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LABORATORY INTERCOMPARISON OF PLEISTOCENE BONE RADIOCARBON DATING PROTOCOLS

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ABSTRACT. Since its invention in the late 1940s, radiocarbon (^{14}C) dating has become an important tool for absolute dating. A prerequisite for the acceptance of this method is consistency between, and compatibility of, ^{14}C dates from different laboratories. To meet these requirements, international laboratory intercomparison studies with different sample materials are frequently performed (e.g. TIRI, FIRI, VIRI and, most recently, SIRI). Intercomparison is especially relevant and difficult for samples close to the dating limit of ~50 kBP, not least for bone samples. A ^{14}C intercomparison study between the Leibniz-Laboratory in Kiel (Germany), the Center for Isotope Research (CIO) in Groningen (the Netherlands), and the Oxford Radiocarbon Accelerator Unit (ORAU, United Kingdom) was performed on three Pleistocene (MIS3) mammal bone samples from the Brick Quarry site Coenen (BQC) in Germany. The comparison of individually prepared and measured bone collagen ^{14}C activities, results from shared collagen measurements, and respective background signatures and correction points to the latter as the main factor responsible for observed differences in final given radiocarbon estimates.

KEYWORDS: Pleistocene bone radiocarbon dating, laboratory intercomparison, background correction.

INTRODUCTION

During the 1960s, various large mammal remains were found in the Brick Quarry site in Coenen, Körrenzig, Germany (Figure 1). The inventory contains samples of horse (*Equus* sp.), bos/bison, woolly rhino (*Coelodonta antiquitatis*), giant deer (*Megaloceros giganteus*), mammoth (*Mammuthus primigenius*), hyena (*Crocuta spelaea*), cave bear (*Ursus spelaeus*), and lion (*Panthera spelaea*).

Nine radiocarbon (^{14}C) measurements, performed in the Leibniz-Laboratory, Kiel, and the Center for Isotope Research (CIO), Groningen, gave ^{14}C ages between 34,000 BP and >45,000 BP, which place the find horizon into the Interpleniglacial (marine oxygen isotope stage MIS3) (Matzerath et al. 2012).

The ^{14}C dates on selected faunal samples point to a rather broad temporal deposition history, while the analysis of the stable isotope composition (δ^{13}C, δ^{15}N, δ^{34}S) seems to indicate a comparably shorter deposition period (e.g. cold MIS3 stadial/possibly Heinrich 5; Wißing et al. 2015).

Considering controversial discussions with respect to bone sample pretreatment for ^{14}C analysis, i.e. with or without ultrafiltration (e.g. Bronk Ramsey et al. 2004a; Higham et al. 2006; Huels et al. 2007, 2009), a ^{14}C intercomparison study between the Leibniz-Laboratory in Kiel (Germany), the Center for Isotope Research (CIO) in Groningen (the Netherlands), and the Oxford Radiocarbon Accelerator Unit (ORAU, United Kingdom) was performed on three

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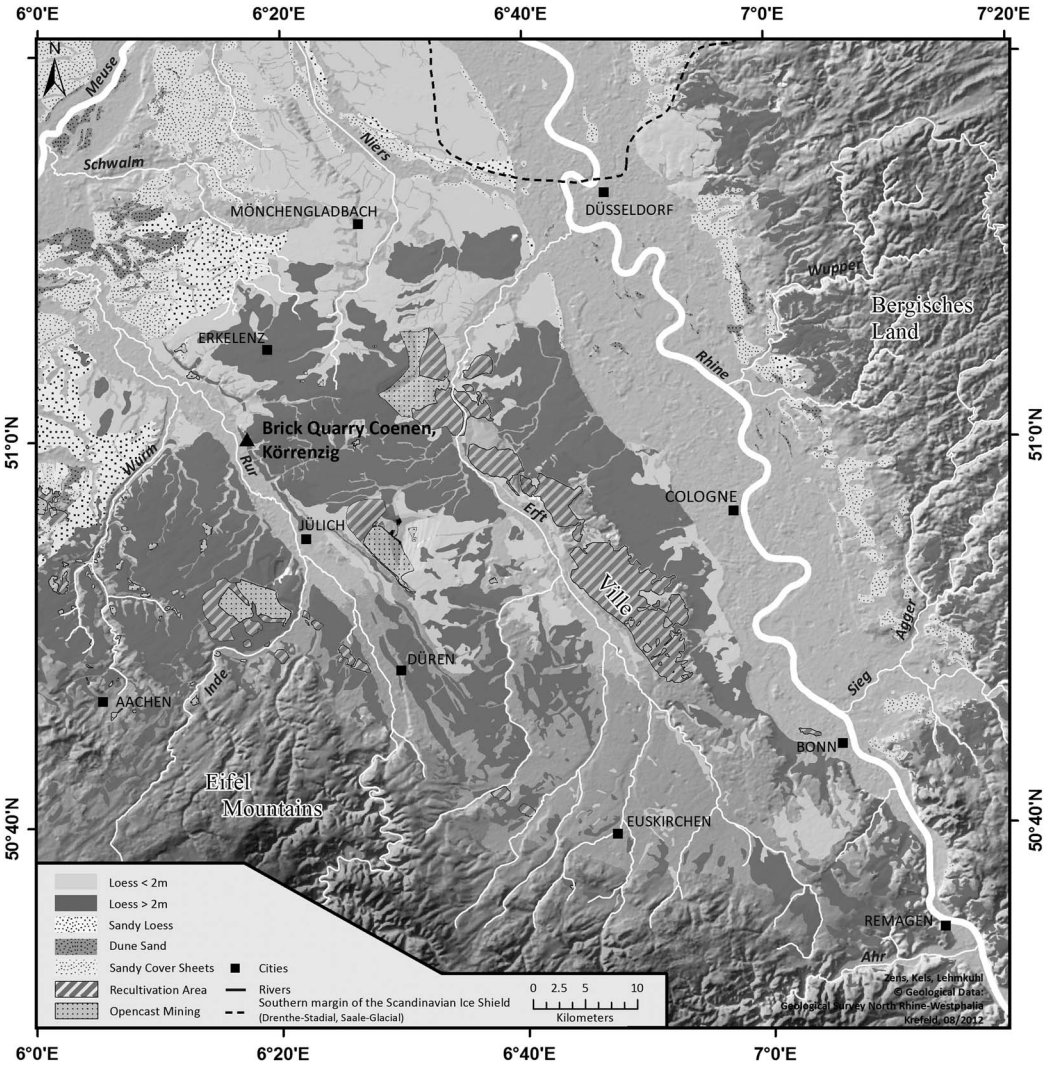


Figure 1 Locality (black triangle) of the Brick Quarry site Coenen, Körrenzig, Germany, and Loess distribution along the left lower Rhine Valley (Lehmkuhl et al. 2016)

Pleistocene (MIS3) mammal bone samples from the Brick Quarry site Coenen (BQC) in Germany, as follows:

- Sample BQC-101, *Equus* sp., right radius, seems to be intentionally fractured by humans, ^{14}C age GrA-53420: >45,000 BP.
- Sample BQC-55, *Equus* sp., right tibia.
- Sample BQC-78, *Bos*/*Bison*, distal piece of left femur, ^{14}C age KIA44874: 34,190 +330/–320 BP.

METHODS

The three samples, each consisting of a single piece of bone, were individually sampled in the participating laboratories, prepared and subsequently measured using in-house accelerator

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mass spectrometry (AMS) systems. In addition to individual measurements, collagen extracted by each laboratory was also sent to the other participating laboratories for AMS measurements.

All three laboratories use a modified Longin protocol (Longin 1971) for collagen extraction, i.e. an acid-base-acid (ABA) treatment for demineralization with small differences in concentration of chemicals used and temperatures for collagen dissolution during the gelatinization step (see Table 1; Mook and Streurman 1983; Grootes et al. 2004; Brock et al. 2010). An additional preparation/cleaning step after collagen gelatinization is applied by the Oxford laboratory using ultrafiltration (Bronk Ramsey et al. 2004a), which intends to remove lower molecular weight (possible environmentally contaminated) protein molecules (molecular weight cut off [MWCO] 30 kDa).

The conversion of extracted sample collagen to CO_2 was done either by closed quartz tube combustion (CTC; with CuO and Ag; Kiel) or using an elemental analyzer and cryogenic separation (Groningen, Oxford). The resulting sample CO_2 was graphitized by the Bosch reaction ($CO_2 + 2H_2 \xrightarrow{550-600\,^{\circ}C;\,Fe\ catalyst} C + 2H_2O$) (Aerts-Bijma et al. 1997; Nadeau et al. 1997, 1998; Dee and Ramsey 2000).

Radiocarbon measurements were performed in each laboratory's own 3 MV HVEE AMS system, normalized to modern oxalic acid II standard (NBS SRM 4990C) and corrected for isotopic fractionation:

$$F^{14}C_{corrected} = F^{14}C_{measured} \times \left[\frac{0.975}{1+\frac{\delta^{13}C}{1000}}\right]^2 \text{ (van der Plicht and Hogg 2006)}$$

Final conventional ^{14}C concentrations ($F^{14}C_{final}$) are calculated by subtracting background effects, i.e. apparent measured ^{14}C concentration measured in fossil sample material, which, according to its age, should not contain ^{14}C:

$$F^{14}C_{final} = F^{14}C_{corrected} - \left[F^{14}C_{Background} \times \left(1 - \frac{F^{14}C_{sample}}{F^{14}C_{standard}}\right)\right]$$

These corrections intend to remove—aside from material specific, intrinsic contamination—any possible effects occurring during the sample preparation, i.e. collagen extraction, CO_2 conversion, graphitization, and AMS measurement. The Kiel laboratory uses fossil bone samples as background material (Huels et al. 2014; Rakowski et al. 2014). For the measurements of shared collagen fractions, i.e. collagen extracted by another laboratory, background corrections in the Kiel AMS facility were performed using crude North Sea oil to correct for contamination effects occurring during CO_2 conversion, graphitization, and AMS measurement. The Oxford laboratory uses CO_2 derived from anthracite to determine an AMS/graphitization background; nylon to determine a combustion background; and fossil bone to determine a pretreatment background (Bronk Ramsey et al. 2004b; Wood et al. 2010). Due to concerns regarding the suitability of background bone standards to represent bone samples from different depositional environments, Groningen uses a pragmatic approach by applying an upper limit of 45 ka BP ($F^{14}C$ concentration ~0.0037) and using anthracite as background sample material (van der Plicht and Palstra 2014).

Final given uncertainties include variance observed during the measurement and the uncertainties in the background correction $\left(\sigma_{final} = \sqrt{\sigma_{meas.}{}^2 + \sigma_{bg_corr}{}^2}\right)$. Kiel uses for background correction uncertainty (σ_{bg_corr}) a factor of 1/3 of the applied background correction (see Nadeau and Grootes 2013); Groningen and Oxford use the standard deviation of measured background signatures.

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Table 1 Sample preparation: collagen extraction procedure, CO_2 conversion, graphitization, AMS system, and applied measurement corrections.

Method	Leibniz-Laboratory, Kiel	Center for Isotope Research, Groningen	Oxford Radiocarbon Accelerator Unit
Collagen extraction	Modified Longin: 0.3M–0.8M HCl, 0.3M NaOH, 0.3M HCl, room temperature; gelatinization 85°C (pH3) 12–24-hr, filtration with 0.45-µm Ag filter	Modified Longin (1–4% HCl, 1% NaOH,1–4% HCl), room temperature; gelatinization 90°C (pH3)	Modified Longin: 0.5M HCl, 0.1M NaOH, 0.5M HCl, room temperature; gelatinization 75°C (pH3) 20 hr, filtration with 60–90 µm Ezee™-filters
Ultrafiltration	No	No	30kDa MWCO, Vivaspin™15 (PES)
Lyophilization	Yes	No, evaporation in hot stove	Yes
CO_2-conversion	CTC (900°C, 4 hr, CuO + Ag)	Elemental analyzer (Isocube, Elementar)	Elemental analyzer (Carbo-Erba NA 2000)
Graphitization	Bosch reaction: (10-mL reactors, 0.9–1.1 mg C/2 mg Fe)	Bosch reaction: (8-mL reactors, 1.5 mg C/1.5 mg Fe)	Bosch reaction: (10-mL reactors, 0.8–1.8 mg C/2–2.5 mg Fe)
AMS measurement	3 MV Tandetron HVEE	3 MV Tandetron HVEE	3 MV Tandetron HVEE
Correction	• Calculating ^{13}C-corrected ^{14}C-concentrations • Background subtraction (for prepared bone sample using extracted background bone collagen; for combusted Groningen and Oxford collagen: combusted fossil oil) • Calculating conventional ^{14}C ages	• Calculating ^{13}C-corrected ^{14}C-concentrations • Background subtraction (anthracite) • Calculating conventional ^{14}C ages	• Subtract AMS/graphitization background (fossil anthracite CO_2; all targets) • Calculating ^{13}C-corrected ^{14}C-concentrations • Background subtraction (combustion background correction all samples [nylon]; pretreatment background correction prepared bones [fossil bone]) (Wood et al. 2010) • Calculating conventional ^{14}C ages

RESULTS AND DISCUSSION

In Table 2, collagen content (estimated in Kiel laboratory), C/N atomic weight ratios (measured by Groningen and Oxford laboratories), ^{14}C concentrations, and conventional ^{14}C ages for samples BQC-101, BQC-55, and BQC-78 are given.

All three bone samples are degraded with respect to organic preservation (collagen content <10 wt% in comparison to >20 wt% in fresh bone; Pasteris et al. 2008). However, measured C/N ratios ~3.2 of extracted collagen and collagen contents above 1 wt% indicate reasonably preserved collagen with intact polypeptide properties (van Klinken 1999; Dobberstein et al. 2009).

For all three bones, final ^{14}C concentrations $\leq$0.011 $F^{14}C$ are measured. Comparatively large uncertainties seen for Kiel measurements stem from background correction uncertainties, i.e. using 1/3 of the background correction value as the background correction uncertainty. This factor is representative of the observed long-term scatter in bone background ^{14}C signature (Nadeau and Grootes 2013). Consequently, Kiel determined for all three bone samples infinite ages, i.e. final ^{14}C concentrations are smaller than two times the measurement uncertainty (so-called 2σ criterion; Olsson 1989; van der Plicht and Hogg 2006). Groningen and Oxford, on the other hand, estimated finite ages. Interlaboratory estimated age differences for BQC-101 and BQC-55 are within given uncertainties, and a somewhat larger scatter is observed for results of BQC-78 (estimated age range from ~39 to ~43 kyr).

A comparison of the results of collagen extracted by one laboratory and measured by another, with in-house prepared and measured collagen, offers a more detailed look into possible causes for observed differences, since possible effects introduced by differences in sample preparation, e.g. with or without ultrafiltration or collagen gelatinization temperatures etc., will not be an issue.

In Figure 2, final ^{14}C concentrations ($F^{14}C$) are shown as stacked column graphs with respective background corrections.

Kiel Collagen

- Measurements made in Groningen and Oxford indicate comparable uncorrected ^{14}C-concentrations, suggesting comparable magnitudes of background contamination introduced by CO_2-conversion, graphitization, and AMS measurement in comparison to Kiel measurements.

Groningen Collagen

- Measurements made in Kiel give slightly lower uncorrected ^{14}C-concentrations, indicating lower magnitudes of background introduced by combustion-graphitization-AMS procedures. The measurements at Oxford imply a comparable background to Groningen.

Oxford Collagen

- Measurements performed in Kiel give lower uncorrected ^{14}C-concentrations for BQC-101 and BQC-55, which seem to indicate a lower background from combustion-graphitization-AMS procedures, and a comparable magnitude of background in BQC-78. Measurements in Groningen indicate a similar size of background effects for BQC-101 and BQC-78 and a lower background effect for BQC-55.

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Table 2 Radiocarbon concentrations ($F^{14}C_{corrected}$, background ^{14}C, and $F^{14}C_{final}$), $\delta^{13}C$ (AMS and IRMS), and conventional ^{14}C ages of samples BQC-101, -55, and -78.

Sample	Lab ID	$F^{14}C_{corrected}$	Background ($F^{14}C_{corrected}$)	$F^{14}C_{final}$	$\delta^{13}C$ AMS (‰VPDB)	$\delta^{13}C$ IRMS (‰VPDB)	Age BP
BQC-101				Kiel collagen			
wt%collagen	KIA50794	0.00613 ± 0.0002	0.00657 ± 0.0022	–0.00040 ± 0.0022	–20.9 ± 0.4		>43,600
(Leibniz-	KIA50794	0.00627 ± 0.0002	0.00657 ± 0.0022	–0.00026 ± 0.0022	–20.6 ± 0.5		>43,600
Laboratory	KIA50794	0.00486 ± 0.0002	0.00582 ± 0.0019	–0.00093 ± 0.0020	–19.8 ± 0.1		>44,550
Kiel): ~6–10	KIA50794	0.00411 ± 0.0002	0.00455 ± 0.0015	–0.00042 ± 0.0015	–18.9 ± 0.1		>46,500
C/N-collagen	GrA62156	0.00660 ± 0.0003	0.00390 ± 0.0003	0.00273 ± 0.0004		–21.2 ± 0.2	>45,000
(Groningen,	OxA_V-2616-52	0.00873 ± 0.0003	0.00492 ± 0.0005	0.00381 ± 0.0006		–20.7 ± 0.2	44,700 ± 1200
Oxford): ~3.3				Groningen collagen			
	GrA59402	0.00600 ± 0.0002	0.00250 ± 0.0002	0.00351 ± 0.0003		–21.17 ± 0.2	>45,000
	GrA59403	0.00660 ± 0.0002	0.00250 ± 0.0003	0.00412 ± 0.0004		–21.15 ± 0.2	44,100 + 750/–700
	KIA50797	0.00393 ± 0.0002	0.00093 ± 0.0003	0.00300 ± 0.00034	–20.2 ± 0.1		46,700 + 950/–850
	KIA50797	0.00413 ± 0.0002	0.00120 ± 0.0004	0.00293 ± 0.0004	–21.0 ± 0.2		46,900 + 1300/–1100
	OxA_V-2581-57	0.00571 ± 0.0002	0.00389 ± 0.0005	0.00182 ± 0.0005		–20.9 ± 0.2	50,700 ± 2300
				Oxford collagen			
	OxA30241	0.00775 ± 0.0003	0.00487 ± 0.0010	0.00288 ± 0.0010		–20.9 ± 0.2	47,000 ± 2900
	OxA30474	0.00942 ± 0.0004	0.00742 ± 0.0010	0.00200 ± 0.0010		–20.9 ± 0.2	>44,300
	KIA50800	0.00618 ± 0.0002	0.00093 ± 0.0003	0.00526 ± 0.0004	–20.7 ± 0.1		42,200 + 550/–500
	KIA50800	0.00585 ± 0.0002	0.00120 ± 0.0004	0.00466 ± 0.0004	–21.0 ± 0.5		43,100 + 800/–700
	GrA61745	0.00950 ± 0.0003	0.00410 ± 0.0003	0.00540 ± 0.0004		–21.0 ± 0.2	41,900 + 650/–600
BQC-55				Kiel collagen			
wt%collagen	KIA50795	0.00868 ± 0.0002	0.00657 ± 0.0022	0.00217 ± 0.0022	–20.6 ± 0.2		>40,400
(Leibniz-	KIA50795	0.00788 ± 0.0002	0.00657 ± 0.0022	0.00136 ± 0.0022	–20.6 ± 0.2		>41,400
Laboratory	KIA50795	0.00477 ± 0.0001	0.00582 ± 0.0019	–0.00102 ± 0.0019	–19.8 ± 0.1		>44,600
Kiel): ~3-5	KIA50795	0.00446 ± 0.0002	0.00453 ± 0.0015	–0.00005 ± 0.0015	–20.7 ± 0.2		>46,600
C/N-C/N-	GrA62158	0.00820 ± 0.0003	0.00390 ± 0.0003	0.00433 ± 0.00042		–21.1 ± 0.2	43,700 + 800/–750
collagen	Ox_V-2616-53	0.01027 ± 0.0003	0.00495 ± 0.0005	0.00532 ± 0.0006		–20.6 ± 0.2	42,100 ± 900
(Groningen,							
Oxford): ~3.2							

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Table 2: (*Continued*)

Sample	Lab ID	$F^{14}C_{corrected}$	Background ($F^{14}C_{corrected}$)	$F^{14}C_{final}$	$\delta^{13}C$ AMS (‰VPDB)	$\delta^{13}C$ IRMS (‰VPDB)	Age BP
				Groningen collagen			
	GrA59397	0.00620 ± 0.0002	0.00250 ± 0.0003	0.00372 ± 0.0004		–20.8 ± 0.2	>45,000
	GrA59400	0.00580 ± 0.0003	0.00250 ± 0.0003	0.00331 ± 0.0004		–20.5 ± 0.2	>45,000
	KIA50798	0.00425 ± 0.0001	0.00093 ± 0.0003	0.00332 ± 0.0003	–20.1 ± 0.1		45,900 + 850/–800
	KIA50798	0.00384 ± 0.0002	0.00119 ± 0.0004	0.00265 ± 0.0004	–20.1 ± 0.2		47,700 + 1450/–1250
	Ox_V-2580-38	0.00682 ± 0.0003	0.00366 ± 0.0005	0.00316 ± 0.0006		–20.8 ± 0.2	46,300 ± 1500
				Oxford collagen			
	OxA30472	0.00878 ± 0.0004	0.00739 ± 0.0009	0.00139 ± 0.0010		–20.8 ± 0.2	>45,700
	OxA30700	0.00891 ± 0.0003	0.00578 ± 0.0009	0.00313 ± 0.0010		–20.5 ± 0.2	46,300 ± 2500
	KIA50801	0.00451 ± 0.0001	0.00093 ± 0.0003	0.00358 ± 0.0003	–20.2 ± 0.1		45,200 + 800/–750
	KIA50801	0.00470 ± 0.0002	0.00120 ± 0.0004	0.00351 ± 0.0004	–20.4 ± 0.6		45,400 + 1050/–950
	GrA61775	0.00710 ± 0.0002	0.00410 ± 0.0003	0.00303 ± 0.0004		–20.9 ± 0.2	>45,000
BQC-78				Kiel collagen			
wt%collagen (Leibniz-Laboratory Kiel): ~4-10 C/N-collagen (Groningen, Oxford): ~3.2	KIA50793	0.00899 ± 0.0002	0.00657 ± 0.0022	0.00248 ± 0.0022	–20.4 ± 0.3		>40,000
	KIA50793	0.00878 ± 0.0002	0.00657 ± 0.0022	0.00227 ± 0.0022	–20.8 ± 0.3		>40,200
	KIA50793	0.00689 ± 0.0002	0.00582 ± 0.0019	0.00111 ± 0.0020	–19.2 ± 0.3		>42,500
	KIA50793	0.00650 ± 0.0002	0.00483 ± 0.0016	0.00170 ± 0.0016	–20.2 ± 0.2		>42,700
	GrA62155	0.00920 ± 0.0003	0.00390 ± 0.0003	0.00534 ± 0.0004		–20.3 ± 0.2	42,000 + 650/–600
	OxA_V-2616-51	0.01096 ± 0.0003	0.00493 ± 0.0005	0.00603 ± 0.0006		–19.8 ± 0.2	41,050 ± 750
				Groningen collagen			
	GrA59398	0.00960 ± 0.0003	0.00250 ± 0.0003	0.00712 ± 0.0004		–20.13 ± 0.2	39,700 + 500/–450
	GrA59401	0.01150 ± 0.0003	0.00250 ± 0.0003	0.00903 ± 0.0004		–20.26 ± 0.2	37,800 + 400/–350
	KIA50796	0.00683 ± 0.0002	0.00093 ± 0.0003	0.00591 ± 0.0004	–20.0 ± 0.1		41,200 + 500/–450
	KIA50796	0.00659 ± 0.0002	0.00120 ± 0.0004	0.00540 ± 0.0004	–19.9 ± 0.4		41,900 + 700/–650
	OxA_V-2580-57	0.00947 ± 0.0003	0.00364 ± 0.0005	0.00583 ± 0.0006		–20.1 ± 0.2	41,300 ± 800
	OxA_V-2581-55	0.01020 ± 0.0003	0.00387 ± 0.0004	0.00633 ± 0.0005		–20 ± 0.2	40,650 ± 650
				Oxford collagen			
	OxA30216	0.00918 ± 0.0004	0.00466 ± 0.0010	0.00452 ± 0.0010		–20.0 ± 0.2	43,400 ± 1800
	OxA30473	0.01300 ± 0.0004	0.00739 ± 0.0009	0.00561 ± 0.0010		–20.2 ± 0.2	41,600 ± 1500
	KIA50799	0.01165 ± 0.0002	0.00093 ± 0.0003	0.01073 ± 0.0004	–19.4 ± 0.1		36,400 ± 300
	KIA50799	0.00852 ± 0.0003	0.00120 ± 0.0004	0.00733 ± 0.0005	–20.3 ± 0.8		39,500 + 550/–500
	GrA61777	0.01110 ± 0.0003	0.00410 ± 0.0003	0.00705 ± 0.0004		–20.5 ± 0.2	39,800 + 500/–450

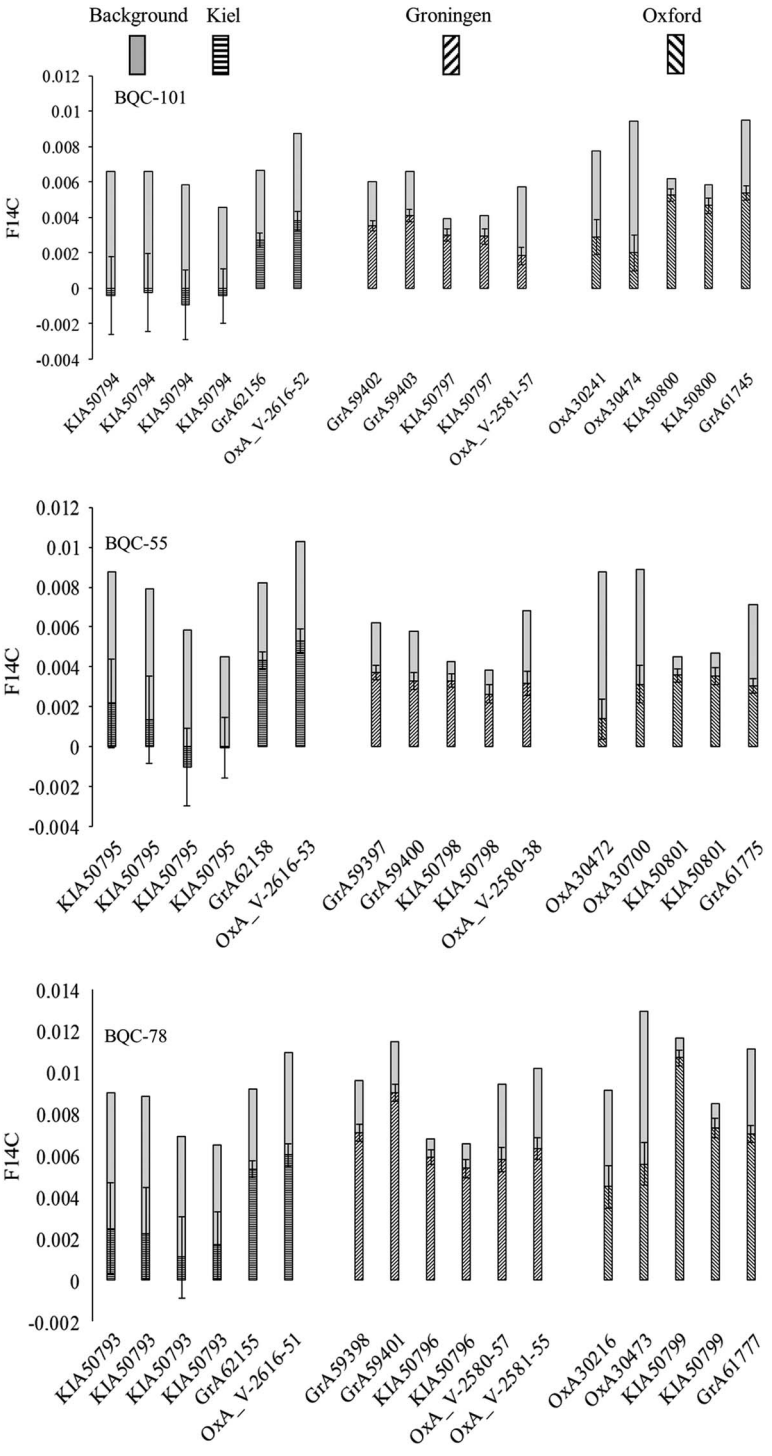


Figure 2 Measured ^{14}C concentrations of BQC-101, BQC-55, and BQC-78. Patterned columns represent Kiel, Groningen, and Oxford (from left to right) extracted collagen $F^{14}C_{final}$ values. The magnitude of applied background correction is shown in gray columns.

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Overall, the observed differences seem to have been caused largely by different apparent background signatures of the participating laboratories. For example, in sample BQC-101, the Leibniz-Laboratory in Kiel measured a $F^{14}C_{corrected}$ between 0.00411 and 0.00627. The same collagen, measured in Groningen and Oxford, gives $F^{14}C_{corrected} = 0.00660$ and $F^{14}C_{corrected} = 0.00873$, respectively. The ORAU, on the other hand, measures slightly more active, non-background corrected ^{14}C concentrations between $F^{14}C_{corrected} = 0.00775$ and $F^{14}C_{corrected} = 0.00942$ on ultrafiltered collagen. The apparent background of about $F^{14}C_{corrected} = 0.00455$–$0.00657$ in Kiel and $F^{14}C_{corrected} = 0.00487$–$0.00742$ in Oxford is comparable in magnitude, however, when background correction is applied, estimated $F^{14}C_{final}$ results in minimum ages of >43,600 BP to >46,500 BP for Kiel measurements and a finite age of 47,000 ± 2900 BP and >44,300 BP for Oxford measurements.

Observed inter- and intralaboratory background signatures are greater, and mask, any differences in applied sample treatment (e.g. whether collagen is ultrafiltered or not).

Limited in the number of samples measured, this intercomparison exercise is far from being representative. However, the results shown indicate the necessity of a more detailed examination of background effects, that is, the measurement of background material, the procedures for correction, and the evaluation of the suitability of background material for a given set of sample materials, in particular for samples close to the limit of the ^{14}C dating method.

CONCLUSIONS

For three Pleistocene mammal bone samples recovered from the Brick Quarry site Coenen, Körrenzig (BQC), Germany, a ^{14}C intercomparison study was performed between the Leibniz-Laboratory in Kiel (Germany), the Center for Isotope Research (CIO) in Groningen (the Netherlands), and the Oxford Radiocarbon Accelerator Unit (ORAU; United Kingdom).

The collagen contents of between 3wt% and 10wt% and C/N ratios ~3.2 indicate a reasonable preservation state of the three bones BQC-101, BQC-55, and BQC-78.

Estimated ^{14}C ages vary between minimum ages ~>40,000 BP to a finite age ~47,000 BP.

The comparison of individually sampled, prepared, and measured bone collagen ^{14}C results as well as the results from shared collagen measurements points to the background correction (e.g. apparent measured background ^{14}C activity and correction applied) as the main factor responsible for observed differences in estimated ^{14}C ages.

With respect to the starting point, measured ^{14}C concentrations and ^{14}C ages are not in contradiction to the assumption of a short deposition period within a cold MIS3 stadial (Wißing et al. 2015).

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REFERENCES

Aerts-Bijma AT, Meijer HAJ, van der Plicht J. 1997. AMS sample handling in Groningen. *Nuclear Instruments and Methods in Physics Research B* 123(1–4):221–5.

Brock F, Higham T, Ditchfield P, Bronk Ramsey C. 2010. Current pretreatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 52(1):103–12.

https://doi.org/10.1017/RDC.2017.23 Published online by Cambridge University Press

Bronk Ramsey C, Higham T, Bowles A, Hedges R. 2004a. Improvements to the pretreatment of bone at Oxford. *Radiocarbon* 46(1):155–63.

Bronk Ramsey C, Higham T, Leach P. 2004b. Towards high-precision AMS: progress and limitations. *Radiocarbon* 46(1):17–24.

Dee M, Ramsey CB. 2000. Refinement of graphite target production at ORAU. *Nuclear Instruments and Methods in Physics Research B* 172: 449–53.

Dobberstein RC, Collins MJ, Craig OE, Taylor G, Penkman KEH, Ritz-Timme S. 2009. Archaeological collagen: Why worry about collagen diagenesis? *Archaeological and Anthropological Sciences* 1:31–42.

Grootes PM, Nadeau M-J, Rieck A. 2004. ^{14}C AMS at the Leibniz-Labor: radiocarbon dating and isotope research. *Nuclear Instruments and Methods in Physics Research B* 223–224:55–61.

Higham T, Bronk Ramsey C, Karavanić I, Smith FH, Trinkaus E. 2006. Revised direct radiocarbon dating of the Vindija G1 Upper Paleolithic Neandertals. *Proceedings of the National Academy of Science of the United States of America* 103(3):553–7.

Huels CM, Grootes PM, Nadeau M-J. 2007. How clean is ultrafiltration cleaning of bone collagen? *Radiocarbon* 49(2):193–200.

Huels CM, Grootes PM, Nadeau M-J. 2009. Ultrafiltration: boon or bane? *Radiocarbon* 51(2):613–25.

Huels CM, Rakowski AZ, Nadeau M-J, Grootes PM. 2014. Background correction for organic samples in Leibniz-Laboratory. Poster presentation at AMS-13 conference, 25–29 August 2014, Aix-en-Provence, France.

Longin R. 1971. New method of collagen extraction for radiocarbon dating. *Nature* 230(5291):241–2.

Lehmkuhl F, Zens J, Krauß L, Schulte P, Kels H. 2016. Loess-paleosol sequences at the northern European loess belt in Germany: distribution, geomorphology and stratigraphy. *Quaternary Science Reviews* 153:11–30.

Matzerath S, Turner E, Fischer P, van der Plicht J. 2012. Radiokohlenstoffdatierte Megafauna aus dem Interpleniglazial der westlichen Niederrheinischen Bucht, Deutschland – Die Funde aus dem Löss der Ziegeleigrube Coenen (Kreis Düren). [Radiocarbon-dated megafauna from the Interpleniglacial in the western Lower Rhine Embayment, Germany – The findings from the loess deposits in the Coenen brick quarry (District of Düren).] *Quartär* 59:47–66 In German.

Mook WG, Streurman HJ. 1983. Physical and chemical aspects of radiocarbon dating. *PACT* 8:31–55.

Nadeau M-J, Grootes PM, Schleicher M, Hasselberg P, Rieck A, Bitterling M. 1998. Sample throughput and data quality at the Leibniz-Labor AMS Facility. *Radiocarbon* 40(1):239–45.

Nadeau M-J, Schleicher M, Grootes PM, Erlenkeuser H, Gottdang A, Mous DJW, Sarnthein M, Willkomm H. 1997. The Leibniz-Labor AMS facility at the Christian-Albrechts University, Kiel, Germany. *Nuclear Instruments and Methods in Physics Research B* 123:22–30.

Nadeau M-J, Grootes PM. 2013. Calculation of the compounded uncertainty of ^{14}C AMS measurements. *Nuclear Instruments and Methods in Physics Research B* 294:420–5.

Olsson IU. 1989. The ^{14}C method, its possibilities and some pitfalls. *PACT* 24:161e177.

Pasteris JD, Wopenka B, Valsami-Jones E. 2008. Bone and tooth mineralization: why apatite? *Elements* 4:97–104.

Rakowski AZ, Huels CM, Schneider R, Dreves A, Meadows J. 2014. Data analysis at Leibniz-Laboratory Kiel: from AMS measurement to radiocarbon age. Poster presentation at AMS-13 conference, 25–29 August 2014, Aix-en-Provence, France.

van der Plicht J, Hogg A. 2006. A note on reporting radiocarbon. *Quaternary Geochronology* 1:237–40.

van der Plicht J, Palstra SWL. 2014. Radiocarbon and mammoth bones: What's in a date. *Quaternary International* 406(B):246–51.

van Klinken GJ. 1999. Bone collagen quality indicators for paleodietary and radiocarbon measurements. *Journal of Archaeological Science* 26:687–95.

Wißing C, Matzerath S, Turner E, Bocherens H. 2015. Paleoecological and climatic implications of stable isotope results from late Pleistocene bone collagen, Ziegeleigrube Coenen, Germany. *Quaternary Research* 84:96–105.

Wood RE, Ramsey CB, Higham TFG. 2010. Refining background corrections for radiocarbon dating of bone collagen at ORAU. *Radiocarbon* 52(2): 600–11.

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