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To Frank McManamon
w/best regards
Tom Stafford

Accelerator Radiocarbon Dating at the Molecular Level*

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Molecular level ^{14}C dating is the isolation of specific classes of molecules for their ^{14}C dating by accelerator mass spectrometry (AMS). Complex matrices such as fossil bone are difficult to date due to their extreme chemical heterogeneity. By isolating individual amino acids, contaminants (humates) are removed and crystalline amino acids result.

Bones with $\geq 0{\cdot}1$–$0{\cdot}2\%$ N and collagenous compositions can be dated accurately because structural collagen is present; contaminants are removable with XAD resin. Bones with $\leq 0{\cdot}1\%$ N and non-collagenous compositions yield dates hundreds to thousands of years too young because most of the preserved organic matter is exogenous. Accelerator ^{14}C dates on collagenous and non-collagenous bones are not comparable due to intrinsic dating inaccuracies.

AMS ^{14}C dating of amino acids demonstrated that (1) post 10,800 year ages for North American megafauna are due to sample contamination, not Holocene ages on extinct fauna, (2) a Clovis age (10,900 years) was established for a human fossil from the Anzick site, Montana, (3) Holocene ages cannot be established absolutely for many North American human fossils because the bones were non-collagenous, (4) accurate ages are attainable on vertebrate fossils as small as passerine birds from Pacific Island localities, (5) well preserved bones are datable without their destruction by extracting protein with water at high temperatures, and (6) stratigraphic anomalies to 45,000 years in European Upper Paleolithic rock shelters are recognizable by dating bone directly.

Keywords: AMS DATING, ^{14}C DATING, QUATERNARY EXTINCTIONS.

Introduction

Accelerator mass spectrometry (AMS) radiocarbon dating is revolutionizing our concepts of timing of geological and environmental events during the Late Quaternary

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Period. Since the development of AMS radiocarbon dating, scientists have enthusiastically accepted AMS dating because it requires 1 mg or less of carbon—1/1000 the mass needed for conventional (β-decay-counting) radiocarbon dating. Carbon-14 dating by AMS has enabled the analysis of specimens too small, too rare or too chemically impure for conventional ^{14}C measurement.

In this paper we summarize experiments at the molecular-level by using ^{14}C AMS to date individual amino acids and proteins from vertebrate fossils. Results are presented from five dating projects: (1) Late Pleistocene faunal extinctions in the New World, (2) ages for early human fossils in North and Central America, (3) establishing chronologies for Late Wisconsinan, New World vertebrate faunas, (4) dating human-caused avifauna extinctions on the Hawaiian Islands, and (5) applying bone dating techniques to Upper Paleolithic sites in Europe. Hypothesis for each topic have been debated for decades; the long-standing controversies may soon be resolved by employing molecular-level radiocarbon dating techniques.

Historical background

Conventional radiocarbon dating, as developed by Libby (1955), measures the β^- particles emitted during the decay of ^{14}C atoms. This indirect measurement of ^{14}C is done commonly by either liquid scintillation or gas proportional counting. In contrast, accelerator ^{14}C dating directly counts the number of ^{14}C atoms present in a sample. Compared to conventional ^{14}C dating, direct counting of ^{14}C by AMS decreases measurement times from weeks to <1–2 h, and lowers sample size requirements by a factor of 1000 and theoretically extends age measurements to $>60{,}000$ years.

The feasibility of radiocarbon dating by accelerator mass spectrometry was first suggested independently by Purser (Purser, 1976; Purser *et al.*, 1977, 1979) and Muller (1977). AMS ^{14}C dating was first demonstrated by Bennet *et al.* (1977), Nelson *et al.* (1977) and was developed quickly by others (Bennett *et al.*, 1978; Purser *et al.*, 1977, 1979; Muller *et al.*, 1978; Bennett, 1979; Gove *et al.*, 1979, 1980, 1987; Muller, 1979; Stephenson *et al.*, 1979; Hedges & Gowlett, 1986). The present state of AMS dating for several radioactive isotopes has been reviewed by Elmore & Phillips (1987). Instrumentation and ^{14}C applications are compiled in conference proceedings (Currie & Klouda, 1982; Stuiver & Kra, 1983, 1986*b*; Wölfli *et al.*, 1984; Gove *et al.*, 1987; Litherland *et al.*, 1987).

AMS dating has fostered novel applications for measuring ^{14}C and include: foraminifera from deep sea cores (Andrée *et al.*, 1986*b*; Duplessy *et al.*, 1986), atmospheric particles and gases (Klouda *et al.*, 1986; Lowe *et al.*, 1988*a*; Currie *et al.*, 1987), textiles (Donahue *et al.*, 1987), archaeological seeds (Betancourt *et al.*, 1984; Conard *et al.*, 1984; Wendorf *et al.*, 1984), meteoritic carbon (Donahue *et al.*, 1983), glacial ice CO_2 (Andrée *et al.*, 1986*a*) oceanic dissolved CO_2 (Schlosser *et al.*, 1987) human skeletons (Taylor *et al.*, 1985; Stafford *et al.*, 1984; Bada *et al.*, 1984; Gowlett, 1986; Stafford & Tyson, 1989), animal fossils (Gowlett & Hedges, 1986; Mead *et al.*, 1986; Emslie, 1987; James *et al.*, 1987), plant fossils (Andrée *et al.*, 1986*c*; Van Devender *et al.*, 1985) and insect fossils (Elias & Toolin, 1990).

Several types of samples are extremely difficult to date, regardless of whether conventional or accelerator methods are used. These materials are chemically heterogeneous and often consist of carbonaceous fractions having multiple origins. Examples include soils, sediments, fresh and marine waters, atmospheric particulates, and bone and shell fossils. Dating these materials often remains an intractable problem because pure chemical phases are difficult to isolate from heterogeneous matrices.

The potential of the AMS method is achieved when organic chemistry and accelerator physics are combined. Dating accuracy is improved by removing trace contaminants, by isolating specific, indigenous molecules, and by understanding diagenetic pathways.

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Research is progressing rapidly in molecular-level studies (Currie *et al.*, 1989) and includes ^{14}C measurements on individual gas species such as atmospheric carbon monoxide, methane, and carbon dioxide (Klouda *et al.*, 1986; Lowe *et al.*, 1988*a*), classes of polycyclic aromatic hydrocarbons (PAHs) from airborne particulates (Currie *et al.*, 1986; Sheffield, 1988); lacustrine lipids (Giger *et al.*, 1984; Fowler *et al.*, 1986; Lowe *et al.*, 1988*b*), groundwater humates (Murphy *et al.*, 1989) and individual amino acids from fossil bones (Gillespie *et al.*, 1984, 1986; Gowlett & Hedges, 1986; Stafford *et al.*, 1987, 1988; Stafford & Tyson, 1989).

Accelerator ^{14}C measurements

The accelerator mass spectrometric measurement of ^{14}C begins by converting the sample into CO_2, then into graphite (Slota *et al.*, 1987) or Fe-C targets (Verkouteren *et al.*, 1987). The targets are mounted in a 10-position target wheel containing two standards, oxalic acid I (OX-I) and oxalic acid II (OX-II). Internal corrections are made assuming the accepted ratio of 1·291 for OX-II/OX-I. Accelerator physics and ^{14}C measurement at the University of Arizona are reviewed in Donahue *et al.* (1983), Zabel *et al.* (1983), Linick *et al.* (1986), and Donahue *et al.* (1987, 1990).

Measurement of ^{14}C by the accelerator mass spectrometer age calculations: The ^{14}C age of a sample is calculated from the formula

$$t = -T\ln(A/A_0)$$

where:

t is age in radiocarbon years for the Libby half-life
T is the mean life of ^{14}C ($T=8033$ for the "Libby" half-life of 5568 years)
A_0 is the initial activity of ^{14}C at 0 BP (1950 AD), corrected to $\delta\,^{13}C = -25‰$.
A is the sample's present ^{14}C activity, corrected to $\delta\,^{13}C = -25‰$.

Corrections to the ^{14}C age include adjustments for (1) natural isotopic fractionation ($+80$ to -400 years), (2) isotopic fractionation that occurs during graphitization of CO_2 ($\sim 1 \pm 1‰$) and (3) secular variations in atmospheric ^{14}C production (-100 to $+800$ years) (Stuiver & Kra, 1986*b*).

Isotopic fractionation results when the $^{13}C/^{12}C$ ratio of a compound changes during physical, chemical or biochemical transformations in nature. The $^{13}C/^{12}C$ ratio is expressed relative to a standard [Pee Dee Belemnite (PDB); Craig, 1953, 1957] and is denoted as $\delta^{13}C$. The formula is:

$$\delta^{13}C = [(^{13}C/^{12}C \text{ sample})/(^{13}C/^{12}C \text{ standard}) - 1] \times 1000‰.$$

Biological materials are depleted in ^{13}C relative to the PDB standard and have more negative $\delta^{13}C$ values. Because ^{14}C dates are normalized to wood having a $\delta^{13}C = -25{\cdot}00‰$ PDB, samples having $\delta^{13}C$ values more positive than $-25‰$ will measure younger than their true age. The measured ^{14}C age differs from the true age by 2% of the mean life of ^{14}C (8033) for each 10‰ difference between the sample and wood ($-25‰$). Because individual amino acids have $\delta^{13}C$ values that range from at least -20 to -5 PDB‰ (Hare & Estep, 1983; Macko *et al.*, 1987), their ^{14}C ages would be 80–320 years too young without a $\delta^{13}C$ correction. Many AMS laboratories measures $^{14}C/^{13}C$ instead of $^{14}C/^{12}C$, thus the fractionation effect is 1% instead of 2% of 8033.

Dating accuracy and precision: The accuracy and precision of the AMS radiocarbon measurements depend upon accelerator physics and sample pretreatment, and the sample's geochemical history, which is discussed separately. The primary components of

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Table 1. Reproduction of computer data sheet for AMS ^{14}C measurements on two standards and one blank graphite sample at the University of Arizona AMS facility

	Standards			Sample				
	1	2						
Target no.:	V3586A	V3553D		Target no.: 87NBS-262				
Material:	OXI	OXII		Sample no.: AA-2936				
^{12}C current:	9·5 μA	9·1 μA		^{12}C current: 7·8 μA				
Wheel position:	1	6		Wheel position: 2				
Run	Counts	14/13	Modern		Run	Counts	14/13	SPL/MOD ± ERR
16,371	8568	18·31	17·49					
				17·61	16,732	5	0·01	0·000 0·000
16,376	10,753	23·91	17·71					
16,381	7974	18·84	18·00					
				17·84	16,382	3	0·00	0·000 0·000
16,386	10,507	23·92	17·72					
16,391	7313	18·97	18·12					
				17·70	16,392	9	0·02	0·001 0·000
16,396	10,519	23·52	17·42					
16,401	7195	18·03	17·22					
				17·40	16,402	3	0·00	0·000 0·000
16,406	9628	23·66	17·53					
16,411	7258	18·73	17·89					
				17·66	16,412	3	0·00	0·000 0·000
16,416	8702	23·59	17·48					
Weighted mean				17·64			0·00	0·000
S.D. MEAN (SCAT)				0·07			0·00%	0·000
% S.D. SCAT				0·41			18·27	18·28%
SUM ^{14}C 88417						23		
% S.D. STAT				0·34%			20·85%	20·85%
Blank factor							−8·151	
Blank sigma							42·58%	

Blank correction basis: contemporary (14/13) = 20·82
Fraction contemporary = 0·0035 +/− 0·0015
Larger error (statistical) in fraction modern: 47·41%
^{13}C-corrected fraction modern = −0·004 +/− 0·002 ^{14}C age BP = 44,470 years.

accuracy and precision are counting statistics, the machine background (^{14}C contributed by the accelerator, mass spectrometer and ion source components), the blank (mass of carbon contributed by sample pretreatment and combustion) and the quality of the graphite or Fe-C target.

The background, blank and limiting ages: The oldest dates that can be reached through radiocarbon measurement are limited by sample size, detection efficiency, and the blank. For AMS, the maximum sample size is ~2 mg of carbon; detection efficiency is controlled by target quality, which is routinely excellent. The blank derives from several sources and its minimization is the aim of much development work.

To examine quantitatively this issue, we refer to Tables 1 and 2. Table 1 is a reproduction of a University of Arizona AMS computer output for results on an atomic absorption graphite blank (National Carbon Graphite). Table 2 contains results derived from Table 1. The ^{14}C signal from the machine blank is 0·06% of that from the standard (4·6/7331 ^{14}C counts); the Fe-C blank is smaller by a factor of 3·5. [Note that the ^{14}C atom

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Table 2. AMS ^{14}C results for selected blanks

	^{14}C counts/cycle	^{12}C (μA)	counts/ (μA × cycles)	f_M	Run no.
Fe-C targets (composite)	8/6 = 1·33 (*c.* 1·6 cpm)	0·005 (Average)	267	0·36*	AA-2680, 2681 -2682, 2683
NC-Graphite	23/5 = 4·6	7·8	0·59	0·00081†,‡	AA-2936
SRM-4990B [OX-I]	7331/1	9·5	770	1·05§	AA-2936

*The 90% confidence interval for f_M, based on "normal" counting statistics, is 0·15 to 0·58; because there are only eight counts, the correct (Poisson) interval is 0·18 to 0·66.
†This is equivalent to a blank of 1·4 μg contemporary (1987 AD) carbon dispersed in a target whose carbon mass is 2 mg.
‡The 90% (normal counting statistics) confidence interval for f_M is 0·00053 to 0·00108, The Blank Equivalent Age is 57,200 BP. The University of Arizona blank quoted in Table 1, 0·0035 contemporary carbon (f_M = 0·0030) gives BEA = 46,800 years. The U of A blank differs in two important respects: it is based on a more extensive data set, and it derives from a different sample preparation system.
§By definition, f_M of OX-I is 1·05.

counting rate from the Fe-C is comparable to the typical AMS "machine blank" (Currie *et al.*, 1985, 1989)]. These results are typical to the extent that chemical blanks nearly always exceed machine plus target blanks, and thus set the basic (upper) limit to ages that may be altered by ^{14}C AMS.

The next three columns of Table 2 include ^{12}C ion current data for calculating average fraction-of-modern carbon (f_M) for each of the samples. The average value for the 2 mg NC-graphite blank is ~0·1% modern, whereas intrinsic Fe-C plus machine blank carbon is relatively young (upper limit *c.* 66% modern). This leads to a very important point—the observed f_M is averaged over all carbon in the sample, which is 10^3 times greater for the NC-graphite blank. This is a crucial difference for small sample dating, as seen below. Also, for understanding and controlling the chemical blank, it is important to recognize that the mass of the actual blank carbon is often much less than the mass of sample carbon within which it is dispersed. For large sample (> 1 mg of C) AMS dating it is generally unnecessary to know f_M for the carbon added during processing. This is not true for small-samples (50–500 μg).

Detection (age) limits for large sample dating: Conventional AMS dating utilizes 1–4 mg C targets, therefore the average blank treatment discussed above is satisfactory. One measures f_M for the chemical blank distributed throughout the ancient carbon host, and this quantity is used directly for the dating-blank correction.

In assessing the influence of the blank on dating limits, two quantities are defined: (1) the Blank Equivalent Age (BEA) [or, Blank Equivalent Mass of carbon (BEM)], and (2) the statistical age detection limit (A_D)—the maximum "detectable" age (Currie, 1973, 1988; Currie *et al.*, 1989). For the NC-graphite blank, the f_M value = 0·00081, which yields a blank equivalent age of 57,200 years BP; assuming a 2 mg carbon target, the blank equivalent mass is 1·4 μg contemporary carbon. If systematic error bounds for the blank f_M are ± 50%, the systematic uncertainty for the blank equivalent age would be +5600, −3300 radiocarbon years and a mass of ± 0·7 μg modern carbon.

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The statistical blank-based, age detection limit (A_D) must take into account random counting (Poisson) error, as well as that related to blank random variability. If we take the mean blank (f_M) to be 0·00081, with a Poisson σ of 0·00017 (based on 23 counts), then the critical value for judging the detectability of a net signal would be 0·00040. The detection limit is approximately twice the critical value, or 0·00080, which is an age of 57,300 years for the maximum (statistically) detectable radiocarbon age, fortuitously similar to the BEA, and the maximum (statistically) detectable radiocarbon age. Lest this seem too good, it must be remembered: (a) that the calculation is based on the single blank which appears in the table—in practice continuing blank quality control data should be used; and (b) that this blank was prepared as part of a programme designed for ultra low contamination levels, to be applied to "molecular dating" of 50–500 μg carbon. The point is that the maximum detectable age is *not* just dependent on method (AMS) and accelerator, it is crucially dependent on the chemical blank deriving from the particular sample preparation reagents and facility.

An example of the chemical blank's effect are ^{14}C measurements on graphite before and after chemical pretreatment. NC-graphite having no chemical preparation has an $f_M = 0{\cdot}081\%$ (BEA = 57,200 years). NC-graphite that is combusted and converted back into graphite has $f_M = 0{\cdot}4\%$ modern (> 49,000 years). This indicates that 4 μg of modern carbon are introduced as a chemical blank.

Detection limits for small-sample dating: The mass *and* isotopic composition of the chemical blank must be known when small samples are dated because the mass of a carbon blank becomes proportionately large in small (50–500 μg C) samples. For example, compare the effect of the same amount of contemporary carbon blank (1·4 μg contemporary carbon) in a 200 μg target as was in the 2000 μg (2 mg) target. The Blank Equivalent Mass would be unchanged (by definition) but the average f_M in the 200 μg target would be increased 10-fold, resulting in a blank-equivalent-age of 38,700 years.

Characterizing the chemical blank is not trivial. It requires measurement of both masses ^{12}C and ^{14}C. The optimal method is direct measurement—collection of sufficient chemical blank carbon to permit its ^{14}C to be determined by AMS. An indirect method is based on non-linear least squares fitting of a series of ancient and modern (or known age) samples of varying mass to the appropriate contamination model (Klouda *et al.*, 1984; Donahue *et al.*, 1990).

Both methods have been employed at the National Institute of Standards and Technology (NIST). The conclusion was that chemical blank carbon is approximately contemporary, i.e. has the same ^{14}C composition as contemporary atmospheric CO_2. Chemical blanks will not necessarily always be contemporary carbon, especially when the pretreatment methods include organic solvents derived from petroleum. The mass of the processing blank carbon (for the NIST laboratory) was about 15 μg in 1984; subsequent improvements in microchemical processing have lowered this to ~2 μg carbon (Verkouteren *et al.*, 1987; Currie *et al.*, 1989). Thus, the blank equivalent ages for 50 μg and 500 μg carbon samples would be *c.* 26,000 years and 44,000 years, respectively.

Radiocarbon Dating of Fossil Bone

The accurate dating of bone will have major impacts on the study of human evolution, and Late Quaternary paleoecology and biogeography. Bone is frequently the only datable material in a geologic deposit and if the fossils are not reworked sedimentologically, it is the only material that directly dates the geologic event. Stratigraphic correlations based on sedimentology, climatic zonation, and artifact typologies are imprecise because the dating is secondary and depends on the accuracy of dates at a type locality. Associated

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charcoal, wood, and plant macrofossils can be displaced physically by bioturbation, cryoturbation, human interference, and sedimentary reworking.

The advantages of directly dating bone were often negated by inaccurate results. Beginning with Libby (1955) and continuing to the present (De Vries & Barendsen, 1954; Münnich, 1957; Tamers & Pearson, 1965; Meltzer & Mead, 1983; Stafford *et al.*, 1988), bone dates have ranked among the most unreliable of all radiocarbon measurements. The problems are due to fossil bones' heterogeneous chemistry and the kg-quantities of bone needed for dating. Unless fossils were well-preserved and relatively contaminant-free as in Arctic environments and dry caves, dates were often inaccurate. Incorrect ages were due to contamination by sediment-derived humates remaining after chemical pretreatments (Stafford *et al.*, 1988). Isolating chemically-specific fractions would have required five to 20 times more bone, an impossible requirement in most archaeological and paleontological applications. The situation actually worsened when AMS dating was applied to small, poorly preserved fossil bones. With exceptions (Gowlett, 1986; Gowlett & Hedges, 1986; Stafford *et al.*, 1988) it was not emphasized that well-preserved and poorly-preserved fossil bones had intrinsically different chemistries and that ^{14}C measurements on each fossil type did not have equal validity. Also misunderstood was the idea that conventional sample pretreatment methods could be scaled-down and the samples dated by AMS methods. AMS ^{14}C dates were considered more accurate than conventional ones because AMS dating was used, not because more chemically-pure fractions were dated.

What led eventually to accurate dating of bone was the suggestion by Ho *et al.* (1969) that a collagen-specific amino acid be dated. The amino acid is hydroxyproline, a secondary amine also termed an imino acid. Hydroxyproline's abundance in bone collagen and its relative rareness elsewhere in nature were justification for its use. Although ^{14}C dating of hydroxyproline has not become a panacea for fossil bone dating, the molecular-level approach was successful. When hydroxyproline was first isolated from fossil bone (Wand, 1981) and AMS radiocarbon dated (Gillespie *et al.*, 1984; Gowlett & Hedges, 1986), ^{14}C ages on hydroxyproline and proline were concordant with ages on total amino acids from hydrolysed bone collagen. Dates on combined imino acids (proline plus hydroxyproline) were similar to the known, 11,000 year age of a collagenous-composition mammoth fossil (Stafford *et al.*, 1987). In subsequent experiments, aspartic and glutamic acids, glycine, serine, and threonine were isolated from poorly preserved, non-collagenous bone (Stafford *et al.*, 1988). The results of these experiments were unexpected. Each of the individual amino acids measured several thousand years younger than the specimen's known age of 11,000 years.

The following experiments are a further examination of ^{14}C dating on individual amino acids isolated from bones of varying degrees of preservation and from diverse geologic and archaeological contexts.

Bone Chemistry

Bone consists of a carbonate hydroxyapatite mineral phase (dahllite) constituting 80% of the bone mass. Its 4–6% weight of indigenous carbonate (Hassan, 1976) is extracted by hydrolysing bone powder with HCl or H_3PO_4. The resulting carbon dioxide is used for ^{13}C and ^{14}C measurements. Despite considerable effort to remove exogenous carbonates and to isolate indigenous bone carbonate, (Hassan, 1976; Hassan *et al.*, 1977; Sullivan & Krueger, 1981; Haas & Banewicz, 1980) the bone apatite phase remains contaminated frequently with secondary carbonate (Stafford *et al.*, 1987) and we consider it to be unacceptable for isotopic analysis.

The remaining 20% weight of bone is the organic fraction comprising approximately 88% collagen, 8–9% glycoproteins, and 3–4% non-collagenous proteins such as osteocalcin and osteonectin and a remainder of peptides, lipids and bone sialoprotein (Urist

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Table 3. Amino acid and % nitrogen analyses for fossil bones. Analyses compare bones with collagenous amino acid compositions to those with non-collagenous amino acid compositions

Sample	Modern bone	Sigma bovine collagen	Dent	Domebo	Escapule	BLM mammoth	Murray Springs mammoth	Del Mar sphenoid	Del Mar tibia	Tepex-pan	Gelatin Anzick white	Gelatin Anzick Fe	Whole bone Pyramid lake camel	H_2O extract Pyramid lake camel	Extracted bone Pyramid lake camel	Whole bone Grotte XVI 162 cm
% N (whole bone)	4·5	15·64	0·83	0·69	0·03	0·01	0·03	0·69	0·06	0·06	—	—	2·95	—	0·53	1·73
Amino acid Residues ‰																
Hydroxy-proline	90	90	91	84	0	0	0	95	0	0	97	89	91	68	55	95
Aspartic acid	53	47	48	54	293	218	223	47	132	244	46	45	49	2	18	48
Threonine	19	17	19	23	29	45	32	17	32	38	17	18	21	10	10	19
Serine	35	31	36	37	0	50	42	29	49	36	29	35	32	0	0	28
Glutamic acid	71	73	71	73	131	150	174	78	111	81	75	76	78	109	78	77
Proline	124	114	124	123	41	0	0	121	74	0	117	113	118	162	113	124
Glycine	322	338	327	322	279	236	189	342	276	359	334	326	323	350	561	346
Alanine	89	113	123	124	84	97	89	118	126	53	114	112	101	169	90	115
Valine	27	26	27	30	12	30	38	31	37	0	24	28	27	37	20	21
Methionine	7	7	5	7	0	29	14	5	0	40	21	10	8	10	1	3
Isoleucine	14	12	11	12	28	32	19	10	37	36	11	11	10	6	4	11
Leucine	32	26	27	33	29	44	36	24	46	40	26	26	27	35	26	24
Tyrosine	6	4	1	5	5	0	0	0	2	10	0	3	4	6	0	0
Phenylalanine	16	20	14	17	13	0	15	7	26	19	18	17	17	24	10	12
Histidine	5	4	2	4	0	0	17	2	1	0	2	5	5	3	1	6
Hydroxy-lysine	5	16	0	0	4	0	0	13	5	5	8	9	6	3	2	4
Lysine	28	21	28	29	51	68	54	30	13	26	27	30	34	7	11	21
Arginine	56	39	44	22	0	0	58	30	32	13	33	47	49	0	0	46
Total	999	998	998	999	999	999	1000	999	999	1000	999	1000	1000	1001	1000	1000

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Sample	Whole bone Grotte XVI 166 cm	Whole bone Grotte XVI 174 cm	Whole bone Grotte XVI 233 cm	H_2O extract Grotte XVI 233 cm	Extracted bone Grotte XVI 233 cm	Whole bone Grotte XVI 293 cm	Whole bone Grotte XVI 301 cm	H_2O extract Grotte XVI 301 cm	Extracted bone Grotte XVI 301 cm	Whole bone arctic whale	Gelatin arctic whale	Whole bone Krapina rhino
% N (whole bone)	2·38	1·03	0·67	—	0·07	1·58	0·89	—	0·20	4·76	—	0·08
Amino acid Residues ‰												
Hydroxyproline	104	88	89	167	54	90	88	84	47	87	88	103
Aspartic acid	46	52	51	0	62	49	51	6	89	48	47	49
Threonine	19	18	18	9	5	18	18	10	7	25	25	17
Serine	29	28	33	0	3	29	28	3	5	38	37	30
Glutamic acid	76	77	77	116	150	77	78	76	137	75	75	76
Proline	118	122	127	208	78	127	128	154	82	113	116	112
Glycine	331	337	335	241	428	328	329	378	402	332	331	343
Alanine	111	116	120	114	79	120	121	155	92	103	105	117
Valine	24	22	23	39	33	21	20	29	29	22	22	20
Methionine	9	5	2	0	29	5	3	11	2	6	7	31
Isoleucine	11	14	10	10	9	14	15	13	18	12	12	14
Leucine	24	28	24	34	28	26	28	32	41	26	25	22
Tyrosine	0	1	0	0	0	0	5	1	7	4	4	0
Phenylalanine	16	14	12	15	6	12	16	16	23	16	18	7
Histidine	1	7	3	9	17	9	1	2	5	4	5	18
Hydroxylysine	15	1	2	14	10	1	9	5	1	9	8	9
Lysine	30	22	31	6	7	27	18	6	7	27	26	19
Arginine	33	47	46	9	1	46	43	19	6	53	51	20
Total	997	999	1003	1001	999	999	999	1000	1000	1000	1002	1001

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et al., 1983; Termine, 1986). The characteristic amino acid composition of modern bone is that of collagen, a protein containing 33% glycine, 9% 4-hydroxyproline, 11% proline, 7% aspartic acid, 9% glutamic acid and 5% hydroxylysine, in addition to 12 other amino acids (excluded is the 0·1% from the 3-hydroxyproline isomer) (Table 3). During diagenesis, the collagenous composition predominates until approximately 5% of original protein remains. Below 5% protein content, which represents approximately 0·2% N in whole bone, a non-collagenous amino acid composition begins to predominate and is characteristic of severely altered bone (Table 3). A non-collagenous composition is exemplified by total loss of hydroxyproline and often proline, a decrease in glycine from 33–20%, and two-to-three-fold increases in abundances of aspartic and glutamic acids (Wyckoff, 1972; Hare, 1974, 1980; Kessels & Dungworth, 1980; Armstrong *et al.*, 1983; Stafford *et al.*, 1988).

The original idea to use hydroxyproline as a collagen-specific amino acid for radiocarbon dating (Ho *et al.*, 1969) was valid. Hydroxyproline's relatively high abundance in bone and the amino acid's relative rarity elsewhere in nature were the principal factors favouring hydroxyproline over other amino acids.

Hydroxyproline occurs in collagen—a connective tissue present in all vertebrate and invertebrate phyla (Adams, 1978; Adams & Frank, 1980; Hunt, 1970)—and in several non-collagenous vertebrate and invertebrate proteins (Hunt, 1970; Kuttan & Radhakrishnan, 1973). Extensin in plant cell walls is the most common non-animal source of hydroxyproline (Kuttan & Radhakrishnan, 1973; Sadava *et al.*, 1973; Rosenthal, 1982); other plant sources of hydroxyproline are less common (White *et al.*, 1978). Chemically bound and free hydroxyproline is present in soils and aqueous environments, where hydroxyproline and other amino acids are often associated with humate phases (Bremner, 1950; Thurman, 1985).

Hydroxyproline is not the absolute answer to bone radiocarbon dating problems for one reason—hydroxyproline is almost always absent in the fossils requiring the most rigorous age-testing. Simultaneous radiocarbon dating of hydroxyproline and proline is an elegant technique, because hydroxyproline is synthesized *in vivo* by hydroxylation of proline (Udenfriend, 1966; Kaska *et al.*, 1987). Consequently, proline and hydroxyproline should have identical $^{14}C/^{12}C$, $\delta^{13}C$, and $\delta^{15}N$ values. If isotopic analyses on the two amino acids were identical, it would be evidence that proline and hydroxyproline were indigenous and that the radiocarbon age was correct. Simultaneous dating of proline and hydroxyproline is not possible for non-collagenous composition bones because hydroxyproline is commonly absent (Table 3).

Based on experimental results, the best approach for dating of fossil bone is measuring radiocarbon in highly purified, total-collagen hydrolysates and verifying this age with dates on individual amino acids.

Chemical Methods for Isolating Bone Protein and Amino Acids

Methods for isolating organic fractions from fossil bone follow those in Stafford *et al.* (1988) as modified below. The goal is to obtain an XAD-purified hydrolysate, the minimum level of purity acceptable for dating by ^{14}C. Individual amino acids are isolated only from XAD-purified hydrolysates.

Physical pretreatment and decalcification

Moderately-well and better preserved cortical bone is demineralized without grinding, thereby increasing protein yield. Small animal bones are left intact, whereas large animal bones are broken into 1–2 cm fragments. Extremely-poorly-preserved bones are powdered and washed extensively in water. Soxhlet extraction with acetone, methanol, petroleum ether or ethanol is used if acetone or alcohol-soluble preservatives or petroleum

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residues exist. In every procedure, carbon contamination from reagents and glassware is minimized by distilling solvents and heating Pyrex glassware 3 h at 550°C.

Bones with <0·2% N are decalcified with 0·2–0·3 *N* HCl whereas 0·6 *N* HCl (where *N* = normal) is acceptable for bones with >0·3% *N*. All decalcifications are done at approximately 4°C. The decalcified residue is lyophilized before further treatment.

Hot water extraction ("gelatinization")

Extracting the decalcified residue with hot water can cause losses of 50% or more of recoverable fossil organic matter; however, the step eliminates clastic sediments and plant detritus. Gelatinization lowers the concentration of humates, which when hydrolysed, would release amino acids that are often complexed to humic and fulvic acids (Thurman, 1985).

Approximately 100–150 mg of lyophilized, decalcified bone are extracted with 2–4 ml of pH 3 H_2O in a N_2-purged, sealed tube at 90°C for 6 h. The soluble phase is passed through 0·45 μm Millipore HV filters and lyophilized. Gelatinization at lower temperatures (58°C) increases yields of the high-molecular weight fraction (Brown *et al.*, 1988) and may also prevent dissolution of exogenous compounds during subsequent hydrolysis. The efficacy of lower-temperature water extraction on moderately-well to poorly preserved fossil bones has not been assessed. The gelatinization step is eliminated for poorly preserved fossil bones because <10% of the decalcified residue is soluble in hot water.

Hydrolysis

The fossil protein is hydrolysed to free amino acids by digesting the decalcified residue or gelatin fraction with 6 *N* HCl for 24 h at 110°C. After filtering the hydrolysate, the supernatant is passed through XAD-resin. The solid, non-hydrolysable residues (humins) are washed with distilled water and lyophilized.

XAD-2 chromatography of the protein hydrolysate

Humates are removed from the hydrolysate by passing the 6 *N* HCl solution through a column of 100–200 μm, Serva XAD-2 resin (Stafford *et al.*, 1988). Approximately 100 g of dry resin are wetted with acetone, then washed extensively with distilled water, and stored in 0·5 *N* HCl. Individual columns are made by pouring 1–3 ml of resin into 5 ml syringes that have 0·45 μm Millex filters attached at the base. After the hydrolysate elutes, the resin is washed with three bed volumes of 6 *N* HCl, which is added to the first eluate. The eluate is dried to a viscous syrup by vacuum-vortexing at 50–60°C.

Chromatographic isolation of individual amino acids

Individual amino acids are isolated from the XAD-purified hydrolysate by using a 9 mm I.D. × 360 mm long column of 10 μm cation exchange resin. Approximately 50–100 mg of XAD-purified amino acids are diluted with 0·05 *N* HCl and injected onto the cation exchange column. The individual amino acids are eluted with HCl whose molarity increases in approximately 0·5 *N* steps from 0·5 *N*–3 *N* HCl (Figure 1). The amino acids elute in 2–20 ml of HCl depending upon their retention times and are detected by UV absorbance at 214 nm. The eluates are dried to crystalline amino acid hydrochlorides by using a vacuum-vortex.

Target Preparation

Approximately 10 mg of sample carbon are combusted in evacuated Vycor tubes that contain 1 g of purified CuO and 0·5 g of Cu^0. Combustion reagents were ultrapurified to eliminate carbon contribution from CuO and Cu^0. Approximately 200 g of commercial CuO wire was combusted at 800°C for 3 h, then transferred to a 5 cm diameter Vycor tube

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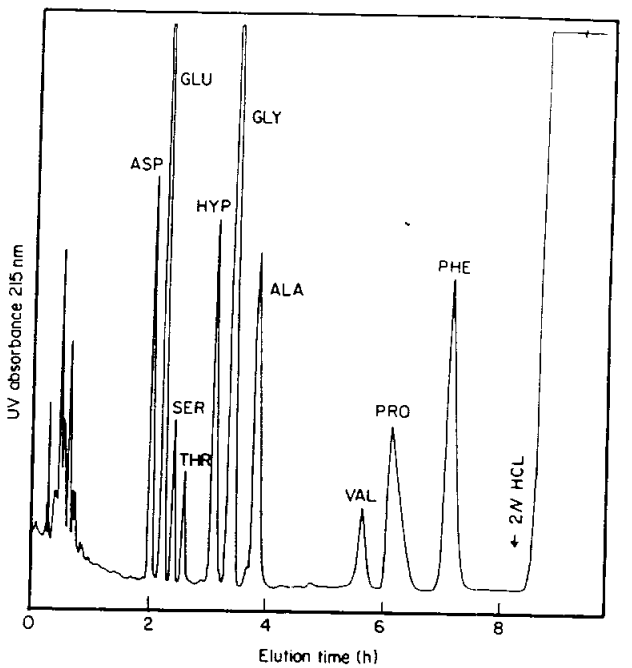

Figure 1. Chromatogram of amino acids from >70,000-year-old Arctic whale. Individual amino acids were isolated from the collagen hydrolysate by injecting 500 µl of 0·05 *N* HCl hydrolysate containing 50 mg of total amino acids onto a 9 × 360 mm column of 9·5 ± 0·5 µm cation exchange resin heated to 70°C. Elution was with 0·6 *N* HCl at 0·6 ml min^{-1}. Amino acids were detected by their UV absorbance at 215 nm. After the elution of phenylalanine, the eluant changed to 2 *N* HCl, which eluted rapidly the remaining amino acids. Abbreviations: ASP, aspartic acid; GLU, glutamic acid; SER, serine; THR, threonine; HYP, hydroxyproline; GLY, glycine; ALA, alanine; VAL, valine; PRO, proline; PHE, phenylalanine.

enclosed in a muffle furnace. The combustion tube was connected to flowing, 99·999% pure O_2 and the CuO combusted for 3 h at 800°C; the CuO was cooled to room temperature with a positive pressure of flowing, purified O_2. The ultra-pure CuO was stored in individual vials under He in a glove box. Purified Cu^0 was made by reducing the ultra-pure CuO with 99·999% H_2 at 300°C for approximately 5 h. Carbon derived from the combustion of 1 g CuO and 0·5 g of Cu^0 was ⩽0·1 µg.

Purified CO_2 was converted to graphitic carbon (Slota *et al.*, 1987). Smaller amounts of CO_2 (<300 µg C) were converted to Fe-C beads by the Verkouteren *et al.* (1987) technique. The reduction reaction was diminished significantly if the combusted samples contained chlorides. Chlorides were eliminated by purifying CO_2 with 1 g of Cu^0 in a sealed Vycor tube at 300°C for 24 h.

Experiments in the ^{14}C Dating of Fossil Bones from Diverse Geological Localities

Late Pleistocene extinctions in the New World

By approximately 11,000 years ago in the New World, 32 genera of large animals in North America and 47 general in South America, became extinct (Martin & Klein, 1984). Extinction of the horse, camel, mammoth, mastodon, ground sloth and sabertooth cats,

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among others, has been attributed to either climatic change at the end of the Pleistocene epoch (*c.* 12,000–11,000 years BP) or over-hunting by the newly-arrived humans in the Americas *c.* 11,500 years BP. The temporal coincidence of human arrivals and megafaunal extinctions is used to support the concept that humans caused the extinctions (Martin, 1984). Proponents of environmental causes of megafauna extinctions (Webb, 1984; Graham & Lundelius, 1984; Guthrie, 1984) consider the 11,000 years BP event the most recent of several extinctions occurring during the last 10 my. The principal fact is the extinction's rapidity—in conformable sedimentary sequences, Pleistocene-age Rancholabrean faunas disappear and are replaced by Holocene faunas within a few hundred ^{14}C years.

A major goal is determining the exact timing of extinction by using stratigraphy and radiocarbon dating. Fine-scale stratigraphic work established precisely the age of the Clovis culture and its associated extinct animals (Haynes, 1984, 1987). When stratification is poorly developed or carbonaceous samples are rare, vertebrate fossils must be dated to establish and corroborate extinction chronologies. Discovering causes for Late Pleistocene extinctions is hampered by a lack of accurate radiocarbon dates, which for Clovis sites are predominately from charcoal, wood, or charred plant remains (Haynes, 1987). Theoretically, direct dates on fossils would eliminate problems of stratigraphic association and would establish the time-of-death for each animal; however, the inaccuracy of bone ^{14}C dates prevented chronologies from being based directly on the fossils. An example of dating problems for bone are Holocene-age radiocarbon dates determined on extinct faunas that are dated stratigraphically as Pleistocene (Hester, 1960; Kurtén & Anderson, 1980).

Holocene ages for extinct mammalian megafauna can be due to (1) inaccurate radiocarbon dates, (2) the extinction event postdated humans arriving in the New World *c.* 11,500 years, and (3) individual species went extinct over hundreds to thousands of years because some species were less vulnerable to extinction or some species survived in refugia. These hypotheses are testable by molecular-level AMS dating of fossil bone (Stafford, 1988) and can establish (1) the time-of-extinction for each major species, (2) whether or not the extinction of all species was contemporaneous, and (3) was the extinction coeval with the earliest appearance of humans?

Experiments on known-age bone

Before unknown-age fossil bones could be dated, causes of dating inaccuracies had to be understood. The best technique is dating known-age fossils and comparing their ages to those for different chemical fractions. Known-age mammoth fossils were selected from three North American Clovis sites—Domebo, Oklahoma (Leonhardy, 1966); Dent, Colorado (Haynes, 1974); and Escapule, Arizona (Hemmings & Haynes, 1969). Two additional sites in Arizona were used—the BLM mammoth site, which is in the same valley and geologic stratum as the Escapule mammoth, and the Murray Springs site, which yielded a 26,000 years BP mammoth. Clovis-age mammoth bones were used for two reasons: (1) the fossils were dated independently to 11,500–11,000 years BP (Haynes, 1984, 1987), and (2) the bones were old enough that trace-levels of modern-carbon contamination would significantly affect the ^{14}C age (Olson & Broecker, 1958; Grootes, 1983). Samples a few thousand years old are too insensitive to modern carbon contamination and are poor tests of pretreatment methods. Because diagenesis substantially affects dating accuracy, fossils with different degrees of preservation and contamination were selected: the Domebo and Dent mammoths had collagenous compositions. The Escapule, BLM and Murray Springs mammoths had a non-collagenous composition and were very poorly preserved (Table 3).

Figures 2–4 and Tables 2–4 summarize dating results for the known-age mammoths. The data show the accuracy achieved by dating individual amino acids and explain why

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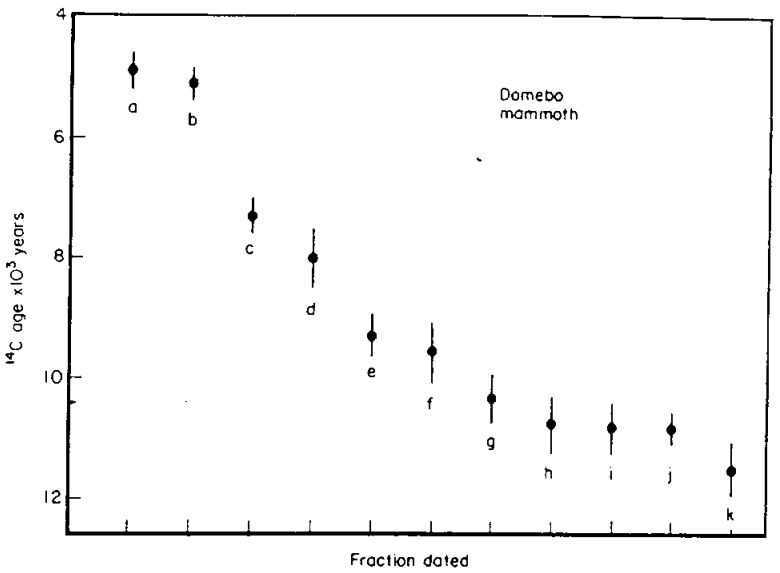

Figure 2. Domebo mammoth AMS radiocarbon dates arranged in order of increasing geologic age. Sample descriptions including Arizona Accelerator laboratory numbers: (a) fulvic acids (AA-812); (b) fulvic acids (AA-819); (c) untreated bone hydroxyapatite (AA-818); (d) total carbon, untreated bone (AA-801); (e) HAc-treated-bone apatite (AA-815); (f) Weak-acid soluble carbon (AA-802); (g) unpurified gelatin (AA-803); (h) total carbon, HAc-treated bone (AA-804); (i) XAD-purified gelatin hydrolysate (AA-805); (j) weak-acid insoluble collagen (AA-824); (k) XAD-purified collagen hydrolysate (AA-825). Error bars are 1 S.D. of the measurement from counting error.

poorly preserved Pleistocene-age fossils often yield ages that are several thousand years too young.

Despite having nearly identical nitrogen contents, amino acid compositions, and humate contamination, the Domebo and Dent fossils have different dating patterns (Figures 2 and 3). Twelve of the 21 fractions dated from the Domebo mammoth bone are within two standard deviations (S.D.S) of its known age, whereas two of the same fractions from the Dent mammoth bone yielded spurious ages (Figure 3 and Table 5). The most accurate date for Domebo bone, based on the averaging of three chemical fractions is 10,940 ± 180 years (Table 4). The most precise date for the sediments containing the Domebo mammoth is on a tree trunk dated at 10,980 ± 70 year BP (Beta-24212) (Hofman, 1988). The significance of the Domebo versus Dent results is that all fossil bones must receive a minimum chemical pretreatment. It is impossible to know when the dates for acid-insoluble-collagen and unpurified gelatin are accurate, as in the Domebo example, or inaccurate, as in the Dent example. When using heterogeneous chemical fractions such as gelatin and collagen, the radiocarbon ages must be tested by dating XAD-purified hydrolysates and constituent amino acids of these proteins.

Dates for individual amino acids from Dent mammoth collagen established the accuracy attainable from collagen-composition bones. The first chemical fractions dated from Dent were HCl-insoluble protein (8250 ± 520; AA-830) and gelatin (9240 ± 350; AA-831) (Figure 3 and Table 5). These isolates are used routinely for isotopic analyses and the preponderance of bone radiocarbon measurements are made on these fractions. Gelatin

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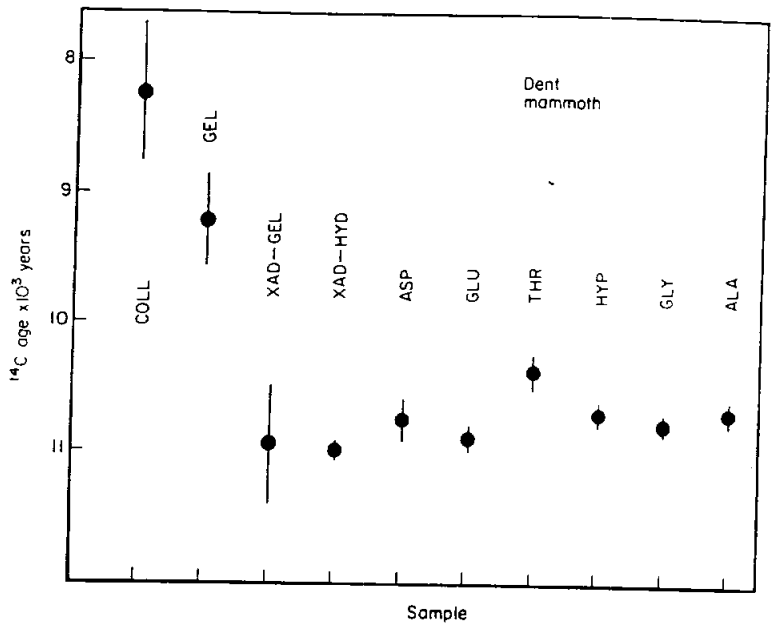

Figure 3. Dent mammoth AMS radiocarbon dates arranged in order of increasingly more pure chemical fractions. Abbreviations: COLL, collagen; GEL, gelatin; XAD-GEL, XAD-2-purified gelatin hydrolysate; XAD-HYD, XAD-2-purified collagen hydrolysate; ASP, aspartic acid; GLU, glutamic acid; THR, threonine; HYP, hydroxyproline; GLY, glycine; ALA, alanine. Error bars are 1 S.D. of the measurement from counting error.

and collagen hydrolysates were purified further and dated 10,950 ± 480 years (AA-833) and 10,890 ± 90 years (AA-2941) respectively. Five amino acids (excluding threonine) dated within 2 standard deviations of the total hydrolysate age (Table 5). Averaging the total hydrolysate (AA-2941) and five amino acid dates yields an age of 10,810 ± 40 years for the Dent mammoth.

Contrasting the Domebo and Dent results are dates for the poorly-preserved Escapule, BLM and Murray Springs mammoths. Their total-bone % nitrogen values were 0·08, 0·03 and 0·03%, respectively. These low nitrogen percentages and non-collagenous compositions (Table 3) are encountered commonly in fossil bones. Many similarly-preserved bones have been radiocarbon dated by AMS, most notably human fossil bones from North America (Bada *et al.*, 1984; Stafford *et al.*, 1984; Taylor *et al.*, 1985; Gowlett, 1986; Stafford & Tyson, 1989). Until know-age analogues such as the Escapule mammoth were dated, the validity of dates on poorly preserved fossil bone was uncertain.

The Escapule and BLM mammoth bone ^{14}C dates confirmed preliminary evidence (Kessels & Dungworth, 1980; Gowlett, 1986; Gowlett & Hedges, 1986; Stafford *et al.*, 1987, 1988) that a dichotomy exists for bone ^{14}C dates—collagenous composition bones like Dent and Domebo will date accurately, whereas non-collagenous fossils like Escapule date inaccurately. The first indication that Escapule-type fossils would not date accurately was that samples dated younger as pretreatment proceeded (Stafford *et al.*, 1987, 1988). The XAD-purified hydrolysates are the most highly purified, total-amino acid fractions. The XAD fraction dated 5000–6000 years too young for the BLM and Escapule mammoths, whereas the same fraction yielded accurate ages for the collagenous fossils.

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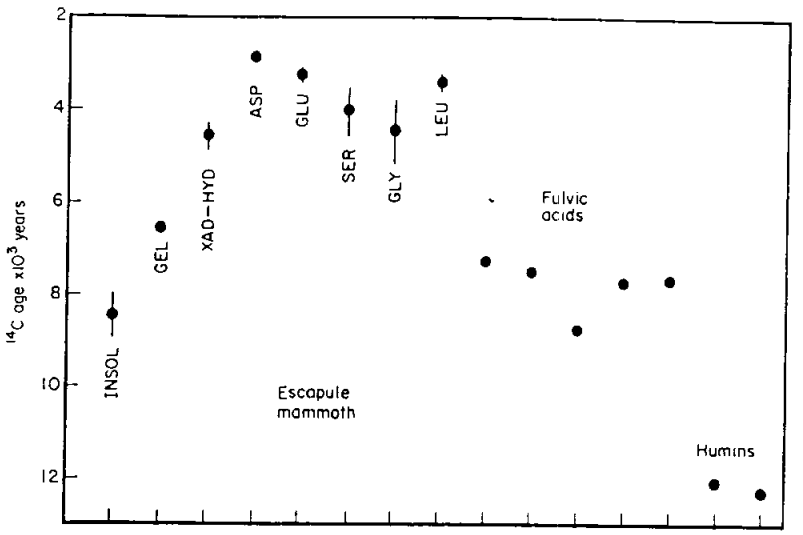

Figure 4. Escapule mammoth AMS radiocarbon dates for sequentially-extracted chemical fractions. Abbreviations: INSOL, weak-acid insoluble fraction; GEL, hot water soluble phase, "gelatin" from INSOL phase; XAD-HYD, XAD-2-purified hydrolysate of INSOL fraction; ASP, aspartic acid; GLU, glutamic acid; SER, serine; GLY, glycine; LEU, leucine. Error bars are 1 S.D. of the measurement from counting error.

Table 4. Domebo mammoth AMS radiocarbon dates. Selected samples are those routinely dated by conventional radiocarbon methods. See Stafford et al. *(1987) for complete date list*

AMS lab no.	Sample description	^{14}C age (years)	Target
AA-812	Fulvic acids from hydrolysed weak acid insoluble collagen; NH_4OH elution from XAD-2 resin	4910 ± 320	Fe-C
AA-819	Fulvic acids from hydrolysed weak acid collagen hydrolysis; NaOH elution from XAD-2 resin	5130 ± 290	Fe-C
AA-818	Hydroxyapatite CO_2; untreated bone	7300 ± 320	Fe-C
AA-801	Total inorganic and organic carbon; untreated bone	8010 ± 500	Fe-C
AA-815	Hydroxyapatite CO_2 from acetic acid extracted bone powder	9310 ± 360	Fe-C
AA-802A	0·6 *N* HCl soluble phase from bone powder	9540 ± 480	Fe-C
AA-803	Unpurified gelatin	10,350 ± 410	Fe-C
AA-804	Total inorganic and organic carbon from acetic acid extracted bone	10,760 ± 440	Fe-C
AA-805*	XAD-2-purified gelatin hydrolysate	10,810 ± 420*	Fe-C
AA-824	0·6 *N* HCl insoluble collagenous residue	10,820 ± 270	Fe-C
AA-811*	Amino acids from AA-805 hydrolysate	10,860 ± 450*	Fe-C
AA-825*	XAD-2-purified, 0·6 *N* HCl insoluble collagen hydrolysate	11, 480 ± 450*	Fe-C

*Symbol denotes dates used to calculate averaged age of 10,940 ± 180 years.

Further dating revealed that Escapule's individual amino acids also dated too young, by up to 9000 years (Table 6 and Figure 4). Data for the Escapule and BLM mammoths fossils are an indication that severely degraded bone has a high probability of molecular level contamination and will yield radiocarbon ages several thousand years too young, regardless what chemical fraction is used.

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Table 5. Dent mammoth AMS radiocarbon dates. All graphite target dates are corrected for $\delta^{13}C$ differences, which varied from −13·6‰ for aspartic acid to −22·4‰ for alanine

AMS lab no.	Sample description	^{14}C age (years)	Target
AA-830	0·6 *N* HCl insoluble collagen	8250 ± 520	Fe-C
AA-831	Unpurified gelatin	9240 ± 350	Fe-C
AA-832	XAD-2-purified collagen hydrolysate	10,590 ± 500	Fe-C
AA-833	XAD-2-purified gelatin hydrolysate	10,950 ± 480	Fe-C
AA-2941	XAD-2-purified collagen hydrolysate	10,980 ± 90	Graphite
AA-2942	Aspartic acid	10,750 ± 170	Graphite
AA-2943	Glutamic acid	10,890 ± 110	Graphite
AA-2944	Threonine	10,380 ± 140	Graphite
AA-2945	Hydroxyproline	10,680 ± 90	Graphite
AA-2946	Glycine	10,780 ± 90	Graphite
AA-2947	Alanine	10,690 ± 120	Graphite

Table 6. AMS radiocarbon dates on three poorly preserved, non-collagenous-composition, known-age fossil mammoths

AMS lab no.	Sample description	^{14}C date (years)	Target
Escapule mammoth (0·03% N) known age = 11,000 years			
AA-2653	0·6 *N* HCl insoluble residue	8460 ± 270	Fe-C
AA-2964	"Gelatin" fraction	6610 ± 90	Graphite
AA-2655	XAD-purified hydrolysate of AA-2653	4750 ± 370	Fe-C
AA-2958	Aspartic acid, HCl insoluble phase	3100 ± 110	Fe-C
AA-2959	Aspartic acid; "gelatin" phase	2080 ± 170	Fe-C
AA-2961	Glutamic acid; HCl insoluble phase	3470 ± 160	Fe-C
AA-2658	Serine; HCl insoluble phase	4070 ± 490	Fe-C
AA-2660	Aspartic and glutamic acids, serine; HCl insoluble phase	2270 ± 360	Fe-C
AA-2661	Glycine; HCl insoluble phase	4540 ± 710	Fe-C
AA-2962	Leucine, isoleucine, lysine, histidine and arginine; HCl insoluble phase	3460 ± 210	Fe-C
AA-2968	Fulvic acids; HCl insoluble phase, acetone eluted from XAD-2 resin	7260 ± 80	Graphite
AA-2970	Fulvic acids; HCl insoluble phase, NaOH-eluted from XAD-2 resin	8780 ± 80	Graphite
AA-2965	Hot water insoluble phase from weak HCl insoluble fraction	9340 ± 90	Graphite
AA-2972	6 *N* HCl insoluble residue from hydrolysis of weak HCl insoluble residue	12,280 ± 110	Graphite
BLM mammoth (0·01% N) known age = 11,000 years			
AA-4937	XAD-2-purified protein hydrolysate	6030 ± 250	Graphite
Murray Springs mammoth (0·03% N) known age = *c.*26,000 years			
AA-4938	"Humin" fraction from weak HCl insoluble residue of decalcified bone	10,580 ± 125	Graphite

The causes of inaccurate bone ages were revealed only when known-age fossils were dated at the molecular-level. The experiments showed two causes for Holocene ages being measured on Pleistocene fossils: (1) pretreatment methods did not remove contaminants (humates) from collagenous bone, and (2) a large proportion of amino acids in poorly-preserved bone are exogenous, thus preventing accurate radiocarbon measurements on these samples.

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Table 7. Del Mar skeleton AMS radiocarbon dates. Samples are tibia and sphenoid fragments of the human burial

AMS lab no.	Sample description	^{14}C date (years)	Target
Sphenoid			
AA-2665	XAD-2-purified collagen hydrolysate	4830 ± 200	Fe-C
AA-2948	Glutamic acid	4900 ± 70	Graphite
AA-2949	Hydroxyproline	5060 ± 80	Graphite
AA-2950	Glycine	4870 ± 60	Graphite
AA-2951	Alanine	4750 ± 100	Graphite
Tibia			
AA-2666	XAD-2-purified hydrolysate of 0·6 *N* HCl insoluble residue	5380 ± 390	Fe-C
AA-2952	Glycine	1150 ± 410	Fe-C

Table 8. Tepexpan human skeleton AMS radiocarbon dates

AMS lab no.	Sample description	^{14}C date (years)	Target
AA-2667	XAD-2-purified weak HCl insoluble collagen hydrolysate	1980 ± 330	Fe-C
AA-2953	Aspartic acid	920 ± 190	Fe-C
AA-2954	Glutamic acid	1090 ± 180	Fe-C
AA-2955	Glycine	960 ± 340	Fe-C
AA-2956	Fulvic acids	1430 ± 60	Graphite

Early Human Occupation of the New World

Ages for early humans in North America are based on: (1) charcoal and wood radiocarbon dates from archaeological sites, (2) dates on associated animal bone from animal kill-sites, and (3) dates directly on human skeletal material. Category (1) includes the earliest accepted dates for human occupation of the New World, 11,500–11,000 years BP (Haynes, 1987) and more controversial sites dating 13–20,000 years BP in North and South America (Adovasio & Carlisle, 1984; Gowlett, 1986; Bryan, 1986; Dillehay & Collins, 1988). Direct dates on human or animal bone would be definitive because secondary emplacement of a bone into a stratum would be identified. The rarity of human bone at Paleoindian sites and uncertainties about bone dating accuracy have restricted the direct dating of human fossils.

Early human skeletal remains in North America consist of two categories—fossils purportedly having considerable antiquity (20,000–70,000 years), yet modern anatomy, and those whose tentative 10,000–11,000 year ages are uncertain because bone preservation is poor or stratigraphic association is uncertain.

One accomplishment of molecular-level AMS radiocarbon dating was establishing the accuracy of ages for several human skeletons from California. The 17-year controversy began when an 18,000 year age was assigned to the Laguna human skull (Berger *et al.*, 1971; Berger, 1975), which was used subsequently to calibrate aspartic acid racemization dates of 20,000–70,000 years BP on other human skeletons (Bada & Helfman, 1975; Bada *et al.*, 1974). AMS ^{14}C dating of the Pleistocene-age fossils revised the ages as Holocene and generally <5000 years (Bada *et al.*, 1984; Bada, 1985; Taylor *et al.*, 1985). A final tabulation of human bone radiocarbon dates apparently supported a Holocene age for all skeletons (Taylor *et al.*, 1985). Because several of the human skeletal fossils were poorly preserved, their AMS ^{14}C ages are considered minimum age estimates. This conclusion is based on experiments elsewhere (Gowlett, 1986) and dating of the Escapule and BLM mammoths, whose non-collagenous composition is analogous to several of the California

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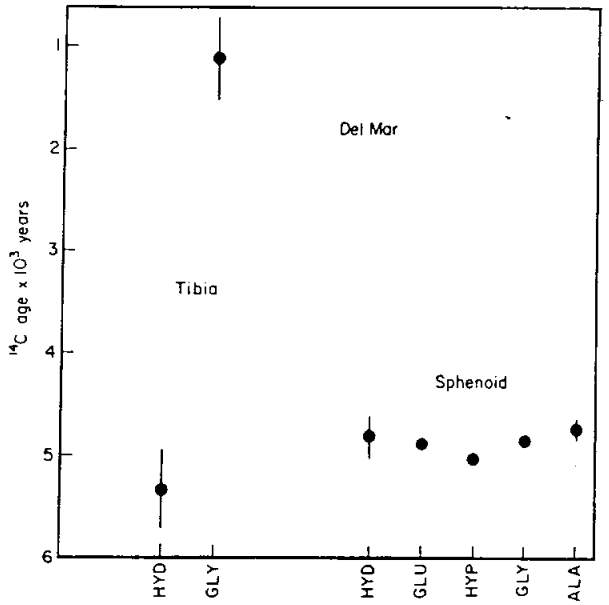

Figure 5. Del Mar, California human skeleton from San Diego Museum collection SDM-16709. Sphenoid fragment is from displayed-skull; tibia is remainder of sample previously dated by uranium series (Bischoff & Rosenbauer, 1981) and aspartic acid racemization (Bada *et al.*, 1974; Bada & Helfman, 1975). Abbreviations: as for Figure 1. Error bars are 1 S.D. of the measurement from counting error.

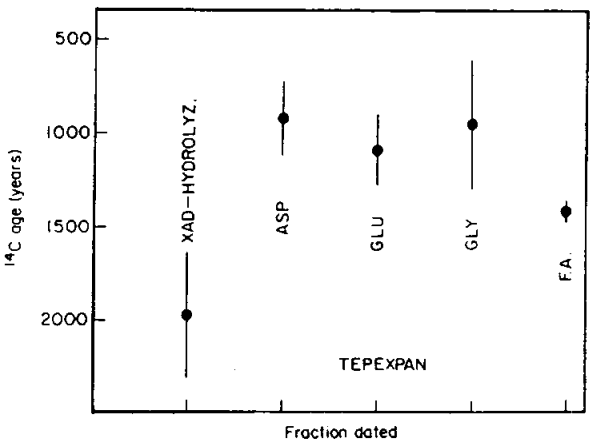

Figure 6. Tepexpan, Mexico human skeleton AMS radiocarbon dates on total organic carbon, individual amino acids and fulvic acids. Abbreviations: XAD-HYDROLYZ, XAD-2-purified hydrolysate of weak acid insoluble residue, ASP, aspartic acid; GLU, glutamic acid; GLY, glycine; FA, fulvic acids. Error bars are 1 S.D. of the measurement from counting error.

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Table 9. Anzick site AMS radiocarbon dates on two human skulls

AMS lab no.	Sample description	^{14}C date (years)	Target
White Calvarium			
AA-313C	0·6 *N* HCl insoluble collagen	8620 ± 340	Fe-C
AA-313D	Untreated gelatin	8940 ± 370	Fe-C
AA-2973	Aspartic acid from hydrolysed gelatin	8510 ± 120*	Graphite
AA-2974	Glutamic acid from hydrolysed gelatin	8740 ± 90*	Graphite
AA-2975	Hydroxyproline from hydrolysed gelatin	8520 ± 80*	Graphite
AA-2976	Glycine from hydrolysed gelatin	8680 ± 90*	Graphite
AA-2977	Alanine from hydrolysed gelatin	8590 ± 90*	Graphite
	Average ^{14}C age based on fractions designated with *	8610 ± 40	
Fe-stained calvarium			
AA-313A	0·6 *N* HCl insoluble collagen	8690 ± 310	Fe-C
AA-313B	Untreated gelatin	10,500 ± 400	Fe-C
AA-2978	Aspartic acid from hydrolysed gelatin	10,240 ± 120*	Graphite
AA-2979	Glutamic acid from hydrolysed gelatin	10,820 ± 100*	Graphite
AA-2980	Hydroxyproline from hydrolysed gelatin	10,710 ± 100*	Graphite
AA-2981	Glycine from hydrolysed gelatin	10,940 ± 90*	Graphite
AA-2982	Alanine from hydrolysed gelatin	10,370 ± 130*	Graphite
	Average ^{14}C age based on fractions designated with *	10,680 ± 50	

fossils. Radiocarbon dating of individual amino acids from the Del Mar fossil bone (Stafford & Tyson, 1989; Table 7 and Figure 5 this paper) and the Tepexpan human fossil (Table 8 and Figure 6) corroborated the conclusion that poorly preserved fossils were contaminated at the molecular level. In contrast, radiocarbon dates from the well-preserved collagenous-composition Del Mar skull were in agreement among all chemical fractions (Table 7 and Figure 5).

Based on bone diagenesis and radiocarbon data from variously-preserved bones, the Holocene dates for several human skeletons (Yuha, Del Mar tibia, Haverty, Truckhaven, Sunnyvale and La Jolla Shores) are questionable. If these human skeletons were Pleistocene in age, they would not have been recognized as such because their chemical fractions would yield Holocene ^{14}C dates. The fossils' non-collagenous compositions indicate a high probability of exogenous carbon contamination. Due to their poor preservation, the small amount of bone remaining, and the loss of some sites to urban development, it probably will never be known if the fossils are Holocene (< 11,000 years) or Pleistocene (11,000–> 20,000 years). The conclusion is that a poorly preserved, Pleistocene-age fossil > 11,000 years in age would go unrecognized because it would yield a Holocene ^{14}C date.

Contrasting with the California skeletons are well-preserved fossils that may represent Paleoindian age (8000–11,500 years) burials. The Wilsall (Anzick) site, Montana, (Taylor, 1969; Lahren & Bonnichsen, 1974) is a rock shelter that yielded crania of two juvenile humans and ocher-stained, Clovis-age artifacts. Although one skull was stained with hematite, its association with the second skull and the Clovis artifacts was uncertain because the site's stratigraphy was largely destroyed before systematic excavations were begun. The presence of Clovis artifacts and ocher (hematite) on bone and lithic tools indicated that one or both skulls could have been from Clovis-age burials (Haynes, 1987).

Each Anzick skull was AMS ^{14}C dated (Table 9 and Figure 7). The dates on these collagenous fossils indicate the existence of two different-age burials—one 8500 years and the other 10,500 years. The dates are accepted for two reasons: (1) both fossils had collagenous compositions (Table 3), and (2) ages on XAD-purified hydrolysates were concordant with dates on individual amino acids (Table 9 and Figure 7). The Anzick fossils had different dating patterns—the younger Anzick skull had concordant ages on all

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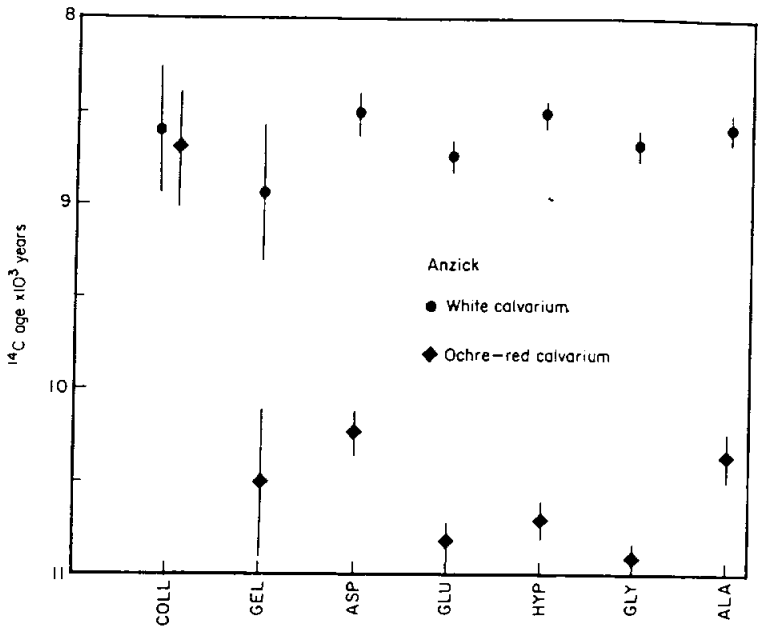

Figure 7. Anzick, Montana human skeleton AMS radiocarbon dates on a bleached white calvarium (dots) and ocher-stained calvarium (diamonds). Abbreviations: COLL, untreated, weak-acid insoluble collagen; GEL, untreated gelatin; ASP, aspartic acid; GLU, glutamic acid; HYP, hydroxyproline; GLY, glycine; ALA, alanine. Error bars are 1 S.D. of the measurement from counting error.

fractions, whereas the older skull's unpurified collagen dated 2000 years younger than subsequent fractions. Without dates on individual amino acids, the 2000 years age difference between the skulls could not have been recognized.

It is unknown why there are two age populations for the ocher-stained bone; the two age groups differ by 500 years. Aspartic acid and alanine have an average age of 10,300 year BP, whereas glutamic acid, hydroxyproline and glycine yield an average age of 10,800 years BP. The older age is considered more correct because young-age contamination is more probable than contamination by older age carbon. These results indicate why an age determination on a single chemical fraction is not absolute proof-of-age, even if the dated fraction is a specific amino acid.

Paleontological Applications of AMS Dating

Faunal assemblages are frequently multi-genetic for two reasons: (1) sedimentary reworking mixes fossils from different-age sediments, and (2) fossils accumulate continuously over hundreds of years in depositional environments that are continually reworked and have very low depositional rates. Solutions to these dating problems are given from sites in the Hawaiian Islands and Nevada pluvial lake basins.

Hawaiian Islands' fossil deposits (Olson & James, 1982) are ideal candidates for AMS radiocarbon dating because: (1) most bird and rodent fossils are too small for conventional radiocarbon dating, (2) fossils occur on sediment-free floors of basalt lava tubes, and (3) the fossils are within poorly stratified alluvium that contains charcoal and wood only in the upper 10–30% of the stratigraphic section.

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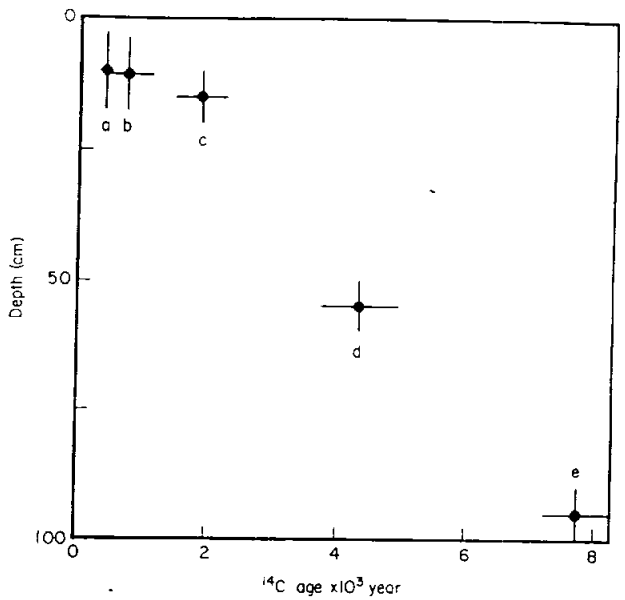

Figure 8. Puu Naio Cave, Maui, Hawaii AMS radiocarbon dates on charcoal, and fossil bird and rodent bones. Symbols: (a) Charcoal (SI-6503); (b) Pacific Rat, *Rattus exulans* (AA-760); (c) Flightless ibis, *Apteribis* sp. (AA-761); (d) Flightless goose, *Thambetochen* sp. (AA-762); (e) Flightless goose, *Apteribis* sp. (AA-763). Horizontal error bars are 1 S.D. of the measurement from counting error for radiocarbon age; vertical error bars represent stratigraphic interval from which sample was collected.

Hawaiian paleontology requires dates for last appearances of extinct avifaunas and the first appearance of human-introduced genera such as *Rattus* and *Mus*. Human-introduced species date younger than *c.* 1800 years BP and it is critical to know the number of years the endemic and introduced species were contemporaneous. Bone dating is essential because sedimentation rates were too slow to resolve 100 year intervals. Figure 8 summarizes bone and charcoal radiocarbon dates from Puu Naio Cave, an alluviated lava-tube on Maui, Hawaii (James *et al.*, 1987). The biogeography of the Hawaiian data is discussed by Olson & James (1982) and James *et al.* (1987). They hypothesize that the Hawaiian avifauna survived late Pleistocene and Holocene climatic changes, only to be decimated when humans destroyed the forest habitats. Historic (post 1778 AD) species records are those of a severely altered avifauna, not those reflecting Pleistocene and Early Holocene species diversity on the Hawaiian islands.

A second paleontological example is the dating of fossils from pluvial lake basins in Nevada (Dansie *et al.*, 1990). Stratigraphic dating was impossible because overlying sediments had been eroded and the lacustrine clays lacked sufficient organic or inorganic carbon for ^{14}C dating. Between 1983–5, the Nevada State Museum collected articulated skeletons of two camels (*Camelops hesternus*), and one horse (*Equus* cf. *pacificus*) from Pyramid Lake, Nevada; the specimens were exposed on the present land surface and were embedded within Sehoo Fm. clays dating *c.* 28,000–5000 years BP (Dansie *et al.*, 1990). The fossils' elevations (3811–3817′) coincide with low lake levels occurring at 28,000, 11,000 and post 8000 years BP. Pluvial lake levels at 13,000 years BP were *c.* 4364′ (1300 m) elevation. The camels were tentatively dated at 11,000–9000 years BP based on the near-

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Table 10. Pyramid Lake, Nevada camel skeleton AMS radiocarbon dates. Two different methods are compared for extracting protein for dating

Fraction dated	Protein extraction method	
	Weak HCL dissolution	Hqt water extraction
XAD-purified hydrolysate	25,870 ± 590 (AA-2663)	25,860 ± 590 (AA-2664)
Aspartic acid	22,400 ± 320 (AA-2983)	—
Glutamic acid	—	22,810 ± 320 (AA-2986)
Glycine	25,230 ± 390 (AA-2985)	24,290 ± 380 (AA-2988)
Hydroxyproline	23,250 ± 360 (AA-2984)	22,270 ± 330 (AA-2987)
Alanine	15,490 ± 200 (AA-3032)	22,890 ± 320 (AA-2989)
Proline	—	25,370 ± 420 (AA-2990)

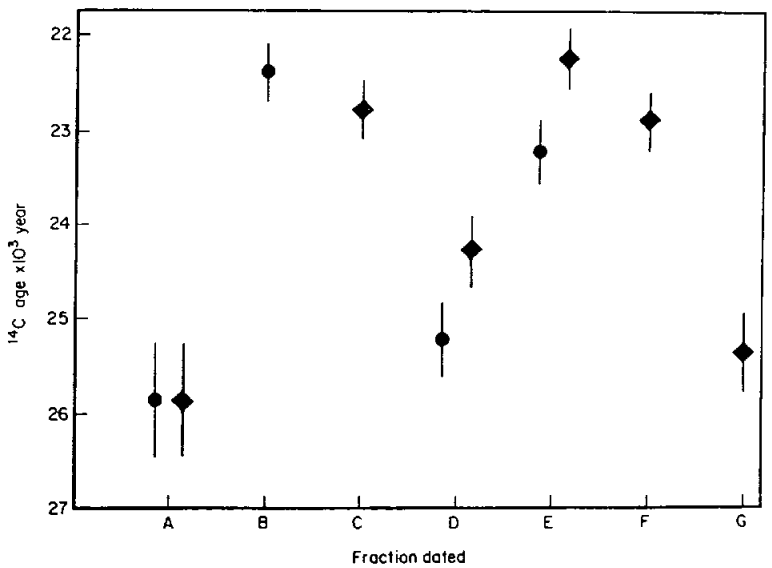

Figure 9. Pyramid Lake, Nevada camel AMS radiocarbon dates on total protein and individual amino acids extracted from collagen and hot water-extracted protein. Error bars are 1 s.d. of the measurement from counting error. (●), Method of extracting collagen extracted by decalcifying bone with weak HCl; (◆), method of extracting protein from whole bone using 150°C water for 7 days. Fractions dated: (A) XAD-2-purified protein hydrolysate; (B) aspartic acid; (C) glutamic acid; (D) glycine; (E) hydroxyproline; (F) alanine; (G) proline.

modern preservation of the bone, by stratigraphic correlation with nearby deltaic gravels, and elevation of the sediments.

Total protein and individual amino acids were dated from one camel. The purified hydrolysate dated 25,870 ± 590 years (AA-2663) (Table 10 and Figure 9), an age substantially older than expected. The ages' validity was tested by dating: (1) individual amino acids from the collagen hydrolysate, (2) hot water-soluble protein isolated from whole bone, and (3) amino acids from water-soluble protein (Figure 9).

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Each extraction method yielded two populations of ages: one of 23,000 years, the other of 25,000 years. Hydroxyproline is the most preferable amino acid for ^{14}C dating of all amino acids because its natural occurrence is limited. Aspartic acid, glutamic acid, and glycine are theoretically less preferable because they are found commonly in sediments, soils and ground waters. Hydroxyproline and aspartic acid had similar ages, which were approximately 2600 years younger than those for glycine and hydrolysed collagen.

Dates on hot water-extractable protein are significant for two reasons: (1) their ages were similar to those on collagen-derived amino acids, and (2) ground-water-borne amino acid contamination is apparently absent—an unexpected discovery. The major importance of the hot water-extraction method is that well-preserved, irreplaceable bone artifacts can be dated without their destruction.

Dating of the European Upper Paleolithic

Establishing chronologies for European Upper Paleolithic rock shelters (Gowlett & Hedges, 1986; Mellars & Bricker, 1986) is a challenge for AMS ^{14}C dating because chronologies are predominately from bone ^{14}C dates, and the cave sediments extend well beyond the present limit of accelerator ^{14}C dating (*c.* 48,000 years). Upper Paleolithic chronologies and tool industries in France's Perigord Region are based on type localities such as Abri Pataud, La Ferrassie, Laugerie Haute, and La Madeleine, where the classic pollen profiles, sedimentary cycles and artifact typologies have been established (Laville *et al.*, 1980). Chronologies for the type sections are based on radiocarbon dating, with Abri Pataud playing an important geochronological role (Movius, 1977). Unknown-age sites are correlated to the type sites by using temporal seriation, climatic zonation, and sedimentological phases. The disadvantages of correlation are: (1) any chronological errors at the type site are repeated throughout a region (Straus, 1987); (2) time transgressive lithic industries would not be identified, and (3) bone artifacts displaced by human interference, bioturbation or cryoturbation would not be recognized unless bone were dated directly.

Experiments at Cénac-et-Saint-Julien (Grotte XVI), a stratified, Upper Paleolithic rock shelter in the Dordogne River Valley of Southern France (Rigaud, 1986), evaluated bone dating for sediments extending from Magdalenian (*c.* 10–17,000 years BP) to Mousterian (>35,000 years) periods. The fossil bones were dated to test for stratigraphic integrity and to establish empirically the maximum dating limits of AMS (Table 11 and Figure 10).

Results from Grotte XVI are (a) upper strata date at 20,000 years and disconformably overlie sediments >39,800-years-old, (2) age inversions occur at 26,000 and 34,000 years, (3) finite dates are limited to *c.* <41,000 years, and (4) non-destructive isolation of bone protein yielded ages concordant with dates on collagen.

The conclusion that the Grotte XVI stratigraphy was disturbed by bioturbation, cryoturbation and human activity was based on dates from XAD-purified hydrolysates (Table 11 and Figure 10). Although these dates were considered accurate because the bones were extremely well preserved, the ages required verification. Sample combustion methods and accelerator physics were proven to be replicable by redating samples, e.g. AA-2991, 2992 and AA-2678, 2679; however, if XAD-purified hydrolysates had been contaminated naturally, redating would yield precisely the same (incorrect) age. The presence of age inversions was tested by isolating and dating individual amino acids and groups of amino acids from the total collagen hydrolysate (Table 11). All dates were within 1 S.D. of ages for the precursor hydrolysate. The second series of dates confirms the validity of the stratigraphic age anomalies, particularly at 34,000 years (AA-2675), and the presence of a disconformity within stratum B. The sample dating 34,000 years is stratigraphically between two infinite radiocarbon ages. The 34,000 year age is substantiated by concordant ages on three individual amino acids (AA-2998, 2999, 3000), each of which is

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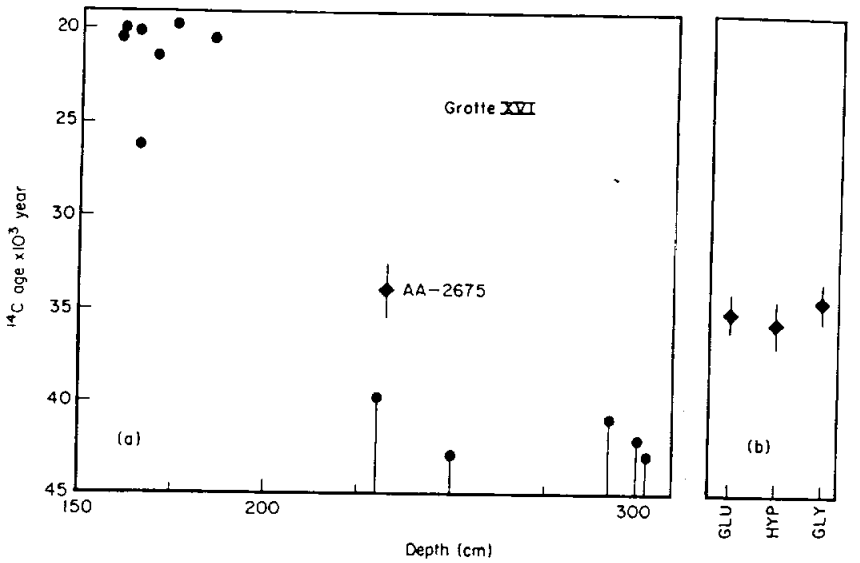

Figure 10. Grotte XVI, France AMS radiocarbon dates of fossil bone arranged by stratigraphic order. (a) Illustrates dates on XAD-2-purified collagen hydrolysates. (b) Shows radiocarbon dates on individual amino acids isolated from collagen from AA-2675. Abbreviations: as for Figure 1. Error bars are 1 S.D. of the measurement from counting error. Points having only bottom of error bars are dates greater than the indicated age.

within 1 S.D. of 34,000 ± 1400 years. The conclusion is the sample at 233 cm depth had been dated correctly and that the bone had been dislocated stratigraphically.

A final experiment on Grotte XVI bone was isolating amino acids from hot water-extracted protein. The test specimen was the 34,000-year-old bone discussed above. Dates on individual amino acids (AA-3001–3003) were unexpectedly similar to dates on amino acids from hydrolysed collagen (AA-2998–3000). Glycine from both extraction methods was concordant at one sigma, glutamic acids agreed in age at two sigma, whereas hydroxyproline ^{14}C ages were discordant. It was unexpected that any hot water-extracted amino acid, particularly glycine, would give an age concordant with one from collagen amino acids.

The Grotte XVI results demonstrate: (1) how molecular-level dates evaluate accuracy of less homogenous chemical fractions, (2) age anomalies in stratigraphic sections are probably due to unrecognized bioturbation or human interference and are not due to sample contamination, and (3) well-preserved, irreplaceable bone artifacts or human skeletons may be datable by extracting protein by non-destructive methods.

Discussion

Experiments presented in this paper are examples of the complexities of measuring ^{14}C in heterogeneous chemical systems such as fossil bone. They illustrate that many problems cannot be addressed successfully except at the molecular level.

Fossil bone is especially well suited for molecular-level ^{14}C dating because it is an extremely complex matrix. This complexity has caused many bone ^{14}C measurements to be questionable, principally due to bone preservation and what chemical fraction was used for dating. These aspects are summarized in Table 12, which compiles the chemical pretreatment used and how bone preservation affects dating accuracy. The table enables

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Table 11. AMS radiocarbon dates from Grotte XVI, France

Depth (cm)	Square	Stratum	^{14}C date for collagen hydrolysate		^{14}C date for seven amino acids	
162	K-10	A^t	20,410 ± 380	(AA-2991)	—	
162	K-10	A^t	20,280 ± 220	(AA-2992)	—	
163	K-10	A^t	20,070 ± 330	(AA-2668)	19,930 ± 160	(AA-3031)
166	K-10	A^t	20,230 ± 270	(AA-2669)	20,460 ± 260	(AA-2993)
167	K-10	A^t	26,340 ± 470	(AA-2670)	—	
172	K-10	A_b	21,490 ± 460	(AA-2672)	21,530 ± 280	(AA-2995)
174	K-10	A_b	19,750 ± 270	(AA-2671)	19,260 ± 240	(AA-2994)
184	J-11	B	20,550 ± 260	(AA-2673)	20,010 ± 230	(AA-2996)
229	I-6	B	> 39,800	(AA-2674)	38,100 ± 1670	(AA-2997)
233	I-6	C	34,000 ± 1400	(AA-2675)	See below	
249	J-5	D	> 43,000	(AA-2676)	—	
293	J-5	E	> 41,900	(AA-2677)	—	
301	I-6	F	> 42,400	(AA-2678)	—	
301	I-6	F	> 43,000	(AA-2679)*	—	
			Individual amino acids isolated from AA-2675 bone			
0·6 *N* HCL insoluble collagen						
	Glutamic acid		35,230 ± 1180	(AA-2998)		
	Hydroxyproline		35,760 ± 1270	(AA-2999)		
	Glycine		34,550 ± 1120	(AA-3000)		
Hot water-soluble protein from whole bone						
	Glutamic acid		31,340 ± 810	(AA-3001)		
	Hydroxyproline		29,060 ± 640	(AA-3002)		
	Glycine		34,690 ± 1150	(AA-3003)		

* Signifies A Fe-C target; all others are graphite. A^t denotes top of stratum A; A_b denotes base of stratum.

one to assess the accuracy of a bone date if bone preservation and chemical pretreatment steps are known.

A bone is categorized as collagenous or non-collagenous by using analytical data on nitrogen content and amino acid composition. Collagenous bones yield accurate ^{14}C dates because chemical pretreatment will eventually isolate a fraction that is free of contaminants. In contrast, non-collagenous bones should not be dated by ^{14}C because foreign organic matter consists of a large proportion to 100% of the bone's organic carbon content. No pretreatment step is presently known that will yield an absolute ^{14}C date for poorly preserved bones.

Once a bone is established as being collagenous or non-collagenous, the appropriate chemical pretreatment steps can be used. The preponderance of erroneous ^{14}C dates on collagenous bone result from using a chemical fraction that retains foreign carbon, usually humic and fulvic acids. Heterogenous and chemically impure fractions such as acid-insoluble-collagen, gelatin, or base-leached-collagen are very likely to contain humate contaminants. Dating results from the Domebo and Dent mammoths, and the Del Mar and Anzick human fossils are evidence that these poorly characterized chemical fractions can date accurately for some fossils and be thousands of years in error for others. Only by dating highly purified protein hydrolysates, individual amino acids, or both, can consistent accuracy be achieved for collagenous fossils.

In contrast, non-collagenous bones have proven undatable by existing techniques. The reason is that they contain little if any endogenous protein. The only fraction that has any

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value from non-collagenous bones is the "humin" fraction, which comprises high molecular weight residues that are resistant to acid hydrolysis. The "humin" residues may be partly derived from endogenous amino acids and will provide a minimum age for the bone.

After assembling all data regarding a bone date, the accuracy of the measurement is estimated. Based on the 55 different chemical fractions that have been used for bone ^{14}C dating (Table 12) a probability-of-accuracy is given. Only nine chemical fractions have a high to extremely high probability of accuracy (rank of 5–6); these comprise purified hydrolysates and individual amino acids from collagenous bone. Fractions ranking 4–5 (moderate to high accuracy) may be accurate for well preserved fossils less than 20,000 years, but bones older than 20,000 years will have their ages underestimated because contaminants were not removed by the less stringent chemical procedures (Gowlett & Hedges, 1986). Dates ranking 3 and less should not be used as absolute geological ages unless corroborating data and additional ^{14}C measurements have been made. Data in Table 12 support the conclusion that most bone radiocarbon dates will be moderate to major underestimates of the fossil's true geologic age. The reason is that chemically impure fractions were dated or that poor preservation precluded accurate dating by any technique.

The difficulty of assessing published bone ^{14}C dates is that (1) the chemical fractions used for dating are not defined, and in terms used by biochemists, (2) the chemical steps used for pretreatment are not specified, thus preventing replication, and (3) % nitrogen and quantitative amino acid analyses are not published, thus preventing preservation to be evaluated. The latter's importance has been stressed repeatedly (Oakley, 1963; Hassan & Hare, 1977; Taylor, 1980; Horvatincic *et al.*, 1983; Gowlett & Hedges, 1986; Stafford *et al.*, 1988); however, the data are reported rarely.

Another difficulty in assessing dating accuracy is that some environmental and diagenetic conditions are too poorly known for generalizations to be made. Although dates on fractions other than purified hydrolysates and amino acids are often inaccurate, exceptions are very-well-preserved fossils that have minor humate contamination and which were treated with NaOH (Vogel & Waterbolk, 1963). These fossils occur frequently in polar environments, dry caves and in European Paleolithic rock shelters. Conventional and AMS ^{14}C dates are generally concordant (Mellars & Bricker, 1986) for European rock shelter fossil bones less than 20,000 years in age (Gowlett & Hedges, 1986).

Geologic environments exist where collagenous compositions are retained at trace levels in fossil bones for thousands to millions of years (Armstrong *et al.*, 1983). Most bones with $<0{\cdot}1\%$ N have non-collagenous compositions, but examples exist where nitrogen is $\leqslant 0{\cdot}1\%$ and a collagenous composition is present (Table 1). Preliminary data support the dates being accurate, but additional samples must be studied before this uncommon class of bones can be dated routinely.

The most important result from our experiments is that no one molecular fraction or pretreatment protocol will guarantee the accuracy of a ^{14}C measurement. Sedimentary environments, geochemical cycles and diagenetic processes are too complex to dictate any one dating or pretreatment protocol. Molecular-level ^{14}C dating must be combined with high-quality litho- and biostratigraphic data to assure that as many errors as possible are removed. This approach was taken in the French Upper Paleolithic Cave, Grotte XVI, where chronological anomalies were recognized only by combining detailed stratigraphic and radiometric analyses.

Conclusions

Dating experiments on known-age fossil bone from diverse geochemical environments resolved why bone radiocarbon measurements are frequently inaccurate and helped

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Table 12. Chemical fractions used for the radiocarbon dating of fossil bone. All chemical fractions known to have been used for bone ^{14}C dating are listed. The literature references are the earliest citation of a method and also significant experiments relating to that technique. The probability of accuracy refers to the validity of a ^{14}C date determined on a specific chemical fraction for each of three fossil bone classes.

Bones with ≥0·2% N are assumed to have a collagenous composition; fossils with <0·1% N are almost always non-collagenous and are not presently recommended for ^{14}C dating. Fossils that have 0·1–0·2% N can be classified in the 3·0–0·2% N group only if they have a collagenous composition; otherwise, they are included in the third least accurately dated group.

The probabilities for accurate ^{14}C dates are (1) zero to extremely low; no value for ^{14}C dating. (2) Very low; use for research on fossil diagenesis or when a series of dates is applicable. (3) Low; provides a minimum age; considerable contamination may remain in the fraction. (4) Moderate; sample is affected frequently by inorganic carbon or inclusion of humates. (5) High; quantitative removal of contaminants. (6) Highest; specific molecular phases (amino acids) have been isolated

Chemical phase dated	Literature reference	% Nitrogen (%N) >3·0	3·0–0·2	<0·2
		Probability of accuracy (1 = lowest 6 = highest)		
I. Inorganic carbon fractions				
(A) Apatite CO_2 (carbonate hydroxyapatite)				
1. Whole bone without pretreatment	(Rafter, 1955; Olsson, 1959)	2,3	1	1
2. Naturally-burned bone	(Rafter, 1955; Grant-Taylor & Rafter, 1963)	1	1	1
3. Whole bone after acetic acid treatment	(Haynes, 1968)	2–4	2	1
4. Whole bone after triammonium acetate treatment	(Hassan *et al.*, 1977)	2–4	2	1
5. Whole bone: differential thermal release of CO_2	(Haas & Banewicz, 1980)	2–4	2–4	1
6. Sequential hydrolysis with HCl	(Haynes, 1968)	2·4	2–3	1
7. CO_2 from bone pyrolysed artificially at 600°C	(Rafter, 1955)	1	1	1
(B) Secondary carbonate CO_2 (~calcite)				
1. 1st fraction from sequential HCl hydrolysis	(Haynes, 1968)	2	2	2
2. Calcite (caliche) precipitate on fossil bone	(Stafford *et al.*, 1987)	2	2	2
3. Geologically associated caliche	(Bischoff *et al.*, 1976; Stafford *et al.*, 1987)	2	2	2

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II. Organic carbon fractions

(A) Whole bone					
1.	Organic + inorganic carbon, unburned bone	(deVries & Oakley, 1959; Tamers & Pearson, 1965)	1	1	1
2.	1–3 *N* HCl-insoluble residue from naturally burned bone	(Arnold & Libby, 1951)	2	1	1
3.	NaOH-treated, weak-HCl-insoluble residue from naturally burned bone	(Vogel & Waterbolk, 1963)	2–3	2	1
4.	Alkali-soluble fraction from weak-HCl-insoluble residue of naturally charred bone	(Vogel & Waterbolk, 1963; Vogel, 1970)	3	1	1
5.	NaOH-$Na_4P_2O_4$-treated, dilute HCl insoluble residue from naturally burned bone	(Steventon & Kutzbach, 1985)	3	1	1
6.	Combustion of organic residue remaining after 600° and 900°C pyrolysis	(Rafter, 1955)	2–3	1	1
7.	1–6 *N* HCl insoluble residue from artificially pyrolysed bone	(May, 1955; Rafter, 1955)	3	1	1
8.	Complete dissolution of whole bone with 12 *N* HCl; removal of salts by precipitation of CaF_2 or dialysis	(Berger *et al.*, 1964)	3	1	1
(B) Decalcified bone ("collagen")					
1.	Weak-HCl-insoluble residue from natural bone	(Rafter, 1955; Münnich, 1957; Berger *et al.*, 1964)	2–3	2–3	1–2
2.	Dialysed weak-HCl-insoluble residue	(Münnich, 1957; Berger *et al.*, 1964; Hassan & Hare, 1977)	2–3	2–3	1–2
3.	NaOH-extraction of bone before decalcification	(Olson & Broecker, 1958)	1–3	1	1
4.	NaOH-extraction of weak-HCl-insoluble residue	(Vogel & Waterbolk, 1963; Berger & Libby, 1966; Haynes, 1967; Gurfinkel, 1987)	4–5	3–4	2
5.	NH_4OH extraction of weak HCl insoluble residue	(Diop, 1974)	4–5	3–4	2
6.	Alkali-soluble fraction from total HCl dissolution of bone	(deVries & Waterbolk, 1958)	3	1	1
7.	Alkali-soluble fraction after NaOH extraction of weak-HCl insoluble residue	(Vogel & Waterbolk, 1963; Taylor, 1983)	3	1	1
8.	EDTA decalcified bone (insoluble residue)	(Sinex & Faris, 1959; Vogel & Waterbolk, 1963; Olsson *et al.*, 1974; El-Daoushy *et al.*, 1978)	3–4	2–3	2
9.	EDTA decalcification during dialysis	(Berger *et al.*, 1964)	3–4	2–3	2
10.	H_2SO_4 decalcification and carbonization	(Kigoshi & Kobayashi, 1966; Sato *et al.*, 1969)	3	1	1
11.	Weak HCl decalcification then H_2SO_4 carbonization	(Alessio *et al.*, 1976)	3	1	1
12.	HCl-soluble-phase after weak HCl decalcification; by precipitation with NaOH or dialysis	(Haynes, 1967; Haynes *et al.*, 1971; Olsson *et al.*, 1974; Taylor, 1983)	3	1	1
13.	Collagenase-digested collagen (peptides)	(DeNiro & Weiner, 1988*b*)	N.D.	N.D.	N.D.
(D) Decalcified bone ("non-collagenous proteins")					
1.	Hydroxyapatite-bound protein	(DeNiro & Weiner, 1988*a*)	N.D.	N.D.	N.D.
2.	Non-collagenous protein	(Masters, 1987)	N.D.	N.D.	N.D.

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Table 12. (Continued)

Chemical phase dated	Literature reference	% Nitrogen (%N) >3·0	3·0–0·2	<0·2
		Probability of accuracy (1 = lowest 6 = highest)		
(E) Gelatin fraction from decalcified bone				
1. Untreated gelatin	(Longin, 1971)	3–4	2–3	1–2
2. Trichloracetic acid precipitated gelatin from dialysed, EDTA insoluble residue	(Sinex & Faris, 1959)	3	2–3	1
3. Low-temperature (58°C) extraction, > 1000 Da gelatin fraction	(Brown *et al.*, 1988)	4–5	2–4	2
4. Gelatin from NaOH-washed decalcified bone	(Protsch, 1975; Taylor, 1983)	4–5	2–3	1–2
5. Gelatin from NaOH-$Na_4P_2O_4$ extracted decalcified bone	(Steventon & Kutzbach, 1985)	4–5	2–3	1–2
6. Hot (90 °C) water insoluble residue after gelatin extraction	(Taylor, 1983; this report)	3	3	2–3
(F) Hydrolysed weak-HCL-insoluble residue (total amino acids)				
1. Amino acids eluted from cation exchange resin by using NH_4OH	(Ho *et al.*, 1969; Gillespie *et al.*, 1984)	5	4–5	2–3
2. Charcoal-purified hydrolysate of decalcified bone	(Gillespie *et al.*, 1984)	5–6	5	2–3
3. XAD-2-purified hydrolysate of decalcified bone	(Stafford *et al.*, 1987)	5–6	5	2–3
4. XAD-2-purified gelatin hydrolysate	(Stafford *et al.*, 1987)	5–6	5	2–3
(G) Specific amino acids				
1. Hydroxyproline (imino acid)	(Gillespie *et al.*, 1984; Stafford *et al.*, 1982; this report)	6	5–6	N.A.
2. Proline (imino acid)	(Gillespie *et al.*, 1984; this report)	6	5–6	2
3. Combined proline and hydroxyproline	(Stafford *et al.*, 1987)	5–6	5–6	N.A.
4. Hydroxyacids from primary amines	(Gillespie *et al.*, 1984; Stafford *et al.*, 1987)	2	1	1
5. Individual primary amino acids, e.g. aspartic and glutamic acids, glycine, alanine	(this report)	5–6	5–6	2–3
6. Suites of several amino acids, e.g. aspartic acid through alanine (seven amino acids)	(this report)	6	5–6	2–3
(H) Non-protein fractions				
1. Fulvic acids, sephadex separation	(Haynes, 1968)	2–3	2–3	2–3
2. Fulvic acids, XAD-2 chromatography	(Stafford *et al.*, 1988)	2–3	2–3	2–3
3. Humic acids	(Haynes, 1967)	2–3	2–3	2–3
4. Lipids (fats)	(Rafter, 1955; Olsson *et al.*, 1974; Stafford *et al.*, 1987)	2–3	2–3	2–3
5. Insoluble residue ("humins") from 6 *N* HCl hydrolysis of decalcified bone	(this report)	3–5	2–5	2–5

Abbreviations: N.D.: Not determined; fraction has been proposed for ^{14}C dating and would be suitable; however, no measurements have been made to date. N.A.: Not applicable; signifies that this fraction can not be dated from a fossil bone with a non-collagenous composition. Bones with <0·1% N often have no hydroxyproline, thus preventing simultaneous dating of proline and hydroxyproline.

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establish protocols for the ^{14}C dating of fossil bone. Inaccurate dates from collagenous bone are due to impurities remaining in heterogeneous fractions such as gelatin and acid insoluble collagen. Purification of these fractions' hydrolysates and isolation of individual amino acids removes the humate contaminants and results in accurate ^{14}C ages.

Inaccurate dates on non-collagenous bone result from the large amount of foreign organic matter and amino acids in poorly-preserved fossil bone. Radiocarbon ages assigned to poorly preserved bones can be hundreds to thousands of years younger than the bone's true geologic age. The "humin" fraction from non-collagenous bones is the only fraction presently identified that will give a minimum age estimate for fossils of this preservation. These results on non-collagenous bone are evidence that some ^{14}C dating problems may be unsolvable by the most sophisticated ^{14}C measurement and chemical pretreatment techniques.

Protocols for dating fossil bone should include the following: (1) bone should have $>0{\cdot}1$–2% N *and* a collagenous amino acid content and these analyses should be published with the bone ^{14}C date; (2) the XAD-purified fractions from collagenous bones should be used exclusively to obtain ^{14}C measurements that are comparable among all geologic environments, (3) age measurements on non-collagenous bone with $<0{\cdot}1\%$ N are minimum-age estimates and (4) individual amino acids should be radiocarbon dated to verify measurements on purified hydrolysates, to date single specimens lacking stratigraphic provenance, and to achieve the accuracy and precision that only multiple dating of individual amino acids can provide.

General conclusions from molecular-level radiocarbon dating of bone are: (1) AMS radiocarbon dates are not intrinsically more accurate than conventional radiocarbon dates, (2) the chemistry employed in sample pretreatment and the fossil's geochemical history determine the accuracy of the radiocarbon measurement and (3) molecular-level dating does not guarantee that the radiocarbon age will be identical to the fossil's geologic age because exogenous molecules could comprise the predominant percentage of the organic fraction.

Molecular-level ^{14}C dating does guarantee that the same chemical fraction (molecule) can be isolated consistently by different laboratories and that diagenesis and sample contamination can be modelled at the molecular level. Most importantly, molecular dating will enable geochemists to understand the geochemical cycling of organic matter and to determine which molecular fractions are most suitable for radiocarbon dating.

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