right.

here is whether the changes in atmospheric ^{14}C would have been rapid enough to be evident during the ca. 5-year life span of the elk. Additionally, an age of 13,100 cal BP for the elk and the LST would require a date of 12,900 cal BP for the onset of the Younger Dryas in central Europe. It would also require de-coupling the climatic-biotic signal of Younger Dryas onset from the steep slope in the calibration curve that is currently dated at 12,760 cal BP (Hua et al., 2009; Hogg et al., 2016b; Capano et al., 2017).

Also, the possibility of large, rapid variations in the ^{14}C content in the atmosphere should not be ignored. Recently, such spikes have been identified in the Late Glacial at ca. 14,300 and 14,700 cal BP using tree ring samples (Adolphi et al., 2017), as well as in the Holocene (Miyake et al., 2017). A New Guinea coral dated by the U–Th method to 13,010 to 13,090 cal BP (Burr et al., 2004), with two ^{14}C dates for each annual growth ring, shows several episodes when the radiocarbon ages jump between ca. 11,200 and 10,800 BP within a few years. However, these spikes are more likely attributable to rapid fluctuations in the local marine carbon reservoir, not in the atmosphere. Nevertheless, in the near future annually resolved high-precision dates for tree rings might (or might not) reveal corresponding atmospheric ^{14}C spikes.

The volcanic carbon and ^{14}C spike or slope explanations of the range of ^{14}C dates would imply variability of carbon uptake and inhomogeneity at a cellular scale within the sampled bone which are theoretically possible, but not demonstrated in this case. Bone regrowth is a continual process of cell replacement or remodelling (Manolagas, 2000). In humans, the average rate of remodelling of rib bone has been estimated as 4.7% per year. Hillman et al. (1973) reported a heightened rate of rib remodelling (22.9%) in mule deer during the period of antler growth. These rates imply that the ribs of a 4 or 5-year-old elk would probably retain some percentage of the cells formed during the first year of its life (elk males grow their first set of antlers 10 months after birth). Still, the spike model would require two very unlikely circumstances: 1) a spike — a rare event — would have to have occurred within the brief 4 or 5 year span of the elk's life; 2) relatively old and new cells would have to be segregated and thus differentially represented within the sub-samples of a small segment of bone. More likely, the date span could simply indicate more or less complete removal of the dead carbon from the PVA, which, as discussed above, would account for about 140 years. It should be emphasized in this regard that in the first inter-comparison, Groningen (the only laboratory that participated in both experiments) obtained a date of 10,915 ± 45 BP on the untreated bone. In the present study, Groningen's dates, obtained by the same method as before, are 11,030 ± 50 and 11,190 ± 50 BP. The first overlaps with the previous date at 2-sigma, but is noticeably if not significantly older; the second does not overlap with, and it is 275 years older than the date from the 2013 study. Again, it seems necessary either to postulate differential absorption and bonding of PVA at a micro-scale, or to accept that practically identical chemical procedures have had substantially different outcomes. In view of the complications raised by these alternative

Table 2
Proposed dates for the LST and equivalent ^{14}C dates based on IntCal13.

LST age (cal BP) and dataset used	Expected ^{14}C age (BP)	Reference
12,842 (Suigetsu–Soppensee)	11,025	Bronk Ramsey et al. (2012)
12,880 (± 40) (Meerfelder Maar) 12,893 (± 3) (Towai and Kruft9)	11,035	Brauer et al. (1999); Hogg et al. (2016b)
12,916 (Hämelsee, GRIP, GISP2)	11,045	Baales et al. (2002)
12,972 (Lake Lucerne–NGRIP)	11,060	Blaga et al. (2013)
13,035 (Gerzensee–NGRIP)	11,120	van Raden et al. (2013)

approaches, we prefer to explain the discordant dates as a matter of statistical error.

Finally, we can reverse the inference process to see which of several plausible alternatives for dating of the Laacher See eruption offers the best fit with our results (Table 2). This comparison is based on the premise that the IntCal13 calibration is accurate, although it must again be noted that there is no annually-dated tree ring sequence in the Northern Hemisphere that stretches uninterrupted across the Younger Dryas onset. Our results appear to be more consistent with a relatively early date for the eruption (12,972 or 13,035 cal BP) rather than the widely cited date of 12,880 cal BP (Brauer et al., 1999). This older date would allow a simple synchronous correlation of the relative position of the LST in several Swiss lake sediment cores with the closely matching oxygen isotope curve in the NGRIP core (van Raden et al., 2013), and would further imply that vegetation shifts marking the Younger Dryas onset in central Europe occurred at ca. 12,780–12,835 cal BP. It should be noted that the next update of the IntCal calibration curve is likely to shift the calibrated ages in the older direction (Hogg et al., 2016a).

4. Conclusions

Five laboratories have obtained 14 new ^{14}C dates on collagen extracted from two ribs of the Miesenheim IV elk. These dates range from 10,920 ± 31 to 11,270 ± 69 BP; their weighted mean is 11,092 ± 19 BP. This mean age is effectively indistinguishable from the age of 11,100 ± 45 BP previously determined by ORAU on the HYP fraction; one of the new dates is actually identical (RICH-22121.2.1). The known presence of a conservant substance, PVA, does not appear to have significantly affected the outcome.

Therefore, the results of this inter-comparison, with samples unaffected by contamination (even with the presence of PVA) support the ORAU HYP-based ^{14}C date from the first study by Fiedel et al. (2013). It looks pretty obvious that the results of the first inter-comparison (Fiedel et al., 2013) are clearly flawed, except for the ORAU HYP-base ^{14}C date, and must be affected by the waxy/dark, presumably humic/organic-based contaminant. Hence, the results of this second inter-comparison, with samples unaffected by that contamination (even with the presence of PVA) support the HYP-based ^{14}C date from the original study, which was the only one not affected by that contamination.

The results of this inter-comparison dating of the Miesenheim IV elk are important in two respects. First, they demonstrate that collagen processed by traditional methods can yield accurate ages. When the collagen preservation is good, as it is in our case, it may not be necessary to use either ultrafiltration as it is routinely employed by several AMS ^{14}C dating laboratories, or the isolated hydroxyproline fraction (e.g., Nalawade-Chavan et al., 2014; Devièse et al., 2017). For comparison, we also note the results of an analogous collaboration by the laboratories of Oxford and Groningen, which dated Neanderthal bones from various locations. The bones were well-preserved and yielded good quality collagen. Oxford treated the samples with ultra-filtration; Groningen did not. Both methods yielded consistent ages, ranging between 32,000 and 36,000 BP (Semal et al., 2009; Crevecoeur et al., 2010; Maroto et al., 2012). Second, additional ^{14}C values for the Miesenheim IV elk provide a new suite of dates for the Laacher See volcanic eruption, a crucial anchor for Late Glacial chronology.

This work clearly demonstrates how different pretreatments of bone may influence the resulting ^{14}C dates, although in our case no major discrepancies were observed. This study also has shown that one should expect that even a well-preserved terminal Pleistocene bone sample may yield ^{14}C ages scattered across a few hundred years when a multitude of dates is obtained by different laboratories. In view of this outcome, some laboratories may consider whether they should increase the stated uncertainty in radiocarbon ages for bones.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.quageo.2018.07.008.

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