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SIZE MATTERS: RADIOCARBON DATES OF <200 µg ANCIENT COLLAGEN SAMPLES WITH AIXMICADAS AND ITS GAS ION SOURCE

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ABSTRACT. For many of archaeology's rarest and most enigmatic bone artifacts (e.g. human remains, bone ornaments, worked bone), the destruction of the 500 mg material necessary for direct accelerator mass spectrometry (AMS) dating on graphite targets would cause irreparable damage; therefore many have not been directly dated. The recently improved gas ion source of the MICADAS (MIni CArbon DAting System) offers a solution to this problem by measuring gaseous samples of 5–100 µg carbon at a level of precision not previously achieved with an AMS gas ion source. We present the results of the first comparison between "routine" graphite dates of ca. 1000 µg C (2–3 mg bone collagen) and dates from aliquots of gaseous samples of <100 µg C (<0.2 mg bone collagen), undertaken with the highest possible precision in mind. The experiment demonstrates the performance of the AixMICADAS in achieving reliable radiocarbon measurements from <0.2 mg collagen samples back to 40,000 ^{14}C BP. The technique has great implications for resolving chronological questions for key archaeological artifacts.

KEYWORDS: accelerator mass spectrometry, archaeology, collagen, gas ion source, radiocarbon.

INTRODUCTION

The development of accelerator mass spectrometry (AMS) revolutionized the field of radiocarbon (^{14}C) dating by reducing required sample sizes from grams to milligrams. This was an especially crucial improvement for the field of archaeology, and for decades the technique has been central for establishing reliable chronologies back to 50,000 cal BP (calibrated years before 1950). In order to produce enough high-quality collagen for AMS dating on solid targets, current pretreatment protocols for archaeological bone samples require ca. 500 mg material for collagen extraction, ultrafiltration, and graphitization (Longin 1971; Brown et al. 1988; Ramsey et al. 2004a; Higham et al. 2006; Talamo and Richards 2011). However, rare and precious bone samples of such antiquity (including Middle-Upper Paleolithic human remains, bone tools, worked bones and ornaments) are often small or fragmented and the destruction of even 500 mg would result in irreparable damage.

Several AMS labs have worked on developing techniques for measuring samples <0.5 mg carbon on graphite targets (Pearson 1998; Hua et al. 2004; Santos et al. 2007a; Santos et al. 2007b; Smith et al. 2007; Ertun et al. 2005; de Rooij et al. 2010; Genberg et al. 2010; Smith et al. 2010; Delqué-Količ et al. 2013; Liebl et al. 2013; Walter et al. 2015). However, the latest developments in AMS technology now offer an alternative solution for the high-precision measurement of samples of 100 µg carbon or less. AMS instruments with a gas ion source have offered a practical way to measure ^{14}C since the 1980s (Middleton 1984; Bronk and Hedges 1987; Ramsey and Hedges 1997). The direct measurement of sample CO_2 in a gas ion source cuts out the graphitization step, reducing the required sample size and risk of contamination while speeding up the dating procedure, making it a highly attractive prospect. Although successful in measuring ^{14}C of small samples in environmental applications, the low ion currents obtained during initial use (<5 µA compared to currents of >40 µA using graphite) meant that the precision required for archaeological questions was not possible (Ramsey et al. 2004b; Uhl et al. 2005). However, AMS has considerably improved over the past decade.

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The MICADAS (MIni CArbon DAting System), the first compact AMS with a hybrid ion source, was developed at ETH Zurich (Ruff et al. 2007; Synal et al. 2007). Initial use demonstrated the extraordinary reproducibility and stability of the instrument, and thus its suitability for high-precision measurement (Wacker et al. 2010b). Measurements over a 2-yr period in Zurich indicated that contamination issues were much smaller for gaseous samples compared to small graphite samples, as well as more constant (Ruff et al. 2010a). Following several years of operation, the gas ion source was updated for increased precision (Fahrni et al. 2013). The MICADAS offers a way to measure gaseous samples of 5–100 µg carbon (Wacker et al. 2013b), and the newest improvements resulted in a more than threefold increase of the ion current (15–20 µA) compared to the previous versions, essential for precision (Fahrni et al. 2013; Hendriks et al. 2016).

These gas ion sources have thus far been utilized for the measurement of small (<100 µg carbon) and ultra-small (<10 µg carbon) samples of gaseous carbon from ice samples (Hoffmann 2016), aerosols (Zhang et al. 2015; Bonvalot et al. 2016) and carbonates (Wacker et al. 2013a; Bard et al. 2015) where samples sizes were small (generally <30 µg C) but precision was not of highest concern. On the contrary, the gas ion source of the MICADAS has neither been tested for samples towards the limit of the method e.g. Middle-Upper Paleolithic transition, nor for collagen samples.

Our primary goal for this present study was therefore to test the instrument capabilities using this updated measurement technique specifically for collagen samples toward the ^{14}C limit. In order to test the precision and accuracy achievable across the range of the ^{14}C method, we converted collagen from medieval human bone and Pleistocene faunal bone samples to CO_2 using three different preparatory techniques and dated them using the gas interface system (GIS) coupled to the gas ion source of AixMICADAS (Bard et al. 2015). We present here a comparison of "routine" 2–3 mg collagen dates (≥1000 µg carbon on graphite targets) with dates from small gaseous samples of <100 µg carbon, demonstrating the reliable measurement of precise ^{14}C dates across the breadth of the method with a greater than tenfold decrease in sample size.

METHODS

Archaeological Samples

We selected a human bone and a human tooth sample from two early medieval burial contexts in San Martino and Palazzo Fulcis, Northern Italy. In order to test the method on samples of Pleistocene age we selected mammoth and bison bones from Brown Bank on the North Sea plains. These samples were previously described and dated by Talamo and Richards (2011).

Pretreatment

Many preparation issues concerning collagen yield, contamination, reproducibility, and blanks are associated with the extraction of small bone samples (<100 mg). However, as this paper focuses on the AMS measurement techniques, initially a large quantity of collagen was prepared as outlined below, and from these batches microgram-size samples were selected for MICADAS analysis. This strategy was adopted to allow us to differentiate between the instrumental limitations and those associated with the pretreatment of small bone samples. Pretreatment of <100 mg bone samples will be discussed elsewhere (Fewlass et al. in prep.).

Bones (500–700 mg material) were pretreated in the Department of Human Evolution at the Max Planck Institute for Evolutionary Anthropology in Leipzig, Germany (lab code: R-EVA),

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following our standard collagen pretreatment protocol: acid-base-acid followed by ultrafiltration (Talamo and Richards 2011). In order to monitor contamination introduced during the pretreatment stage, a background cave bear bone (R-EVA 800) kindly provided by D. Döppes (Mannheim, Germany) was extracted with each batch of samples (throughout we refer to measurements of this bone as "background," in contrast to "blank," which refers to blank instrumental levels). Elemental and stable isotopic data (C% and N% content, C:N, $\delta^{13}C$, and $\delta^{15}N$) of extracted collagen from all samples was measured in-house at the MPI-EVA. Collagen yields were sufficiently high from all samples to allow the collagen to be split into multiple aliquots and submitted for dating using a range of techniques (Table 1).

Graphitization

Our initial step was to date the collagen via our regular dating routine. In order to obtain independent dates, collagen was sent to two AMS laboratories. Ca. 5 mg collagen from each sample was weighed into pre-cleaned tin cups at the MPI-EVA and sent to the Klaus-Tschira-AMS facility in Mannheim, Germany (lab code: MAMS). The samples were combusted in an elemental analyzer (EA) and CO_2 was converted catalytically to graphite. The samples were dated using the MICADAS-AMS (Kromer et al. 2013). The error calculation was performed using BATS software (Wacker et al. 2010a), with background collagen samples and standards used for the age calculation of the unknown samples, plus an added external error of 1‰, as per their standard practice (R. Friedrich, personal communication).

Collagen was also measured at the Centre de Recherche et d'Enseignement de Geosciences de l'Environnement (CEREGE) in Aix-en-Provence, France (lab code: AIX), where two samples of ca. 2 mg collagen from each bone were weighed into tin cups and graphitized using the AGE III (Automated Graphitization Equipment, IonPlus AG, Switzerland) (Wacker et al. 2010c) and dated using the AixMICADAS (Bard et al. 2015). Oxalic acid standards and background collagen samples run in the same batch were used in the age calculation of the unknown samples. An additional external error of 1‰ was also propagated in the uncertainty calculation.

Conversion to CO_2

We employed three methods of extracting and purifying CO_2 from collagen in order to monitor sources of contamination and identify the optimum route.

Method 1. CEREGE in Aix-en-Provence: EA directly coupled to the gas ion source via zeolite trap

Four collagen aliquots (each 170 μg) from each bone sample were weighed into cleaned (800°C, 2 hr) silver cups. These were placed into the auto-sampler of an Elementar Vario MICRO cube EA (Elementar Analysensysteme GmbH, Germany) directly coupled to the gas ion source of the AixMICADAS via a gas interface system (GIS). Following combustion, sample CO_2 was adsorbed on a zeolite trap. After heating of the trap, the CO_2 was released and expanded to the syringe of the GIS (Ruff et al. 2010b; Wacker et al. 2013b).

Method 2. MPI-EVA in Leipzig: EA coupled to cryogenic gas collection system

For the second method of CO_2 preparation, collagen was converted to CO_2 at the MPI-EVA using a SerCon ANCA SL EA coupled to an Oxford gas collection system. From each sample four aliquots of 170 μg collagen were weighed out on a microbalance into cleaned (800°C, 2 hr) silver cups and placed in the auto-sampler of the EA. Samples were combusted and CO_2 and N_2 were separated. A small proportion of CO_2 and N_2 gas was diverted for isotopic measurement

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in a SERCON 20-20 mass spectrometer. The rest of the CO_2 was diverted to the gas collection system where it was cryogenically purified and trapped into borosilicate glass ampoules (80 mm length, 4 mm diameter) which were flame-sealed. These ampoules were then measured by means of the cracker of the AixMICADAS in Aix-en-Provence (Wacker et al. 2013b). Phthalic acid (≥99.5%) blank samples were run prior to and following sample runs. Blanks (cleaned silver cups) were run between aliquots to monitor instrumental contamination and purge the system.

Method 3. University of Heidelberg: sealed tube combustion and vacuum line

The extraction and purification of CO_2 from bone collagen was also achieved manually using a vacuum line at the Institute of Environmental Physics, University of Heidelberg, adapted from the CARMEN (Carbon AeRosol Muffel Extraction liNe), designed by Hammer (2003) for aerosol filters. This method was carried out for background and medieval samples only due to time constraints. Silver wool was inserted to the bottom of cleaned quartz tubes (150 mm length, 6.5 mm internal diameter; 850°C, 2 hr) to catch sulfur and halides during combustion. Collagen was weighed out using a microbalance and inserted to the bottom of the quartz tubes. Individual sample tubes were inserted into the vacuum line. The line was evacuated while the sample tube was heated to 70°C. The quartz tube was flooded with oxygen (450–550 mbar) and flame-sealed, as wire-form copper oxide was previously found to introduce tiny amounts of carbon to the sample (Hoffmann, personal communication). Samples were combusted for 6 hr at 800°C. Quartz tubes were then broken in the vacuum line and sample CO_2 was isolated from the other combustion products using liquid nitrogen (77 K) and acetone dry ice (195 K) cold traps. The CO_2 was trapped in a region of known volume and quantified through temperature and pressure readings. The sample was then cryogenically captured in the final sample ampoule (80 mm length, 4 mm diameter) which was flame-sealed, and measured via the cracker of the AixMICADAS.

AMS Measurement with the Gas Ion Source of AixMICADAS

Oxalic acid II NIST standards (gas canister) were measured to normalize and correct samples for fractionation and blank CO_2 (gas canister) was measured to purge the system and check the blank level of AixMICADAS in gas configuration prior to measurement of samples (0.4 pMC threshold) (not used in sample age calculation). Samples containing carbonate reference material (blank IAEA-C1) were run prior to samples of method 1 to begin the measurement of old samples under optimal conditions. The different samples were measured in order of increasing activity (i.e. from oldest to youngest), as per standard procedure (Wacker et al. 2013a). Sample CO_2 released from the ampoules or zeolite trap was expanded to the syringe where it was mixed with He (5% CO_2). The mixture was introduced to the gas ion source at a flow rate of ca. 2 µg C/min. The system was flushed with helium between samples. The target magazine can hold up to 39 new titanium (Ti) gas targets which can be changed during measurement. Targets were pre-sputtered for ca. 2 minutes in the ion source to remove any remaining surface contamination before the sample CO_2 injection. All steps of the process were fully controlled via the gas-interface handling software. In the software BATS (Wacker et al. 2010a) the uncorrected background collagen samples (cave bear bone R-EVA 800) were used in the age calculation of the four unknown archaeological samples (shown in Tables 3–6).

The gas ion source of the MICADAS has been predominantly used for measuring samples limited by C amount (<30 µg C), whereas for collagen samples a reduction in sample size to 50–100 µg C still represents a sizeable decrease compared to standard dating on graphite targets (>500 µg C). Therefore, for this exploratory test relatively large samples were combusted in order to reach

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maximum precision. However, as any C above the limit of 100 µg C in the syringe after combustion/cracking leads to a flushing of excess sample, only around 170 µg collagen (ca. 70–80 µg C) was measured out. During measurement only 30–40 µg C was consumed for the AMS due to a typical degradation of the Ti target performance (Fahrni et al. 2013) and the rest was lost. In future we would measure out a suitable sample size (30–40 µg C in 70–80 µg collagen) for one target. The measurement of a large sample (>40 µg C) over a second or even a third Ti target has been performed on carbonate samples using the AixMICADAS with positive outcomes (Fagault et al. 2017; Tuna et al. 2017). Although this was not carried out for collagen samples during this preliminary study, such a strategy is an interesting avenue for further exploration.

RESULTS AND DISCUSSION

Preservation

For all samples the elemental and stable isotopic data indicate well-preserved collagen, and are well within the acceptable range (C:N = 2.9–3.6) (van Klinken 1999) (Table 1). All samples produced a collagen yield of >10%, confirming a high level of preservation, hence their suitability for dating (Ambrose 1990; van Klinken 1999) (Table 1).

Dating on Graphite Targets

The results of samples measured on solid targets in the two labs, MAMS and AIX, are in agreement (Table 2; Figure 1). The Italian samples date to the early medieval period as expected from the archaeological context. The dates of the mammoth bone fall perfectly within the range found previously (Talamo and Richards 2011). The ages of the bison bone reported here are the oldest yet for this specimen. The oldest dates obtained by Talamo and Richards (2011) were >44,800 BP (conventional ^{14}C yr before AD 1950) from collagen extracted, ultra-filtered, graphitized and dated at the Oxford Radiocarbon Accelerator Unit (ORAU) and from collagen extracts pretreated at the MPI-EVA and subsequently graphitized and dated at ORAU (47,300 +910/–820 BP) and MAMS (47,000 +1190/–1040 BP). All measurements in the previous study were also corrected for collagen extraction backgrounds and standards measured in the same batch. The older ages of the bison bone obtained on graphite targets in this study may be a reflection of the updated pretreatment method now employed at the MPI-EVA, as well as stringent contamination criteria observed at MAMS and AIX during the graphitization

Table 1 Elemental and stable isotopic data (C%, N%, C:N, $\delta^{13}C$ and $\delta^{15}N$), and collagen yields of the collagen extracts measured in-house at the MPI-EVA on a ThermoFinnigan Delta V Advantage isotope ratio mass spectrometer coupled to a Flash 2000 EA. Stable carbon isotope ratios were expressed relative to VPDB (Vienna PeeDee Belemnite) and stable nitrogen isotope ratios were measured relative to AIR (atmospheric N_2), using the delta notation (δ) in parts per thousand (‰). Repeated analysis of both internal and international standards indicates an analytical error of 0.2 ‰ (1σ) for $\delta^{13}C$ and $\delta^{15}N$.

Material	MPI-EVA lab code	Site	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	C%	N%	C:N	Collagen (%)
Background	R-EVA 800.30	Austria	−21.1	0.0	46.7	17.1	3.2	14.1
Cave bear bone	R-EVA 800.33	Austria	−21.3	−0.2	46.4	17.5	3.1	7.6
Bison bone	R-EVA 124.43	North Sea Plains	−20.0	3.3	45.9	17.2	3.1	11.7
Mammoth bone	R-EVA 123.53	North Sea Plains	−21.1	7.1	45.6	16.9	3.2	11.2
Human tooth	R-EVA 1516.1	Belluno Palazzo Fulcis	−16.5	9.7	44.8	16.4	3.2	17.7
Human bone	R-EVA 1489.1	San Martino Lundo Lomaso	−16.4	8.8	45.4	16.7	3.2	17.9

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Table 2 Results from collagen samples measured on graphite targets at MAMS and AIX. Both labs used ^{12}C currents on graphite targets in the order of 40 µA (low energy side). In Aix, the collagen background measurements (R-EVA 800) had a standard deviation of 0.01 pMC (5%). Rather than propagating this variation in the error calculation of the unknown samples, a conservative value of 0.04 pMC (20%) was used based on observed long-term reproducibility of Phthalic acid standards. An additional 0.1 pMC relative variability was included in the error propagation to take into account the long-term variation on OXA2 standards. In MAMS, samples were corrected for collagen background measurements (cave bear R-EVA 800) and standards run in the same batch using BATS software, with an added external error of 0.1 pMC as per their standard practice. Asymmetrical age uncertainties are shown where pMC ≤ error × 10. All ages >15,000 BP are rounded to nearest 10 yr.

		MAMS					AixMICADAS				
Material	MPI-EVA lab code	Lab code	pMC	±	^{14}C age BP (yr)	± (yr)	Lab code	pMC	±	^{14}C age BP (yr)	± (yr)
Background cave bear bone* (used in correction of unknown samples)	R-EVA 800.30	MAMS-26330	0.27	0.02	47430	480	Aix-12001.1.2	0.21	0.01	49630	410
		MAMS-26331	0.27	0.02	47590	470	Aix-12001.1.3	0.22	0.01	49310	400
		MAMS-26332	0.33	0.02	45920	470					
			weighted mean		**47020**	**270**					
	R-EVA 800.33	MAMS-26878	0.20	0.01	50120	600	Aix-12000.1.2	0.20	0.01	49990	360
							Aix-12000.1.3	0.19	0.01	50280	370
								weighted mean		**49850**	**190**
Bison bone	R-EVA 124.43	MAMS-26877	0.19	0.04	50150	+2080/−1650	Aix-12002.1.2	0.22	0.04	49300	+1610/−1340
							Aix-12002.1.3	0.23	0.04	48800	+1530/−1290
								weighted mean		**49040**	**+1040/−920**
Mammoth bone	R-EVA 123.53	MAMS-26876	1.4	0.05	34360	300	Aix-12003.1.1	1.38	0.04	34390	240
							Aix-12003.1.2	1.40	0.04	34320	240
								weighted mean		**34350**	**170**
Human tooth	R-EVA 1516.1	MAMS-26328	83.6	0.2	1436	23	Aix-12005.1.1	82.99	0.18	1498	18
							Aix-12005.1.2	83.38	0.18	1460	18
								weighted mean		**1479**	**13**
Human bone	R-EVA 1489.1	MAMS-26317	83.2	0.2	1481	23	Aix-12004.1.1	83.07	0.18	1490	17
							Aix-12004.1.2	83.28	0.18	1470	17
								weighted mean		**1480**	**12**

*R-EVA 800.30 and R-EVA 800.33 represent two separate collagen extractions from one bone (R-EVA 800). R-EVA 800.30 was extracted alongside the medieval samples, and R-EVA 800.33 was extracted alongside the Paleolithic samples.

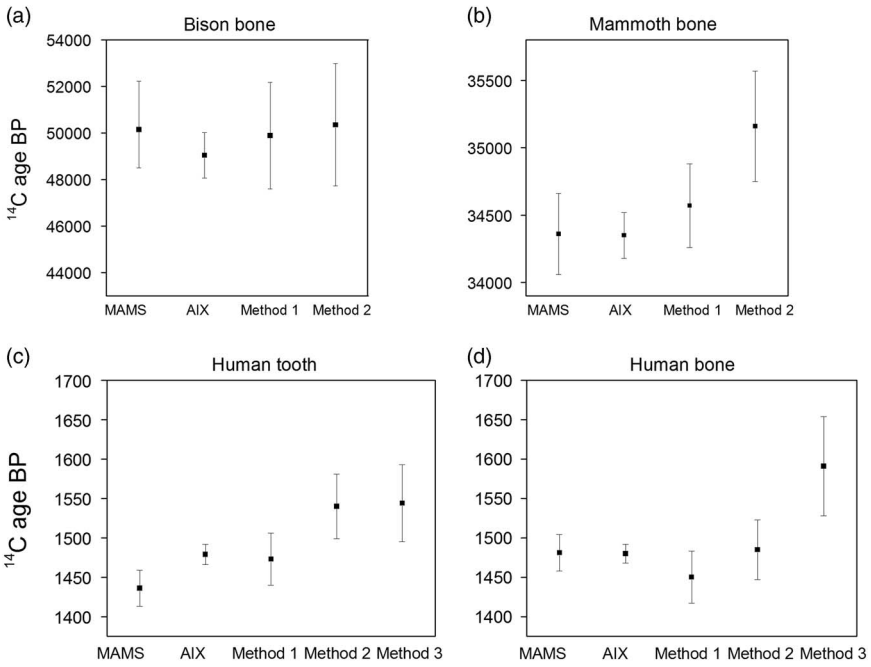

Figure 1 Comparison of graphite dates from MAMS and AixMICADAS against the CO_2 weighted mean dates and weighted errors (error 2 in Tables 3–5) of replicates for the four bone samples: (a) R-EVA 124.43, (b) R-EVA 123.53, (c) R-EVA 1516.1, and (d) R-EVA 1489.1. MAMS graphite dates are the results of a single run, whereas AixMICADAS graphite dates are the weighted mean of two replicates, shown in Table 2. Errors are shown to 1σ. In part (d) the mean value for method 3 is somewhat older and less precise than all other values. This mean for method 3 is only based on two replicates, which are not overlapping at 1σ: 1521 ± 80 and 1708 ± 100 BP. The first replicate agrees with those of other methods, while the second and older value is clearly an outlier. More data and work are needed to decipher the cause of this.

process, and further instrumental improvements. We conclude that the agreement between results of large samples measured on solid targets at MAMS and with the AixMICADAS provide a suitable reference dataset for comparison to small gaseous samples measured with the gas ion source of AixMICADAS.

CO_2 Dating

Tables 3–5 show the results of measurements of collagen CO_2 samples, prepared via three different techniques (methods 1–3). Results are shown in both ^{14}C years and percent modern carbon ($pMC = F^{14}C \times 100$). The first error column (error 1) in the tables shows the error calculated in BATS (Wacker et al. 2010a) propagating only the variance of the standards and collagen backgrounds included in the same batch as the samples. A second error (error 2 column in Tables 3–5) has also been calculated based on observed data. This added external error has been calculated from the long term variabilities observed on CO_2 blanks (0.1 pMC long-term standard deviation of blanks is used as the absolute blank error) and oxalic acid standards (3.5‰ relative error added). While the minimal error propagation of the first error column is optimistic, the second column may represent an overestimation of error as these measurements were made over a short period of time. A comparison of dates from each method is shown in Figure 1, using the weighted means and weighted errors (error 2) of the data in Tables 3–5.

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Table 3 Results of AMS measurements using the gas ion source of AixMICADAS for collagen CO_2 samples prepared via method 1. The background cave bear concentrations have been subtracted from all four unknown samples, including the bison bone. The measured mass shows the amount of carbon (μg) trapped in the syringe after expansion; in reality only 20–40 μg C was used for each measurement. All errors are shown to 1σ: the error 1 column shows the minimal error, corrected for standards and backgrounds measured in the same batch. The error 2 column includes an external error taking into account long-term variability on standards (3.5‰ relative error added) and blanks (the 0.1 pMC long term standard deviation of blanks is used as the absolute blank error). The results with lab codes including asterisks (*) were measured as preliminary runs of limited duration which explains their lower precision and higher scatter (hence, error 2 is equal to error 1). Asymmetrical age uncertainties are shown where pMC ≤ error × 10. "Older than" ages have been calculated at 2σ, according to convention in van der Plicht and Hogg (2006). All ages >15,000 BP are rounded to nearest 10 yr.

Method 1: EA directly coupled to the gas ion source via zeolite trap

Material	MPI-EVA lab code	AIX lab code	Measured mass (C μg)	Run time (s)	pMC	Error 1 pMC ±	Error 2 pMC ±	^{14}C age BP (yr)	Error 1 (yr) (1σ)	Error 2 (yr) (1σ)
Background cave bear bone	R-EVA 800.33	Aix-12000.2.1*	88	374	0.72	0.11		39580	+1320/−1140	
(used in correction of	R-EVA 800.33	Aix-12000.2.2*	92	446	0.74	0.10		39450	+1170/−1020	
unknown samples)	R-EVA 800.33	Aix-12000.2.3*	96	446	0.53	0.07		42120	+1140/−1000	
	R-EVA 800.33	Aix-12000.5.4	87	576	0.61	0.05		40950	660	
	R-EVA 800.30	Aix-12001.5.1	84	403	0.66	0.06		40290	760	
	R-EVA 800.30	Aix-12001.5.2	86	748	0.68	0.05		40130	570	
			weighted mean		**0.64**	**0.03**		**40550**	**330**	
Bison bone	R-EVA 124.43	Aix-12002.4.1	84	331	0.11	0.10	0.12		>46400	>45430
		Aix-12002.4.2	89	561	0.21	0.08	0.11	49530	+3850/−2590	>43770
		Aix-12002.4.3	80	547	0.24	0.09	0.11	48610	+3780/−2560	+4930/-3030
		Aix-12002.4.4	74	547	0.22	0.08	0.11	48980	+3630/−2490	>43590
			weighted mean		**0.20**	**0.04**	**0.06**	**49890**	**+1790/−1460**	**+2690/-2010**
Mammoth bone	R-EVA 123.53	Aix-12003.2.1*	89	418	1.32	0.18	0.18	34750	+1180/−1030	+1180/-1030
		Aix-12003.2.2*	96	475	1.25	0.17	0.17	35210	+1170/−1020	+1170/-1020
		Aix-12003.2.3*	96	575	1.41	0.15	0.15	34250	+900/−810	+900/-810
		Aix-12003.5.1	89	490	1.41	0.11	0.13	34260	620	750
		Aix-12003.5.2	78	590	1.31	0.10	0.13	34820	620	770
		Aix-12003.5.3	75	993	1.33	0.08	0.11	34710	510	675
		Aix-12003.5.4	98	633	1.41	0.11	0.13	34260	630	760
			weighted mean		**1.35**	**0.04**	**0.05**	**34570**	**260**	**310**
Human tooth	R-EVA 1516.1	Aix-12005.3.1	71	619	83.25	0.61	0.69	1473	59	67
		Aix-12005.3.2	72	590	83.07	0.68	0.75	1490	65	73
		Aix-12005.3.3	69	978	82.88	0.51	0.60	1508	49	59
		Aix-12005.3.4	69	431	84.11	0.69	0.77	1390	66	73
			weighted mean		**83.25**	**0.30**	**0.35**	**1473**	**29**	**33**
Human bone	R-EVA 1489.1	Aix-12004.3.1	84	561	84.00	0.72	0.79	1401	68	75
		Aix-12004.3.2	74	561	82.65	0.67	0.74	1530	65	72
		Aix-12004.3.3	77	921	83.03	0.53	0.62	1494	51	60
		Aix-12004.3.4	74	633	84.34	0.59	0.68	1368	56	65
			weighted mean		**83.50**	**0.31**	**0.35**	**1450**	**30**	**33**

Table 4 Results of AMS measurement using the gas ion source of AixMICADAS for collagen CO_2 samples prepared via method 2. Columns: see Table 3.

Method 2: EA coupled to cryogenic gas collection system										
Material	MPI-EVA lab code	AIX lab code	Measured mass (C µg)	Run time (s)	pMC	Error 1 pMC ±	Error 2 pMC ±	^{14}C age BP (yr)	Error 1 (yr) (1σ)	Error 2 (yr) (1σ)
Background cave bear bone (used in correction of unknown samples)	R-EVA 800.33	Aix-12000.3.1	75	475	0.64	0.06		40560	700	
	R-EVA 800.33	Aix-12000.3.2	74	489	0.73	0.07		39550	770	
	R-EVA 800.30	Aix-12001.2.1	61	504	0.69	0.06		39980	740	
	R-EVA 800.30	Aix-12001.2.2	76	417	0.54	0.07		41910	+1120/−980	
	R-EVA 800.30	Aix-12001.2.4	81	403	0.59	0.07		41280	+1010/−900	
			weighted mean		**0.64**	**0.03**		**40590**	**360**	
Bison bone	R-EVA 124.43	Aix-12002.2.2	69	561	0.29	0.09	0.11	47080	+2980/−2170	+3830/−2580
		Aix-12002.2.3	77	633	0.08	0.09	0.11		>47810	>46660
		Aix-12002.2.4	77	576	0.21	0.09	0.11	49420	+4500/−2870	>43770
			weighted mean		**0.19**	**0.05**	**0.06**	**50350**	**+2450/−1880**	**+3050/−2200**
Mammoth bone	R-EVA 123.53	Aix-12003.3.1	67	576	1.16	0.11	0.13	36120	800	+950/−850
		Aix-12003.3.2	79	504	1.25	0.11	0.13	35180	720	+880/−790
		Aix-12003.3.3	81	547	1.26	0.12	0.13	35140	760	+870/−790
		Aix-12003.3.4	69	561	1.42	0.12	0.13	34160	670	750
			weighted mean		**1.26**	**0.06**	**0.06**	**35160**	**370**	**410**
Human tooth	R-EVA 1516.1	Aix-12005.2.1	69	489	82.45	0.88	0.92	1561	86	90
		Aix-12005.2.2	74	403	82.29	0.95	0.99	1577	93	96
		Aix-12005.2.3	67	532	83.60	0.70	0.75	1449	68	72
		Aix-12005.2.4	71	533	82.07	0.70	0.79	1599	73	77
			weighted mean		**82.57**	**0.40**	**0.42**	**1540**	**39**	**41**
Human bone	R-EVA 1489.1	Aix-12004.4.1	71	547	82.43	0.75	0.79	1563	73	77
		Aix-12004.4.2	79	576	83.00	0.76	0.80	1507	73	78
		Aix-12004.4.3	74	590	83.60	0.73	0.77	1449	70	74
		Aix-12004.4.4	72	561	83.87	0.74	0.77	1424	71	75
			weighted mean		**83.12**	**0.37**	**0.39**	**1485**	**36**	**38**

Table 5 Results of AMS measurement using the gas ion source of AixMICADAS for collagen CO_2 samples prepared via method 3. Columns: see Table 3. A limited samples set was prepared using this method due to time constraints.

Method 3: sealed tube combustion and vacuum line										
Material	MPI-EVA lab code	AIX lab code	Measured mass (C µg)	Run time (s)	pMC	Error 1 pMC ±	Error 2 pMC ±	^{14}C age BP (yr)	Error 1 (yr) (1σ)	Error 2 (yr) (1σ)
Background cave bear bone (used in correction of unknown samples)	R-EVA 800.30	Aix-12001.4.1	101	835	0.42	0.04		43950	750	
	R-EVA 800.30	Aix-12001.4.2	61	533	0.50	0.04		42620	710	
			weighted mean		**0.45**	**0.03**		**43340**	**520**	
Human tooth	R-EVA 1516.1	Aix-12005.4.1	99	461	81.72	0.97	1.03	1623	96	102
		Aix-12005.4.2	51	878	82.40	0.67	0.75	1557	65	73
		Aix-12005.4.4	51	345	83.30	0.83	0.90	1469	80	87
			weighted mean		**82.51**	**0.46**	**0.50**	**1544**	**45**	**49**
Human bone	R-EVA 1489.1	Aix-12004.5.1	48	504	82.76	0.75	0.82	1521	73	80
		Aix-12004.5.2	101	461	80.86	0.96	1.02	1708	95	101
			weighted mean		**82.03**	**0.59**	**0.64**	**1591**	**58**	**63**

Comparison between AMS Measurements

The results agree between measurements on graphite targets and gaseous collagen samples for all four samples, as seen in Figure 1. The dates between replicates are internally consistent for all samples prepared via methods 1 and 2 (Tables 3 and 4) (chi^2 test, $p > 0.05$ in all cases; Ward and Wilson 1978) and the weighted mean ages for each of the gas methods are statistically identical for all four samples (Mann-Whitney U test, $p > 0.05$ in all cases).

The background collagen samples (R-EVA 800) averaged 0.65 pMC for method 1 and 0.6 pMC for method 2 (see Table 6), both with a standard deviation (1σ) of 0.07 pMC, well within the long-term variability (0.1 pMC) observed on standards measured with the gas ion source. The same background collagen measured on graphite targets in Aix averaged 0.2 pMC with a standard deviation of 0.01 pMC.

Table 6 Comparison of AMS measurements obtained from the background cave bear bone R-EVA 800 for each method. R-EVA 800.30 and 800.33 denote two collagen extractions from the same bone; R-EVA 800.30 was extracted alongside the medieval samples, and R-EVA 800.33 was extracted alongside the Paleolithic samples. At MAMS, R-EVA 800.30 was used for background correction of the graphite measurements of the medieval samples and R-EVA 800.33 was used for background correction of the bison and mammoth samples as these batches were run on separate occasions. In Aix, measurements performed with AixMICADAS on samples R-EVA 800.30 and 800.33 were both used for background correction of the bison, mammoth and medieval human samples, measured on graphite or CO_2 gas, as all samples were measured in the same batch. Asymmetrical age uncertainties are shown where pMC ≤ error × 10. All ages >15,000 BP are rounded to nearest 10 yr.

Method	MPI-EVA lab code	AMS lab code	pMC	±	^{14}C age BP (yr)	Error (yr) (1σ)
Graphite	R-EVA 800.30	Aix-12001.1.2	0.21	0.01	49630	410
	R-EVA 800.30	Aix-12001.1.3	0.22	0.01	49310	400
	R-EVA 800.33	Aix-12000.1.2	0.20	0.01	49990	360
	R-EVA 800.33	Aix-12000.1.3	0.19	0.01	50280	370
		weighted mean	**0.20**	**0.005**	**49850**	**190**
	R-EVA 800.30	MAMS-26330	0.27	0.02	47480	480
	R-EVA 800.30	MAMS-26331	0.27	0.02	47630	470
	R-EVA 800.30	MAMS-26332	0.33	0.02	45970	470
	R-EVA 800.33	MAMS-26878	0.20	0.01	50120	600
		weighted mean	**0.28**	**0.01**	**47200**	**250**
Gas Method 1	R-EVA 800.30	Aix-12001.5.1	0.66	0.06	40290	760
	R-EVA 800.30	Aix-12001.5.2	0.68	0.05	40130	570
	R-EVA 800.33	Aix-12000.5.4	0.61	0.05	40950	660
		weighted mean	**0.64**	**0.03**	**40460**	**330**
Gas Method 2	R-EVA 800.30	Aix-12001.2.1	0.69	0.06	39980	740
	R-EVA 800.30	Aix-12001.2.2	0.54	0.07	41910	+1120/−980
	R-EVA 800.30	Aix-12001.2.4	0.59	0.07	41280	+1010/−900
	R-EVA 800.33	Aix-12000.3.1	0.64	0.06	40570	700
	R-EVA 800.33	Aix-12000.3.2	0.73	0.07	39550	770
		weighted mean	**0.65**	**0.03**	**40590**	**360**
Gas Method 3	R-EVA 800.30	Aix-12001.4.1	0.42	0.04	43950	750
	R-EVA 800.30	Aix-12001.4.2	0.50	0.04	42620	710
		weighted mean	**0.45**	**0.03**	**43340**	**520**

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Although the results for the collagen background (R-EVA 800) are statistically the same between methods 1 and 2, those from method 3 are not, being older by ca. 3000 ^{14}C yr (0.2 pMC lower). This may relate to the absence of C contribution from the silver cups used for sample combustion in methods 1 and 2. It is clear that one of the two aliquots of the medieval human bone (R-EVA 1489.1) prepared using method 3 is an outlier (Aix-12004.5.2: 1708 ± 101 BP) compared to all other measurements for this bone, with the two replicates not overlapping at 1σ (Table 5). Due to this outlier the weighted mean for method 3 is older than the weighted means of methods 1 and 2 (Figure 1d). This aliquot was prepared in the Heidelberg vacuum line following the first preparation of the same bone (Aix-12004.5.1), interspersed with overnight evacuation of the system. Likewise, the outlier was measured with the GIS following Aix-12004.5.1. It is therefore unlikely that the older age is a result of a memory effect from an older sample. As the method 3 data set is limited, further analysis of small samples prepared via method 3 will be undertaken to expand the data set and explore the phenomenon observed in the "cleaner" collagen backgrounds. The results agree within statistics between the graphite and CO_2 techniques (methods 1 and 2) for the medieval samples and for the mammoth bone at ca. 34,500 BP (calibrated age ca. 39,000 cal BP), with low error ranges.

As shown by the graphite measurements in Table 2, the bison bone is very close to the cave bear background value (ca. 0.2 pMC). In Tables 3–4, the bison gas analyses are corrected for a more sizable background value (ca. 0.65 pMC). Consequently, the CO_2 results vary widely between replicates although this variation is still within the quoted 1σ errors (see Tables 3 and 4). Nevertheless, after propagation of the blank scatter in the error calculation (error 2 discussed above), the gas measurements (weighted mean and error of 50120 +2950/–2150 BP for the 7 replicates in Tables 3 and 4) are compatible with those performed on solid graphite (49,040 +1040/–920 BP based on duplicates in Table 2) at the limit of the ^{14}C timescale. In any case, this sample suggests that the realistic limits of the gas source for relatively precise measurements is ca. 0.6 pMC, equivalent to an age of 41,000 BP (and a calibrated age of ca. 44,000 cal BP). Beyond that limit, the ^{14}C can still be detected and quantified, but the uncertainty of the background correction dominates accuracy and precision.

Precision

Although ion currents remain higher for measurements of large samples on graphite targets (around 40 µA for these samples on the Low energy side), various modifications to the gas ion source (Fahrni et al. 2013), such as the addition and adjustment of the immersion lens, mean that currents from the MICADAS gas ion source are now achievable which were impossible eight years ago (in the range of 15 µA for this study), and the use of helium as a stripper gas has further increased transmission (48% for AixMICADAS in gas configuration).

While ca. 80 µg C (170 µg collagen) was weighed into each aliquot for these tests, only approximately 30 µg C was consumed during measurement. For future samples, an appropriate amount of collagen (ca. 70–80 µg) would be weighed out or measurements could be extended for the duration of a second or third titanium target to exhaust the whole sample. With such a reduction in sample size (e.g. half the amount combusted in this study), any external carbon in the EA-GIS system will make an increased contribution for samples prepared via methods 1 and 2. This will be explored in future tests using such sample sizes.

Although a single gaseous measurement of <100 µg C is not yet directly competitive with a 1000 µg C graphite measurement in terms of error, the level of precision we achieved with one

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aliquot is still highly applicable for answering many archaeological questions. This is especially important for Paleolithic fossils and bone artifacts where 500 mg material is not available for sampling. This is demonstrated by the mammoth bone at ca. 34,500 BP, where a single gaseous measurement of <0.2 mg collagen has a precision of approximately ±800 yr (error 2).

For this test, four aliquots per sample were measured to test the consistency of the measurements. Although we are principally interested in the precision and accuracy we can reliably achieve with one run (<100 μg C), when we take the weighted mean and error of the four gaseous replicates for method one, the measurement error of the gas technique is more or less comparable with a graphite date (see Figure 1). For example, for the mammoth bone, the weighted mean of the four ca. 80 μg C (total 320 μg C combusted, ca. 120 μg C consumed) gas samples (method 1) was 34530 ± 300 BP, while the graphite date from MAMS was 34360 ± 300 BP and from Aix was 34350 ± 170 BP (each ca. 1000 μg C). This is especially apparent when considering the calibrated ranges. For the medieval tooth, the calibrated range of the weighted mean age and error (1473 ± 33 BP) of the method 1 gas samples is 1389–1320 cal BP (1σ) and the weighted mean of the graphite measurements (1479 ± 13 BP) from Aix is 1380–1346 cal BP (1σ) (OxCal, v4.2). The strategy for dating gaseous samples could therefore be adjusted depending on the level of precision required for each individual sample and the amount of material available.

Choice of Optimal CO_2 Preparation

The preparation of samples using method 3 is very labor-intensive (overnight combustion is followed by around 3 hr of elaborate lab work for the preparation of one sample). However the collagen background suggests this may be the "cleaner" route of CO_2 preparation and further preparations using this method are planned for future tests. The larger data sets from methods 1 and 2 produced results in good agreement for the background cave bear bone and all four samples. The direct coupling of the EA to the gas ion source in method 1 reduces the time for combustion and isolation of collagen CO_2 to around 10 min per sample, reducing both time investment and minimizing handling steps (fully automated process with no sealing step). Considering the practicalities alongside the agreement of results between techniques in this study, method 1 is the preferable route of sample CO_2 isolation, allowing us to go from collagen to a high precision date in around an hour per sample (including a series of replicates and flushing).

CONCLUSION

We can now date gaseous samples of bone collagen of <100 μg C due to the improved design of the MICADAS hybrid ion source. Consistent agreement between replicate measurements in this preliminary study demonstrates the level of accuracy and precision that can be achieved using the gas ion source. The results here demonstrate the applicability of the method, particularly for Paleolithic bone samples, at least back to 40,000 BP. The directly coupled EA and gas ion source offer a fast, efficient method of sample preparation. This study opens the way for the direct dating of extremely precious and small archaeological bone objects.

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