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FROM THE EDITOR

In this issue, we round out the year 2003 and include the usual summary of known radiocarbon laboratories and their contact information. This issue contains several interesting papers.

The French group of Tisnérat-Laborde et al. discuss their improvements to bone chemistry using the methodology developed by Nelson et al. in 1991. Hatté et al. discuss an automated combustion system to convert organic material to CO₂, with various options. This system is an example of developments being undertaken in several laboratories, to use current computer technology to improve the repetitive processes in radiocarbon laboratory chemistry.

Fischer et al. studied food residues on pottery and found significant "reservoir effects", presumably from the use of fresh fish used in cooking. These results indicate the reservoir effect might be 100–500 years in Denmark, so that dating using food residues from such contexts has an additional caveat, as well as the usual ones.

Hua et al. have studied the differences in the bomb ¹⁴C record in tree rings from *Pinus radiata*, from New South Wales. They compare these records to oceanic and other atmospheric data. They are able to derive estimates of the air-sea exchange time in the southern Pacific mid-latitudes based on these results. In a more oceanographic vein, von Rad and coauthors report on AMS ¹⁴C dating of a laminated marine sediment, which records Heinrich events 1 and 2. This allowed the authors to establish a floating marine varve chronology for this core.

Vandergoes and Prior discuss methods for concentrating pollen and successful AMS pollen dating, using a peat bog in New Zealand as the source of pollen, which had previously been difficult to date. The pollen ages are systematically older than other organic fractions, which leads these authors to conclude the organic fractions are contaminated by incorporation of younger humic materials.

In a note on the next radiocarbon intercalibration to be called VIRI, Scott et al. discussed the need for continued intercomparisons. In VIRI, ¹⁴C laboratories have a chance to determine how well their procedures result in ¹⁴C ages within the expected norms, or whether changes to their protocols are needed. The ¹⁴C intercalibration exercises have been most successful in the past, and indeed this successful model of blind intercomparisons is now being copied for other contexts.

Rasmussen et al. continue the earlier discussions in *Radiocarbon* about the accuracy of the dates on the Dead Sea Scrolls, a matter which surely will continue to generate interest. It also emphasizes the importance of good intercomparisons of protocols and measurements between laboratories.

Lastly, Solow presents a simple expression for the variance in the estimated age due to dating errors and bioturbation.

I trust everyone will enjoy a happy and peaceful New Year,

A J Timothy Jull



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January 5, 2004

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AMS RADIOCARBON DATING OF BONES AT LSCE

N Tisnérat-Laborde^{1,2} • H Valladas¹ • E Kaltnecker¹ • M Arnold³

ABSTRACT. In this paper, we explain our routine pretreatment of bone for radiocarbon dating by accelerator mass spectrometry (AMS), based on the specific reaction between amino acids and ninhydrin described by Nelson (1991). The values and uncertainties of the total system background are presented as a function of the carbon sample mass and the reliability of this method is discussed.

INTRODUCTION

Since the first ¹⁴C dates were obtained (Arnold et al. 1951), radiocarbon laboratories have developed many methods of bone pretreatment. Usually, these methods are based on the extraction of the bone organic matter. The extract can consist of the whole collagen (Longin 1971; Brown et al. 1988; Hedges et al. 1989; Law et al. 1989; Kretschmer et al. 1998), a mixture of collagen amino acids (Gillespie et al. 1986; Gurfinkel 1987; Long et al. 1989; Redvers-Newton et al. 1994), specific individual amino acids (van Klinken et al. 1990), or non-collagenous proteins (Ajie et al. 1992). These extracts are oxidized to CO_2 , then reduced to graphite and dated.

For more than 10 years at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), we have prepared bone by the method described by Nelson (1991), based on a chemical reaction that extracts CO_2 from carboxylic groups of proteinaceous molecules. This chemical treatment is preceded by elemental analyses (%N, %C, C/N) in order to quantify the bone collagen, and, consequently, to determine if the bone is datable.

In this paper, we describe the protocol of bone preparation. We present the blank values obtained on bones from 2 sites, Sclayn and Gerde. Finally, we discuss the reliability of the ¹⁴C ages obtained by this method by comparing some of them to other ¹⁴C dates available for the same archeological layers. These samples are either charcoal, burnt bones, or bones treated differently.

MATERIAL AND METHOD

Material

On the basis of porosity, bone may be classified as cortical bone (also known as compact bone) or trabecular bone (also called cancellous or the spongy part). The cortical bone, which is much denser and less porous than the cancellous bone, is preferred for ¹⁴C dating since it is generally less altered by diagenesis.

The fossil bones used to estimate the degree of contamination introduced by our protocol come from 2 sites. Five bones were collected in Scladina Cave (Sclayn, Belgium), under a stalagmitic floor in layer 4A, which was dated by thermoluminescence to approximately 100,000 yr ago (Debenham 1998). Another bone comes from layer 2b of Carrière cave (Gerde, France), which is below a stalagmitic floor and dated to 52,500 yr ago by U/Th (Clot 1987).

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Method

The protocol used for the bone treatment is summarized in Figure 1.



Figure 1 Diagram showing pretreatment steps of bones for AMS 14C dating

Mechanical Treatment and Elemental Analyses

A piece of bone sample (\sim 1–2 cm) is cleaned mechanically with an airbrasive system with 27 µg aluminum oxide to remove superficial contaminants (roots, glue) and the spongy part, which is considered to be the most contaminated.

A sub-sample of approximately 5 mg is drilled out and subjected to elemental analysis. It is introduced in a tin capsule into a Carlo-Erba NA 1500 elemental analyzer. The other part of the mechanically cleaned bone (1-3 g)—if it contains enough collagen—is ultrasonically rinsed in Milli-Q water to remove aluminum oxide and dried at 45 °C. This bone is then finely ground in a planetary micro-mill composed of bowls and balls of zirconium oxide (ZrO₂).

Chemical Treatment

The powdered bone is repeatedly treated with 0.5M HCl and stirred at room temperature to remove carbonates, phosphates, and fulvic acids until the residue becomes colloidal. The acid-insoluble collagenous residue is then rinsed with Milli-Q water until neutral pH is reached.

Next, 50 mg of ninhydrin (2,2-dihydroxy–1,3-indandione) in a 2-ml sodium citrate buffer (pH = 4.8) is added to the residue, which is heated at 100 °C for 10 min. The ninhydrin reacts specifically with the free amino acids, which come from either degraded collagen or contaminants. The ninhydrin reacts with the α -NH₂ of amino acids to give α -imino acids, which react with water to give α -ceto acids (Moore et al. 1950). These α -ceto acids are unstable and release CO₂ from the α -carboxyl group:



The CO₂ is not collected and the residue is rinsed until the solution is decolorized.

Next, this "pure" residue is hydrolyzed to free amino acids with hot acid (HCl 6M at 100 °C overnight). The solution of free amino acids is filtered on a precleaned glass filter and collected in a glass reactor. This filtrate is evaporated at 80 °C under nitrogen. The free amino acid residue is rinsed 5 times with Milli-Q water, which is then evaporated at 80 °C under nitrogen.

The reactor is connected to a vacuum line (Figure 2) and heated to 100 °C with heating coils. Once the vacuum reaches $\approx 2.10^{-4}$ mb after ~ 2 days, 2 ml of ninhydrin solution is injected through a septum. The released CO₂ is dried by passing through 2 "water traps" (-78 °C, mix of dry ice and ethanol), trapped in a liquid nitrogen trap (-196 °C), quantified into the calibrated volume, and then collected in a glass vial. The entire treatment and the CO₂ transformation take more than 8 days.

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The CO_2 was reduced to graphite (Arnold et al. 1989) and the ¹⁴C ages were obtained by accelerator mass spectrometry (AMS) at the Gif-sur-Yvette Tandetron Facility (UMS 2004).

RESULTS AND DISCUSSION

Blanks

Results of Elemental Analyses

Several sub-samples were removed from different parts of the Sclayn and Gerde bones for elemental analyses (%N, %C, C/N). The results are reported in Table 1.

Nitrogen concentrations in the Sclayn bones range from 0.57–2.17%wt, in agreement with previous measurements (Bocherens et al. 1997), and in the Gerde bones from 1.21–2.5%wt. These nitrogen concentrations in the whole bone give some idea of the quantity of collagen (Hedges et al. 1992; Bocherens et al. 1997; Gillespie et al. 1984; Ambrose 1990; Hedges et al. 1995). Indeed, the quantity of nitrogen ranges from about 4% in a fresh bone (Stafford et al. 1988; Ambrose 1993) to below 0.2% in poorly preserved bone, which cannot be dated by the ninhydrin method. With nitrogen amounts ranging from 0.5–2.5%wt, the Sclayn and Gerde bones contain enough collagen for AMS dating.

The scatter of the nitrogen measurements shows that the diagenesis of the organic matter is not homogeneous within any one bone. The C/N ratio of the whole bone can help to estimate the degree of diagenetic alteration. High values (i.e., >5) indicate extensive diagenesis (deamination) or a high proportion of exogenous carbon (humics). For the Sclayn bones, the C/N ratios are statistically similar with a mean value of 4.55 ± 0.4 (n = 14; χ^2 ; P_{0.05} = 9.95/22.40), excluding the value of the

I	Nitrogen	Carbon	
Sample	$(\% \text{wt} \pm \Delta)$	$(\% wt \pm \Delta)$	C/N ratio
SC91-500G30	1.33 ± 0.14	6.6 ± 0.3	5.0 ± 0.8
	0.67 ± 0.07	3.9 ± 0.2	5.9 ± 0.9
SC91-450F28	0.69 ± 0.07	3.1 ± 0.2	4.4 ± 0.7
	0.57 ± 0.06	3.0 ± 0.2	5.3 ± 0.8
	1.33 ± 0.14	5.2 ± 0.3	3.9 ± 0.6
	1.02 ± 0.11	4.5 ± 0.2	4.4 ± 0.7
SC91-503G30	0.59 ± 0.06	3.0 ± 0.2	5.1 ± 0.8
	0.60 ± 0.06	3.3 ± 0.2	5.5 ± 0.9
	$\underline{0.60\pm0.06}$	5.4 ± 0.2	9.0 ± 1.3
SC91-588F27	2.17 ± 0.22	8.2 ± 0.4	3.8 ± 0.6
	0.65 ± 0.07	3.3 ± 0.2	5.0 ± 0.8
	1.07 ± 0.11	4.6 ± 0.2	4.3 ± 0.7
SC91-619F30	1.12 ± 0.12	4.7 ± 0.2	42 ± 0.6
5071 017100	1.21 ± 0.13	4.9 ± 0.2	4.0 ± 0.6
	0.79 ± 0.08	4.0 ± 0.2	5.1 ± 0.8
Garda	1.21 ± 0.14	4.7 ± 0.3	3.9 ± 0.7
Guide	1.21 ± 0.14 2 50 + 0 29	4.7 ± 0.3 8.4 ± 0.4	3.9 ± 0.7 3.4 ± 0.6
	1.66 ± 0.19	6.0 ± 0.3	3.6 ± 0.6

Table 1 Nitrogen and carbon concentrations in bone, expressed as % of bone weight (%wt) and the atomic C/N ratio of the Sclayn (SC91-) and Gerde blank bones. The results of the underlined line correspond to the analyses carried out on the spongy part of the bone.

spongy part of sample SC91-503G30/3 (C/N = 9). This high C/N ratio is attributed to the addition of humic contaminants since the nitrogen concentrations are similar within the compact and the spongy parts; the high C/N ratio confirms the importance of removing this porous part of the bone. This mean C/N ratio of Sclayn bones is approximately equal to the fresh bone (5) and shows the good preservation of these bones. For the Gerde sample, the mean C/N ratio is equivalent to 3.58 ± 0.6 (n = 3, χ^2 ; P_{0.05} = 0.4/5.99), and is slightly lower than the C/N value in Sclayn. This lower value can be explained by a loss of inorganic carbon (decalcification) during burial. The Gerde bone seems less well preserved than the Sclayn bones.

The nitrogen concentrations show that the Sclayn and Gerde bones contain enough collagen for AMS datings and the C/N ratios show their degree of preservation and their non-contamination.

AMS ¹⁴C Results

The ¹⁴C values of the Sclayn and Gerde bones (Table 2) are presented as a function of the carbon mass in Figure 3. These blank values take into account the chemical pretreatment, the conversion into CO_2 , the graphitization, and the machine background contaminants. They increase from 0.10 pMC to 0.80 pMC as the carbon sample size decreases from 2400 µg to less than 300 µg.

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		Fraction modern	
Sample	Mass (µg)	$pMC \pm 1 \sigma$	
SC91-500G30	280	0.60 ± 0.07	
	290	0.31 ± 0.03	
	950	0.15 ± 0.02	
	1760	0.31 ± 0.07	
SC91-450F28	1040	0.32 ± 0.03	
SC91-503G30	460	0.16 ± 0.02	
	460	0.18 ± 0.02	
	970	0.66 ± 0.06	
	1240	0.37 ± 0.04	
	1270	0.24 ± 0.03	
SC91-588F27	2390	0.16 ± 0.02	
SC91-619F30	390	0.79 ± 0.05	
	660	0.28 ± 0.03	
	1300	0.17 ± 0.03	
	1345	0.16 ± 0.03	
	1575	0.19 ± 0.03	
	1630	0.22 ± 0.03	
	1740	0.10 ± 0.02	
	1790	0.18 ± 0.02	
	2050	0.10 ± 0.02	
Gerde	290	0.42 ± 0.06	
	580	0.41 ± 0.05	
	990	0.30 ± 0.04	

Table 2 ¹⁴C results of the Sclayn (SC91-) and Gerde bones, reported in pMC

The data indicate a statistically significant mass dependence relationship, as previously reported by several studies of ¹⁴C background (Vogel et al. 1987; Kirner et al. 1995; Brown et al. 1997; Schleicher et al. 1998; Tisnérat-Laborde et al. 2001). By using the least-squares method, the best fit between ¹⁴C concentrations and the inverse carbon mass is obtained by:

 $y = 119.68 (\pm 28.59) / x + 0.1295 (\pm 0.0486)$

where $y = {}^{14}C$ concentration (pMC) and $x = \text{carbon mass} (\mu g)$. This increase of the ${}^{14}C$ background is due to the addition of 1.3 μg of modern carbon (100 pMC) per mg of sample during the whole process.

All the blank values from Sclayn and Gerde (Figure 3) are consistent, although the C/N analyses showed a lower preservation for the Gerde sample. Such agreement indicates the reliability of our protocol.

These blank values are higher than those obtained from the Carrara marble IAEA C-1, which range from 0.06–0.14 pMC as the size decreases from 2400–300 μ g (Tisnérat-Laborde et al. 2001). The contamination during the chemical treatment and the conversion of bone into CO₂ may be responsible for the high blank values since the graphitization and the machine processing are the same for



Figure 3 ¹⁴C concentration (pMC) as a function of carbon sample mass (μ g). The error bars are shown as $\pm 1 \sigma$ (68% of overall confidence). The inset small figure is the relation between the inverse carbon sample weight and the ¹⁴C concentration (pMC). Dashed lines correspond to the 1 σ error.

these 2 types of sample. We also reject the intrinsic contamination because the same results were obtained for different bones and different sites. We suspect the vacuum line processes before the conversion stage of the amino acids to CO_2 to be responsible for this level of contamination for the following 2 reasons:

- 1. The pumping is less effective for the bone than for the carbonate (by ~1 order) because the residue quickly becomes pasty under the vacuum;
- 2. Atmospheric CO_2 may have been introduced during the addition of ninhydrin, either in the form of dissolved CO_2 in the ninhydrin or when the septum was perforated.

The ¹⁴C ages of bone are calculated using the blank values determined from the mass dependent equation. From this equation, the age limit is about 50,000 BP (0.2 ± 0.08 pMC) for a carbon mass of 1500 µg, and about 45,000 BP (0.37 ± 0.1 pMC) for a carbon mass of 500 µg.

Reliability of the Method

The ¹⁴C ages of bones treated by the ninhydrin method are compared to those obtained for the same archeological layer on associated organic materials (charcoal, burnt bones) and bones treated by other methods. We use the Chi-squared test statistic to check consistency of these determinations (Ward et al. 1978).

In the first test of reliability, 3 sites (Trois-Frères Cave, Laugerie Haute, and Kozarnika) allowed the comparison of ¹⁴C dates of ninhydrin-treated bones with those of associated charcoals or burnt bones. These charcoals or burnt bones underwent the classical AAA treatment. The ¹⁴C results of the 3 archeological sites are reported in Table 3 and Figure 4. At Trois-Frères Cave and Laugerie-

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Haute (Delpech et al. 2001; Roque et al. 2001), the burnt bones and bones have consistent ¹⁴C ages. The Kozarnika site (Fontugne et al. 2002) reveals the ¹⁴C age of the bone to be slightly older than those of the 2 charcoals, but, nevertheless, statistically in agreement.

Table 3 Comparison between ¹⁴C dates from bones (ninhydrin method) and from associated charcoals or burned bones (AAA treatment). All ages are given in ¹⁴C yr BP (before 1950). Statistical errors are given at 1 σ .

			Age	Error		
Site	Lab nr	Material	(yr BP)	(1 o)	Chi-squared test	Reference
Trois-Frères Cave	GifA 99552	bone	14210	110	$6.21/\chi^2_{6.0.05} = 11.1$	
	GifA 99555	bone	13930	110	,	
	GifA 99550	burnt bone	14060	110		
	GifA 99551	burnt bone	13980	120		
	GifA 99553	burnt bone	14210	110		
	GifA 99554	burnt bone	14200	120		
		average	14100	50		
Laugaria Hauta	GifA 100634	hone	10550	340	$0.75/y^2 = -0.40$	Delpech & Pigued 2001
Laugerie Haute	GrN 4442	bone	19550	140	$0.75/\chi 5; 0.05 - 9.49$	Poque et al 2001
	GrN-4495	bone	107/0	200		Roque et al. 2001
	$I_{\rm V} = 1173 (Ov A)$	burnt hone	10525	155		
	$Gif \Delta 100630$	burnt bone	19600	200		
	01111100050	average	19600	200		
		average	17000	00		
Kozarnika	GifA 99662	bone	39310	1000	$3.37/\chi^2_{3:0.05} = 5.99$	Fontugne &
	Gif/LSM-	charcoal	38700	1400	N 5, 0.05	Tisnérat-Laborde,
	10994	charcoal	37170	700		in press
	GifA 101050	average	38000	530		1



Figure 4 From a same archeological level, the average ¹⁴C dates obtained with the ninhydrin method are plotted versus the average ¹⁴C ages obtained with the Oxford bone method (open circles) or associated materials (solid circles). The ages are expressed as yr BP. The error bars are shown as $\pm 1 \sigma$ (for 5 of the data points, these error bars are smaller than the symbols). The dotted line is the 1:1 correlation line.

In the second test, we compared the ¹⁴C dates of bones treated by different chemical methods. The results are reported in Table 4 and Figure 4. A comparison with the Oxford method (Hedges et al. 1989; Law et al. 1989) may be made for 3 sites: Margaux Cave, Flageolet, and Combe Saumière (Delpech et al. 2001) (Table 4). A comparison with the Groningen procedure can be done for the site of Laugerie Haute (Table 3). In all cases, the ¹⁴C ages are similar whatever the chemical treatment, as previously noted by Nelson (1991).

Table 4 Comparison of ¹⁴C ages of bones pretreated by the method used by the Oxford Radiocarbon Laboratory (OxA) and by the ninhydrin method (LSCE, GifA). All ages are given in ¹⁴C yr BP (before 1950). Statistical errors are given at 1 σ .

Site	Lab nr	Material	Age (yr BP)	Error (1σ)	Chi-squared test	Reference
Margaux Cave	GifA 92354 GifA 92355 GifA 92362 OxA-3533 OxA-3534	bone bone bone bone average	9590 9530 9260 9530 9350 9460	110 110 120 120 120 50	$5.76/\chi^2_{5;\ 0.05} = 9.49$	
Flageolet	GifA 95538 GifA 95559 OxA-598	bone bone average	32040 34300 33800 33000	850 1100 1800 630	$2.87/\chi^2_{3;\ 0.05} = 5.99$	Delpech & Riguad 2001
Combe Saumière	GifA 96768 OxA-6507	bone bone average	35500 34000 34560	1100 850 670	$1.16/\chi^2_{2;\ 0.05} = 3.84$	Delpech & Riguad 2001

The 2 tests show the good correlation between the ¹⁴C ages of the ninhydrin-treated bones and those of samples collected at the same archeological level (Figure 4) for time intervals ranging between 9000–45,000 yr BP. All these comparisons confirm the reliability and accuracy of the method for dates up to 45,000 yr BP.

CONCLUSION

In this paper, we described our routine protocol of bone pretreatment for AMS ¹⁴C dating. This routine is applied to fossil bones containing more than 0.2% of nitrogen in whole bone.

The blank level is a function of the mass of the carbon sample. According to the equation (y = 119.68 / x + 0.1295), the blank value is equal to 0.20 ± 0.08 pMC ($\geq 50,000$ yr BP) for a sample mass of 1500 µg and 0.37 ± 0.10 pMC ($\geq 45,000$ yr BP) for a sample mass of 500 µg. The contamination by modern carbon is attributed either to the difficulty of degassing the sample or to the introduction of atmospheric CO₂.

The validity of the method and the protocol is tested by comparing the ¹⁴C ages obtained on bones by this method and those obtained by other methods (Oxford and Groningen bone methods or associated materials). The satisfactory results of these comparisons and the good estimation of the blank level show the reliability and accuracy of the method for dates up to 45,000 yr BP.

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DEVELOPMENT OF AN AUTOMATED SYSTEM FOR PREPARATION OF ORGANIC SAMPLES

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ABSTRACT. We constructed an automated system to transform organic samples to CO₂, which included several options such as: combustion in 2 steps with collection of the 2 fractions, volatile fraction combustion, and ¹³C sampling. The process includes organic matter combustion, CO₂ drying, quantification of the mass of carbon, CO₂ collection in a glass vial, and eventually ¹³C sampling. The system is computer-controlled and -monitored. The apparent background age of the automated system reaches 0.191 ± 0.011 pMC (2 σ), equivalent to a ¹⁴C age of about 51,700 yr BP, and requires only 30 min of handling, instead of the several days needed when using a manual procedure.

INTRODUCTION

The radiocarbon group of the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) previously developed a semi-automated system to transform carbonate samples into CO_2 (Tisnérat-Laborde et al. 2001) in order to reduce the time and effort of sample processing. A further step of the automation consists of the elaboration of a system allowing transformation of all types of organic samples into CO_2 . The system must be able to handle both simple samples (e.g. charcoals and vegetal macrorests) and complex samples (e.g. peat and sediment) requiring step combustion and/or including volatile fractions. An option permitting aliquot collection for further ¹³C analysis is also necessary.

METHODS

Organic Sample Pretreatment

Sample preparation depends on sample type, ranging from classical Acid-Alkali-Acid treatment for routine charcoals to ABOx, for N-rich woods and Fe^{2+} -rich paleosols (Hatté et al. 2001), and ninhydrin extraction for bones (Tisnérat-Laborde et al., this issue).

To validate manual and automated lines and to measure backgrounds, we use a 0-pMC charcoal as an internal standard. This standard, known as "Afrique du Sud," is from inside the Border cave (South Africa) in a Paleolithic level (Middle Stone Age) dated to more than 70 kya. It is routinely prepared by using an Acid (HCl 1N 60 °C)–Alkali (NaOH 0.1N 60 °C)–Acid (HCl 1N 60 °C) treatment.

"Manual" Procedure to Transform Organic Samples into CO₂

Organic samples are sealed in quartz tubes under a vacuum with an excess of CuO and silver wire. Tubes are introduced into a furnace at 835 °C for 5 hr to transform the organic matter into CO_2 . The quartz tubes are then broken under a vacuum to release, dry, measure, and collect CO_2 . This procedure requires complex handling (installation of tubes, sealing of the tubes, vacuum setting, etc.) and is time consuming.

Graphite Target Preparation

The graphite target is obtained by direct catalytic reduction of the CO₂, using Fe powder as the catalyst with a ratio of 1:5. The reduction reaction occurs at 600 °C with excess H₂ (H₂/CO₂ = 3) and is

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complete after 5–7 hr. The iron-carbon powder is pressed into a flat pellet (1-mm diameter) and stored under pure argon in a sealed tube.

To reduce contamination from modern carbon or memory effects, all quartz and glass dishes are burned at 450 °C for at least 12 hr. A turbo-molecular pump reaching 10^{-6} mbar is used to evacuate the vacuum lines.

Results are presented as ¹⁴C activity in pMC (i.e., normalized to a δ^{13} C of –25‰).

AUTOMATED SYSTEM DESCRIPTION AND FUNCTIONALITY

Technical Choices

We developed the automated system based on the manual procedure, rather than derivation from an elementary analyzer (EA) (Aerts-Bijma et al. 1997, 2001; Hedges et al. 1992). This latter technique is susceptible to carbon contamination from Sn capsules and memory effects caused by the gas chromatographic column. The Gröningen team reports a blank value of 0.56 ± 0.17 pMC and a memory effect of a factor 2 with the initial EA system (Aerts-Bijma et al. 1997). Modifications of the protocol (combustion of an empty Sn capsule between each sample) and of the line (elimination of the GC separation) significantly reduced the memory effect and the blank to 0.24 ± 0.05 pMC (Aerts-Bijma et al. 2001). The Oxford team reports a mass-dependent contamination, essentially due to the capsules combustion, of about 0.15 pMC on a 1 mg sample, which one must add to the background of the physical measurement of 0.25 ± 0.1 pMC (Hedges et al. 1992).

The automated system (hereafter, "BMOA") allows: i) combustion of 2–5 samples in the presence of 500 mg of CuO and Ag wire; ii) CO_2 drying; iii) measurement of the carbon amount; and iv) CO_2 storage in glass vials.

The new automated system called for flexible handling to accommodate both routine samples (i.e. charcoals) and decomposable samples or samples showing a volatile fraction (some peats and wood). To allow for different sample types, we motorized the furnace for vertical shifts. This solves the problem of a "cold wall" that exists with a static furnace. Indeed, with a furnace heating only the lower part of the quartz tubes, the vaporized volatile fraction rises and condenses on the quartz tube above the furnace. This fraction is not burned. On the contrary, if the furnace is raised above the sample before the heating phase and lowered only after the combustion temperature is reached, the volatile fraction will first encounter a high temperature zone, where it will be combusted to CO_2 . Thus, volatile fractions never encounter a "cold wall." The obtained CO_2 is then representative of the whole sample.

With the idea of using this automated system for all types of samples, and because it is already shown that it can be advantageous to burn peat in 2 steps (Bird et al. 1999), a 2-step combustion option was added to our system. In addition, we have included a user-definable option to remove an aliquot of obtained CO_2 for ¹³C analysis. Our line allows a partition of 10% for ¹³C and 90% for ¹⁴C.

Finally, the calibrated finger is shaped to optimize CO_2 freezing. Indeed, organic matter combustion evolves not only CO_2 , but also nitrogen and sulphur oxides that interfere with CO_2 during the freezing. The finger shape combines a small volume (permitting good precision of CO_2 measurement) with a high surface area.

Description

The line and storage vials are made of glass. Samples introduced into quartz tubes are connected by a Cajon Ultra-Torr fitting with a Viton o-ring. Glass vials are connected via "Rotulex" unions with Viton o-rings.



Figure 1 Schematic overview of the automated system. 0: movable furnace; 2: cold (-78 °C) or warm (70 °C) water trap; 3: cold (-173 °C) or warm (40 °C) calibrated finger trap; 3: cold (-173 °C) storage vials trap; P.P.: rotary pump; P.S.: turbo-molecular pump.

The vacuum is assured by a rotary and a turbo-molecular pump, and is controlled through 2 Pirani gauges and 1 inverted magnetron gauge (AIM-S). The amount of obtained carbon is calculated from the pressure gauge measurement in a calibrated finger.

All valves are either electro-pneumatic (vacuum system) or vacuum-actuated and connected to a vacuum reservoir emptied by a membrane pump.

The furnace (① on Figure 1) may be operated by a jack system operating as a step-to-step motor.

Five warm and cold traps are operated by a pneumatic-jack system:

- A cold trap (-78 °C, dry ice and ethanol) and a warm trap (70 °C water) to remove H₂O between 2 consecutive samples for the water trap (2 on Figure 1);
- A cold trap (-173 °C, liquid nitrogen) and a warm trap (40 °C water) to expand CO₂ for the calibrated finger (③ on Figure 1);
- A cold trap (-173 °C, liquid nitrogen) for storage vials (④ on Figure 1).

Electro-pneumatic valves control the transfer of liquid nitrogen from an adjacent liquid nitrogen storage reservoir, which is secured by the filling level.

The entire system is monitored by a PC computer and controlled by software written in DELPHI (Turbo Pascal Objet). The computer collects external parameters by an IEEE interface card through a digital multimeter. The electro-pneumatic valves, the vacuum-actuated valves, and the jack systems are connected via actuators to a 24-channel relay Output Board PC, then to a Data Acquisition Board (Digital I/0).

Functionality

The software tests the vacuum and leaks on different parts of the line, monitors organic sample combustion and CO_2 transfers until final storage in a vial, and calculates the amount of produced and stored carbon.



Figure 2 Synoptic of the automated system, including optional ways and user-definable user parameters. In *italics*, user-definable parameters. *Nb*: number of samples (2<Nb<5); Gauge thresholds (*Cap*: capillary to primary pumping, *Pir*: primary to turbo-molecular pumping, *Dyn*: limit vacuum under pumping, *Sta*: limit without pumping, *Freez*: limit pumping on freezing CO₂); furnace parameters: r_i , t_i , T_i : heating time, hold time, and temperature for i = drying (# 100 °C), first combustion step (# 450 °C), the second or single combustion step (# 900 °C) and cooling step (# 150 °C). The grey squares correspond to the following options: ① preliminary line pumping. The diamond boxes correspond to tests that have to be successful in allowing a passage to the following step. If the condition is not satisfied, either the operation continues until satisfaction (pumping, temperature rise, etc.), or a series of steps is carried out again for the following sample (until i = *Nb*), or a message preventing of a leak is sent if the time to obtain satisfaction is exceeded (<3 hr, <7 times).

Different options can be added to the basic run procedures:

- Preliminary line pumping before the combustion step, included in the automated system;
- Combustion in 2 steps with storage of the 2 fractions of obtained CO₂;
- Combustion with a furnace vertical shift (from top to bottom), allowing total combustion of decomposable or volatile fraction containing samples;
- Aliquot sampling of obtained CO₂ for further ¹³C analysis.

Several parameters are user-definable:

- Number of samples (from 2 to 5);
- Timing of the different steps;
- Furnace parameters: heating rate, temperature hold time and temperature for drying, the eventual 2 combustion steps, and the cooling phase;
- The following gauge thresholds allowing continuation of the run:

"Cap" threshold on Pirani 1 allowing a shift from primary pumping through a capillary to a direct primary pumping (necessary for fine sediments);

"Pir1/Pir2" threshold on Pirani 1/2, allowing a shift from primary pumping to a turbo-molecular pumping; "Dyn" threshold on AIM-S, indicating that the limit vacuum is reached through the whole line;

"Sta" threshold on AIM-S, controlling pressure increase on AIM-S in 50 seconds. It allows run continuation *id est* drying and combustions;

"Freez" threshold on AIM-S, controlling the residual gas pumping on freezing CO₂.

Several parameters are logged during the automated protocol and are easily available during and after the run:

- · Sample names;
- Results of combustion in terms of the amount of residual gases (measured in mbar on Pirani 1) and obtained carbon (in mg of carbon);
- Records of AIM-S pressure during leak testing, including results from Pirani 1 during CO₂ transfer from the quartz tube to the calibrated finger, pressure gauge during the CO₂ expanding in the calibrated finger, and Pirani 2 during the CO₂ transfer from the calibrated finger to the glass vial;
- Record of action messages showing progress and timing of the run.

RESULTS

Background Level of Manual Procedure

Figure 3 presents ¹⁴C activity versus mass or inverse mass of carbon obtained for different amounts of the Afrique du Sud standard through a manual procedure. As expressed by the very low correlation coefficient, there is no relationship between carbon mass and activity. Considering a 2 σ error margin, all data are consistent (χ^2 test with 56 observations) with a mean of 0.138 ± 0.006 pMC (2 σ), equivalent to a ¹⁴C age of about 54,400 yr BP.

For the common size range (between 0.8 and 2 mg) a mean apparent background age of 0.134 ± 0.006 pMC (about 54,700 yr BP) is measured.

Background Level of BMOA

The Afrique du Sud standard was used extensively to test different options and to cover a large range of mass. Results ranging between 430 and 1640 μ g of carbon are presented in Figure 4.



Figure 3 Background level of manual procedure. (1), above: ¹⁴C activity (pMC) as a function of carbon sample mass (μ g); (2), below: ¹⁴C activity (pMC) as a function of inverse carbon sample mass (1/ μ g). The error bars are shown $\pm 1 \sigma$ (68% of overall confidence). Full lines represent regressions (equations and coefficients are noted above). Dotted lines are the range of variation within 2 σ . The grey bar represents the mean value (0.138 \pm 0.006 pMC).

The results show that the relationship between mass and ¹⁴C activities may be represented by:

¹⁴C activity =
$$(194 \pm 28) \times (1/\text{mass}) + (0.022 \pm 0.040)$$
 (1)

with the mass in μ g of carbon (r² = 0.67). However, this empirical relationship is not valid for samples containing more than 800 μ g of C, as exhibited by the very low regression coefficient (r² = 0.0015) between ¹⁴C activities and 1/mass. Considering the 2 σ error margin, all data are consistent (χ^2 test with 11 observations) with a mean of 0.191 ± 0.011 pMC (2 σ), equivalent to a ¹⁴C age of about 51,700 yr BP.



Figure 4 Background level of BMOA. (1), above: ¹⁴C activity (pMC) as a function of carbon sample mass (μ g). Open circles represent memory effect tests, whereas open triangles are for 9-mm tubes (see text). (2), below: ¹⁴C activity (pMC) as a function of inverse carbon sample mass ($1/\mu$ g). The grey line represents the linear regression tying ¹⁴C activity and inverse carbon mass for all tests (equation and coefficient are noted below). The error bars are shown ± 1 σ (68% of overall confidence). Full black lines represent the couple of equations tying ¹⁴C-activity and inverse mass (see text). Equations and coefficient are noted black lines are the range of variation within 1 σ .

Consequently, it is more appropriate to replace Equation 1 by the following 2 equations:

mass
$$\leq 800 \ \mu g^{-14}C \ activity = (300 \pm 55) \times (1/mass) + (-0.16 \pm 0.09)$$
 (2)

mass
$$\ge 800 \ \mu g^{-14}C$$
 activity $= 0.191 \pm 0.035$ (3)

Mass dependencies can be appreciated as a constant addition of $1.8 \pm 0.4 \,\mu\text{g}$ of modern carbon (112 pMC as 2002 atmospheric CO₂) into a 0-pMC charcoal.

Memory Effects

In Figure 4, open circles symbolize the "memory effect" tests. These were performed using a small amount of the Afrique du Sud, which was run just after a large sample of "Sucrose" (IAEA-C6, 150.6 pMC). Values obtained are consistent with mean standard values obtained during normal runs, indicating that the procedure timing is well calibrated to induce no memory effect.

Quartz Tube Evaluation

Due to differences in dimensions between the international metric and imperial systems, tests were conducted to define the type of quartz tubes to be used. Cajon Ultra-Torr fittings correspond to a tube with an external diameter of 3/8", but common quartz tubes are manufactured in international metric units with an external diameter of 9 mm (i.e., 0.54 mm smaller than the Cajon fitting). Our tests showed that values obtained using the metric tubes (9 mm, open triangles in Figure 4) are consistent with values obtained using the 3/8" tubes. This indicates that no extensive leak exists with the association of Cajon Ultra-Torr fittings and the 9-mm tubes. The use of metric tubes allows for substantial lab-cost savings.

DISCUSSION

Ranges of background variation of the BMOA and the manual procedure are consistent for samples containing more than 800 μ g of carbon (Figure 5). Nevertheless, the mean level of BMOA is definitely higher than that of the manual process, 0.191 ± 0.011 pMC versus 0.138 ± 0.006 pMC (2 σ). The small number of manual measurements for the lowest masses (5 lower than 800 μ g of carbon) do not allow us to confirm an apparent background activity as low as that of the heavier samples. Nevertheless, it seems that the difference in background between the manual process and the BMOA is even larger for the samples lower than 800 μ g than it is for the largest samples. Nevertheless, the BMOA background is lower than the blank value of the EA-based systems, even modified, which show a value of 0.24 ± 0.05 pMC. (Aerts-Bijma et al. 2001).

The particular nature of the BMOA procedure may explain its apparent greater background age compared to the manual procedure for 2 reasons:

- The major difference between the manual procedure and the BMOA is that for the former, combustion occurs in a sealed tube, while in the latter, it occurs under a valve and an Ultra-Torr Cajon. Undoubtedly, flame-sealed tubes are more airtight than a "closed valve–Ultra-Torr Cajon" assembly. In particular, an increase of Viton o-ring porosity can occur consecutively with an increase of temperature (around 50 °C) during the combustion step and can allow small contamination by o-ring degassing. Perhaps a preliminary heating of the Viton o-rings would be sufficient to decrease the background level.
- 2. A leak due to differential thermal expansion between quartz, Viton and Stainless of Cajon is not very probable. Indeed, a more significant leak would be expected to occur in the case of the 9-mm tubes, for which the pressure on the o-ring is weaker than for the 3/8" tubes. Such leaking is not observed. Consequently, at this stage of the development, it does not seem necessary to implement a room with double walls around the Cajon connection, as proposed by Bird et al. (1999).

Nevertheless, the constancy and relatively low background obtained for samples containing more than 800 μ g on BMOA allows for the treatment of the majority of organic samples. Moreover, this configuration requires minimal handling to obtain, dry, measure, and collect CO₂ from 5 samples; thus, only 30 min of human handling is necessary. Furthermore, an automated run of only 10 hr is



Figure 5 Background level of manual procedure and of BMOA with the ¹⁴C activity (pMC) as a function of the carbon sample mass (μ g). The error bars are shown $\pm 1 \sigma$ (68% of overall confidence). Full lines are the range of variation within 1 σ for the BMOA. Dotted lines are the range of variation within 2 σ for manual procedure.

necessary to obtain the collected CO₂, compared with the more than 8 hr distributed over 4 days necessary to arrive at the same result "manually."

CONCLUSION

We developed an automated system to obtain, dry, measure, and collect CO_2 from organic samples. This new procedure considerably reduces the human handling time, while preserving a background level sufficiently low to treat samples containing more than 800 µg of carbon, with a limiting age of approximately 51,700 yr. This system includes many options, such as allowing aliquot extraction for ¹³C measurement and step combustion of specific samples.

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BOMB RADIOCARBON IN TREE RINGS FROM NORTHERN NEW SOUTH WALES, AUSTRALIA: IMPLICATIONS FOR DENDROCHRONOLOGY, ATMOSPHERIC TRANSPORT, AND AIR-SEA EXCHANGE OF CO₂

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ABSTRACT. We have analyzed by radiocarbon 27 consecutive single rings, starting from AD 1952, of a preliminarily crossdated section (DFR 021) of *Pinus radiata*, which grew in Armidale, northern New South Wales, Australia. The bomb ¹⁴C results suggested the possibility of 2 false rings, and, consequently, 2 misidentified rings in the preliminary count for this section. This possibility was supported by a better ring-width correlation between the revised DFR 021 count and other *Pinus radiata* chronologies in the study region. This indicated that bomb ¹⁴C is a useful tool to complement the standard techniques of dendrochronology in tree species where annual rings are not always clearly defined.

Our accelerator mass spectrometry (AMS) ¹⁴C results for Armidale *Pinus radiata*, on a corrected timescale, can be compared with previously published atmospheric and oceanic ¹⁴C data. The data show interesting features of atmospheric circulation and the regional air-sea exchange of CO₂ for the bomb period. On average, the difference between Δ^{14} C values for Armidale (30°S) and those for Tasmania (42°S) was negligible, implying a small latitudinal ¹⁴C gradient in the Southern Hemisphere. However, small offsets between Armidale and Tasmania were observed for some periods. The variation of these offsets suggests some slight changes in the relative contributions of the 2 excess ¹⁴C sources (the northern troposphere and southern stratosphere) to the southern troposphere. In the decay of bomb ¹⁴C, atmospheric ¹⁴C reached a global equilibrium at the end of the 1960s and decreased exponentially, halving every 16 years. The time for air-sea exchange of CO₂ for southern Pacific mid-latitudes was found to be about 7.5 yr, which was equivalent to a CO₂ flux from the atmosphere to the oceans of 21.5 moles m⁻²y⁻¹ for the 1970s.

INTRODUCTION

Hundreds of nuclear weapons were detonated in the atmosphere between 1945 and 1980. The radiocarbon produced around the nuclear fire ball was directly injected into the atmosphere. As a result, the concentration of ¹⁴C in the atmosphere increased dramatically in the late 1950s and early 1960s. The atmospheric ¹⁴C level reached a maximum in the Northern Hemisphere in 1963–1964, almost double its pre-bomb level. Since then, the ¹⁴C concentration in the atmosphere has been decreasing due to rapid exchange between the atmosphere and other carbon reservoirs (mainly the oceans and biosphere), and the absence of major atmospheric nuclear explosions.

Bomb ¹⁴C was recognized as a useful tracer for the study of atmospheric circulation (Nydal and Lövseth 1983; Levin et al. 1985; Manning et al. 1990), air-sea exchange of CO₂ (Nydal 1968; Druffel and Suess 1983), and the global carbon cycle (Oeschger et al. 1975; Broecker et al. 1980; Levin and Hesshaimer 2000). To contribute to the global effort, we have recently published the first long records of ¹⁴C in tree rings from the northern tropics (Thailand, 19°N) and the southern temperate region (Tasmania, Australia, 42°S) for the bomb pulse period (Hua et al. 2000). Here we present the results of new measurements on a series of annual tree rings from Armidale, Australia (30°S). This is the first time that a site in inland Australia has been used to examine the rise in atmospheric ¹⁴C due to atmospheric nuclear explosions. The accelerator mass spectrometry (AMS) ¹⁴C results were used to correct the preliminary ring boundary assignments in this cross-section, made first by using the standard techniques of dendrochronology. We then discuss the features of bomb ¹⁴C in the Southern Hemisphere and their implications for atmospheric transport. Finally, we esti-

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mate the air-sea exchange of CO_2 for southern Pacific mid-latitudes, based on our measured ¹⁴C data from Armidale tree rings and those from Great Barrier Reef corals for the bomb period reported by Druffel and Griffin (1995).

SAMPLE DESCRIPTION

An introduced species of pine in Australia, Pinus radiata, was used for this study. The tree was on the New England Tableland of northern New South Wales, Australia (30°S, 152°E). This mediumsized tree, catalog nr DFR 021, grew near a fence along a quiet countryside road from Armidale to Dangar Falls. The sampling site is at moderate altitude, about 1000 m above sea level and about 5 km east-southeast of Armidale. The tree was a sapling in 1922 and was felled in mid-winter (July) 1998, when the 1997 ring was complete but the 1998 ring had not yet begun to form. We chose DFR 021 over sections from neighboring trees because the rings were wider and easier to sample for 14 C analysis. The cross-section used for ¹⁴C analysis is shown in Figure 1. The heartwood-sapwood transition for DFR 021 is around rings 1962-1966. Note that organic materials (e.g., lignin, waxes) in the outermost sapwood rings may be added to heartwood at the time of conversion from sapwood to heartwood (Cain and Suess 1976), but should be removed by pretreatment to pure cellulose (Hua et al. 1999 and references therein). This pretreatment was employed for this study (see below), so that the ${}^{14}C$ measurements are unaffected. The outer rings, where samples were taken for ${}^{14}C$ measurement, are typically 2-3 mm wide, necessitating the use of AMS for ¹⁴C analysis. During the summer growing season of Armidale Pinus radiata, the air mass movement is predominantly from the northeast/southeast sector (Linacre and Geerts 1997).



Figure 1 Cross-section of Armidale *Pinus radiata* DFR 021 with rings from AD 1922 to 1997, from which a subsection was used for AMS ¹⁴C analysis.

AMS 14C ANALYSIS AND THE DENDROCHRONOLOGY OF PINUS RADIATA

The ring pattern of *Pinus radiata* is clear and well-defined for the inner part of the DFR 021 section, where the rings are wide. For this part of the section, a typical ring width is 5–10 mm. As the tree became older and the outer rings became narrower, the ring pattern was less clear, with many doubtful ring boundaries. There are many bands of small dark cells, which are similar to ring boundaries, across the section. This made it difficult to date the DFR 021 section using the standard techniques of dendrochronology because these uncertain ring boundaries might result in false (or intra-annual) rings being counted in one part of the section and true rings not being counted in other parts of the section or vice versa. The cross-dating of DFR 021 against other *Pinus radiata* trees in the region was carried out at the NWG Macintosh Centre for Quaternary Dating of the University of Sydney and a preliminary ring count (pc) for DFR 021 was achieved.

Fortunately, the narrow rings in the section, where the potential problems occur, are in the bomb pulse period. There are 2 unique features of bomb ¹⁴C, which can be used to examine the preliminary chronology of DFR 021. The first one is that atmospheric ¹⁴C contents are similar for similar latitudes in the Southern Hemisphere. We employed atmospheric ¹⁴C records for Pretoria 26°S (South Africa, Vogel and Marais 1971) and Wellington 41°S (New Zealand, Manning and Melhuish 1994) as a norm for the ¹⁴C level for Armidale. The second feature is the significant difference in ¹⁴C levels between consecutive annual tree rings during the bomb period, especially for the period of rising atmospheric ¹⁴C and a decade after the major bomb peak (1955–1965 and 1966 to the late 1970s). These features are very effective for detecting misidentified rings.



Figure 2¹⁴C in tree rings versus atmospheric ¹⁴CO₂ at similar latitudes. Lines represent Δ^{14} C values for atmospheric samples. Data for Pretoria and Wellington are from Vogel and Marais (1971) and Manning and Melhuish (1994), respectively. Triangles depict Δ^{14} C values for tree rings. Δ^{14} C values for Armidale *Pinus radiata* are shown for the preliminary ring counts (pc) and revised chronology (RC).

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Twenty-four consecutive single tree ring samples, starting from AD 1952, were prepared for AMS ¹⁴C analysis using the protocols set up by Hua et al. (1999). Our sampling strategy was to avoid the ring boundary areas due to very different levels of ¹⁴C between consecutive rings. The woody material of each ring, well clear from ring boundaries, was selected for ¹⁴C analysis. The samples were pretreated to alpha-cellulose using the method of Hua et al. (2000). The pretreated material was converted to graphite using methods described in Hua et al. (2001). The AMS ¹⁴C measurements were performed using the ANTARES facility at ANSTO (Lawson et al. 2000; Fink et al. 2003), with a precision of 0.35–0.45%.

The AMS ¹⁴C results for DFR 021 were reported in Δ^{14} C values, after corrections for isotopic fractionation using δ^{13} C and radioactive decay of both sample and standard (Hua et al. 1999, and the Δ term of Stuiver and Polach 1977). The results are presented in Table 1 and illustrated in Figure 2. The Δ^{14} C values for tree rings are plotted as points in the middle of the presumed growing period of December–January. For ease of comparison, the atmospheric ¹⁴C records from the Southern Hemisphere temperate regions, namely Pretoria 26°S (South Africa) and Wellington 41°S (New Zealand), are also shown in Figure 2.

Table 1 Measured Δ^{14} C from *Pinus radiata* in Armidale, Australia (30°S, 152°E), for both preliminary ring counts and revised chronology.

		Ring forma		
Laboratory	$\delta^{13}C$	Preliminary	Revised	
code	(‰ PDB)	ring counts (pc)	chronology (RC)	Δ ¹⁴ C (‰)
OZE208	-22.1	1952	1952	-28.8 ± 4.5
OZE209	-21.9	1953	1953	-21.8 ± 4.1
OZE210	-21.5	1954	1954	-22.0 ± 4.3
OZE211	-22.6	1955	1955	-17.0 ± 4.6
OZE212	-22.4	1956	1956	18.7 ± 4.5
OZE213	-19.9	1957	1957	40.5 ± 3.3
OZE214	-21.0	1958	1958	98.1 ± 4.2
OZE215	-21.8	1959	1959	186.8 ± 4.2
OZE216	-20.4	1960	1960	195.5 ± 3.4
OZE217	-22.3	1961	1961	191.2 ± 4.1
OZE218	-22.9	1962	1962	251.6 ± 4.6
OZE219	-22.1	1963	1963	435.8 ± 5.2
OZE220	-21.8	1964	1964	606.6 ± 5.9
OZE221	-20.7	1965	1965	628.2 ± 5.7
OZE222	-20.5	1966	1966	615.4 ± 5.6
OZE223	-21.9	1967	1967 (early wood)	586.9 ± 5.4
OZE224	-21.9	1968	1967 (late wood)	580.7 ± 5.3
			1967	583.8 ± 3.9
OZE225	-21.1	1969	1968	556.6 ± 5.6
OZE226	-21.7	1970	1969	531.6 ± 5.7
OZE227	-22.7	1971	1970	516.1 ± 5.1
OZE228	-23.0	1972	1971	475.6 ± 6.0
OZE229	-22.2	1973	1972	448.1 ± 5.3
OZE230	-22.3	1974	1973	416.7 ± 5.4
OZE231	-21.8	1975	1974	396.0 ± 5.6
OZG572	-22.9	1976	1975	378.7 ± 4.4
OZG573	-22.5	1977	1976 (early wood)	351.9 ± 4.9
OZG574	-23.4	1978	1976 (late wood)	340.5 ± 4.9
			1976	346.2 ± 5.2

Excellent agreement between measured ¹⁴C data for Armidale tree rings and atmospheric ¹⁴C records for Pretoria for the period of 1952 to 1967 (pc) was found. However, for the period of 1968 to 1975 (pc), Δ^{14} C values for the Armidale tree rings were significantly higher than those of atmospheric ¹⁴C records for Pretoria and Wellington. In addition, Δ^{14} C value for ring 1967 (pc) was equal to that for ring 1968 (pc) (Table 1). These results suggested that 1967 (pc) ring boundary was a false one and that rings 1967 and 1968 (pc) were in fact a single 1967 ring.

To test this hypothesis, we shifted results one year back for rings 1968–1975 (pc) and plotted their Δ^{14} C values in Figure 2. A very good agreement with the atmospheric data sets was then found, indicating that the hypothesis was correct. We therefore adopted a revised ring count, with the (new) 1967 ring consisting of the 2 rings, 1967 and 1968 of the preliminary count (Figure 3). We then noted the similarity between rings 1967–1968 (pc) and rings 1977–1978 (pc) (see Figure 3), and inferred that the 1977 (pc) ring boundary may also be a false one. To confirm this, the 3 single rings, 1976–1978 (pc), were prepared and measured by AMS. The ¹⁴C results from these rings, which are also presented in Table 1, showed that the Δ^{14} C value for ring 1977 (pc) was similar to that for ring 1978 (pc). These results confirmed that the 1977 (pc) ring boundary was also a false one.

Table 2 Ring-width correlation between DFR 021 and other *Pinus radiata* trees in the study region. Calculation was performed for 25-yr segments lagged 12 yr.

	Statistical correlation			
Counted segment (year AD)	Preliminary ring counts (pc)	Revised chronology (RC)		
1923–1947	0.79	0.79		
1935–1959	0.82	0.82		
1947-1971	0.79	0.83		
1959–1983	0.54	0.69		
1971–1995	0.52	0.63		
1973–1997	0.53	0.65		

¹⁴C contents for rings 1952–1976 of the revised count (rc), equivalent to rings 1952–1978 (pc), agreed well with the atmospheric records for Pretoria and Wellington. This therefore meant that 2 later true rings were not counted, somewhere between rings 1979 and 1997 (pc). Using the standard techniques of dendrochronology, and the fact that ring 1982 in other trees from this site was a very narrow ring influenced by a strong El Niño event (low rainfall from November 1982 to January 1983 for the Armidale region, data files provided by Bureau of Meteorology 1999), we inferred that the correct ring boundaries were those shown in the revised count (Figure 3). Unfortunately, we could not use additional ¹⁴C measurements to confirm the revised count because the ¹⁴C levels between consecutive rings in this period are not so different (the atmospheric ¹⁴C bomb curves for the Southern Hemisphere from 1980 onwards decreases less steeply; Vogel and Marais 1971; Manning and Melhuish 1994). However, after the identification of 2 false ring boundaries in 1967 and 1976 (rc), and new ring boundaries for 1982 and 1991 (rc), the revised count was supported by statistical correlation, with a significant improvement in ring-width correlation between DFR 021 and other *Pinus radiata* trees in the region for rings 1947 outwards (Table 2). This gave us confidence in the revised chronology (RC).



Figure 3 Tree-ring pattern of Armidale Pinus radiata DFR 021. Preliminary ring counts (pc) versus revised chronology (RC).

IMPLICATIONS FOR ATMOSPHERIC TRANSPORT

Measured Δ^{14} C values for Armidale *Pinus radiata* (RC only) are shown in Figure 4, together with previously published Δ^{14} C data for tree rings at different latitudes from the Northern and Southern Hemisphere. They are, respectively, the data for Hungary (48°N, 1951–1978, Hertelendi and Csongor 1982), Germany (49°N, 1966–1982, Levin et al. 1985), Japan (38°N, 1960–1969, Muraki et al. 1998), Thailand (19°N, 1952–1975, Hua et al. 2000), and Tasmania (Australia, 42°S, 1952–1975, Hua et al. 2000). These data are plotted in the middle of the growing period: June–July for the Northern Hemisphere and December–January for the Southern Hemisphere.

The difference between Armidale (30°S) and Tasmania (42°S) was generally small or negligible (Figure 4). The weighted average of the difference of the 2 data sets for the period influenced by atmospheric nuclear detonations (rings 1954–1975) was $0.3 \pm 2.9\%$ (Armidale is higher). The magnitude of this difference is similar to the mean monthly difference of $0.5 \pm 1.1\%$ between Pretoria (26°S) and Wellington (41°S) for the period of 1957–1993 (Hua and Barbetti 2003). This indicated a small latitudinal gradient in terms of Δ^{14} C for the Southern Hemisphere. The reason for the low latitudinal gradient in the Southern Hemisphere is that the sources of bomb ¹⁴C, which are mainly in the Northern Hemisphere, are far from the south (Manning et al. 1990), and once the ¹⁴C diffuses rapidly with fast mixing in the Southern Hemisphere and does not allow for a large gradient there (Hua et al. 1999). This feature of bomb ¹⁴C in the Southern Hemisphere is in contrast to that for the Northern Hemisphere, where there is a large latitudinal gradient of Δ^{14} C—note the significant difference between Δ^{14} C values for Hungary (48°N) and those for Japan (38°N) at least for the bomb peak period (Figure 4).

Although the average difference between Armidale and Tasmania was negligible, small offsets between the 2 data sets were observed during the rise and fall of bomb ¹⁴C. Note that the excess ¹⁴C produced by bomb tests was mostly injected into the stratosphere, then returned to the troposphere through the mid- to high-latitude tropopause gap in both hemispheres during the spring and summer time of each hemisphere. Because the main sources of bomb ¹⁴C were in the Northern Hemisphere, the southern troposphere received excess ¹⁴C from the northern troposphere reached Armidale (30°S) before it reached Tasmania (42°S), meanwhile Tasmania was more sensitive to the injection from the southern stratosphere (compared to Armidale) because Tasmania is located further south and is close to the injection areas (mid- to high-latitudes) in the Southern Hemisphere.¹ Due to a very similar growing season between Armidale *Pinus radiata* and Tasmanian Huon pine (approximately from November to February), the variation of the small offsets between Armidale and Tasmania during the bomb period might indicate some indications about relative contributions of the 2 excess ¹⁴C sources to the southern troposphere.

¹The seasonal structure for the Wellington record (41°S, New Zealand), which is close to Tasmania in latitude, was well determined with a maximum in March and a minimum in August (until 1980; Manning et al. 1990). This seasonality reflected the injection of excess ¹⁴C from the southern stratosphere into the southern troposphere. Meanwhile, the seasonal structure for the South Pacific sites including Funafuti 9°S (Tuvalu) and Suva 18°S (Fiji), which is close to Armidale in latitude, were not well determined (Manning et al. 1990). It is likely that these sites received more excess ¹⁴C from the Northern Hemisphere, which became diffused when transferred to the Southern Hemisphere across the broad ITCZ. As a result, atmospheric ¹⁴C over these sites lost the Northern Hemisphere seasonal pattern: maximum in July–August and minimum in January–March (Meijer et al. 1995), which mainly reflected the seasonality of the injection of excess ¹⁴C from the northern stratosphere to the northern troposphere.



Figure 4 ¹⁴C in tree rings at different latitudes and atmospheric nuclear detonations AD 1950–1980. Symbols depict Δ^{14} C values for tree rings. Data sources are Hertelendi and Csongor (1982) for Hungary, Levin et al. (1985) for Germany, Muraki et al. (1998) for Japan, and Hua et al. (2000) for Thailand and Tasmania. Measured Δ^{14} C values for Armidale *Pinus radiata* are shown for the revised chronology (RC) only. Error bars are too small to be shown. Bars represent effective yield of atmospheric nuclear detonations for 3-month periods (for 1945–1976, Enting 1982; for 1977–1980, Yang et al. 2000).

 Δ^{14} C values for Armidale were slightly lower than those for Tasmania at the ends of 1954, 1957, and 1961 (Figure 4). Unfortunately, the 2 atmospheric ¹⁴C records for Pretoria and Wellington shown in Figure 2, which have latitudes similar to Armidale and Tasmania, respectively, are not detailed enough at those times to determine if there are similar ¹⁴C offsets between the 2 records. It is interesting that the ends of 1957 and 1961 were times when there were changes in the rates of increase of ¹⁴C in Armidale *Pinus radiata*: a small rise from the end of 1955 to the end of 1957, an intermediate increase from the end of 1957 to the end of 1959, a plateau from the end of 1959 to the end of 1961, and a steep rise from the end of 1961 to the end of 1965 (Figure 4). These changes suggest variations in the amount of excess ¹⁴C transferred from the northern troposphere to the southern troposphere. There was a plateau in Δ^{14} C in the northern troposphere during 1956, followed by a small increase during 1957. There was effectively no increase in the amount of ¹⁴C transferred to the Southern Hemisphere during 1957 because there is a time lag for the transfer of excess ¹⁴C between the 2 hemispheres of the troposphere. Meanwhile, Δ^{14} C values of the southern stratosphere increased slightly during 1957 (Figure 5). A similar situation was noted for 1961, when there was no increase in the amount of ¹⁴C transferred from the Northern Hemisphere to the Southern Hemisphere (see Figure 4), and a slight increase of ${}^{14}C$ in the southern stratosphere (see Figure 5). These slight changes in the relative contributions of the 2 excess ¹⁴C sources to the southern troposphere might explain the negative Armidale-Tasmania offsets at the ends of 1957 and 1961 (and perhaps also 1954, for which there are no data on stratospheric ¹⁴C; see Figure 5; Telegadas 1971; Hesshaimer and Levin 2000).


Figure 5 Δ^{14} C values in the stratosphere and troposphere for the bomb period (after Manning et al. 1990). The upper 2 curves are for the stratosphere and the lower 2 for the troposphere. The solid and dotted lines denote the Northern and Southern Hemisphere, respectively.

In contrast, during the steepest rise of bomb 14 C, Δ^{14} C values for Armidale were slightly higher than those for Tasmania (at the ends of 1963, 1964, 1968, and 1969). It was clear that this steep rise of 14 C was due to high-yield nuclear weapon tests in 1961–1962 (Figure 4). These detonations injected a large amount of artificial 14 C into the upper and high stratosphere in the Northern Hemisphere. As a result, the major transport of excess 14 C was from the northern stratosphere to the northern troposphere then to the southern troposphere. During this period of time, the concentration of excess 14 C in the northern stratosphere was much higher than that in the southern stratosphere (Figure 5), so the amount of excess 14 C injected into the southern troposphere from the southern stratosphere would be smaller than that from the northern troposphere. This would explain why there were positive Armidale-Tasmania offsets for the steep rise of bomb 14 C (at the ends of 1963 and 1964). Bomb 14 C reached a maximum at the end of 1965, then decreased. There were no differences between Armidale and Tasmania at the ends of 1965, 1966, and 1967. However, there were positive Armidale-Tasmania offsets at the ends of 1965, 1968, and 1969.

In the decay of bomb ¹⁴C, there were some disturbances (Figure 6). A small peak in tree ring Δ^{14} C was found in German pine in the middle of 1970. Levin et al. (1985) suggested that a nearby nuclear power plant caused this effect (see Table 6 of Levin et al. 1985). This Δ^{14} C peak was also found in Hungarian tree rings in the middle of 1970 and in Thai tree rings in the middle of 1971 as the transport time of bomb ¹⁴C from northern temperate region to the tropics is ~1 yr (Hua et al. 2000). These disturbances were also observed around 1970 in the atmospheric records for Fruholmen, Norway, at 71°N (Nydal and Lövseth 1983). These features indicate that the effect was not local or regional, but global, and that it was caused by sporadic atmospheric nuclear tests after 1963 performed by China in the Northern Hemisphere and France in the South Pacific (Enting 1982). A small bomb peak is

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expected to be found in the Southern Hemisphere temperate region at the end of 1971 as the transport time of bomb ¹⁴C from the tropics to the southern temperate region is ~0.5 yr (Hua et al. 2000). However, as mentioned above, the ¹⁴C excess becomes diffused when it is transported over the broad ITCZ; no small bomb peak was found in either the Armidale or the Tasmanian series at the end of 1971.



Figure 6 Influences of sporadic atmospheric nuclear tests after the 1963 Test Ban Treaty and decay of bomb ¹⁴C. Measured Δ^{14} C values for Armidale *Pinus radiata* are shown for the revised chronology (RC) only. Sources of Δ^{14} C data for tree rings and effective yield of atmospheric nuclear detonations are shown in Figure 4.

There were small upward fluctuations in Tasmanian Huon pine at the ends of 1970 and 1972 and the Δ^{14} C value for Tasmania was slightly higher than that for Armidale at the end of 1972. These fluctuations might be due to atmospheric nuclear tests in the South Pacific in 1968 and 1970, and 1971, respectively (Figure 6). However, there were no significant fluctuations for Armidale *Pinus radiata* (except perhaps for a small upward fluctuation less pronounced than that for Tasmania at the end of 1970). As mentioned above, Tasmania is more sensitive to the injection from the southern stratosphere and, therefore, to atmospheric nuclear bomb tests in the Southern Hemisphere. As a consequence, Tasmania became equal to Armidale at the ends 1970 and 1971 (Tasmania was lower than Armidale at the end of 1972. This would also explain why no pronounced fluctuations in atmospheric ¹⁴C between 1970–1976 were found in Armidale tree rings.

Most of the Armidale-Tasmania offsets discussed above (negative at the ends of 1954, 1957, 1961 and 1972; positive at the ends of 1964, 1968, and 1969) were small, as the 2 data sets did not overlap within 1 σ error but did overlap within 2 σ error. Only one significant offset, where the 2 data sets did not overlap within 2 σ error, was found at the end of 1963. This significant difference between Armidale and Tasmania might be due to large amount of excess ¹⁴C transferred from the Northern to Southern Hemisphere during the steep rise of bomb ¹⁴C at the end of 1963.

Although there were some small disturbances between 1970–1972, bomb ¹⁴C reached a global equilibrium at the end of 1968 (Telegadas 1971) and decreased exponentially, halving every 16 yr (Figure 6). This estimate is very similar to those of previous work: 17 yr from Manning et al. (1990) and Dai et al. (1992), 18 yr (inversion of a decay constant of 0.055 yr⁻¹) from Nydal and Gislefoss (1996), and 16 yr from Levin and Kromer (1997) and Park et al. (2002).

AIR-SEA EXCHANGE OF CO2 FOR SOUTHERN PACIFIC MID-LATITUDES

Measured Δ^{14} C values for Armidale tree rings and those for corals from the Great Barrier Reef are shown in Figure 7. The coral Δ^{14} C were the average values of 3 different sites: Heron Island (23°S, 152°E), Abraham Reef (22°S, 153°E), and Lady Musgrave Island (24°S, 153°E) (Druffel and Griffin 1995). Atmospheric Δ^{14} C for Armidale increased from –22‰ at the beginning of 1955 to 186.8‰ at the beginning of 1960. As a result of the transfer of bomb ¹⁴C from the atmosphere to the surface ocean, Δ^{14} C in Great Barrier Reef corals slightly increased from –54.7‰ in early 1955 to –22.8‰ in early 1961. Then, atmospheric Δ^{14} C dramatically increased from 191.2‰ at the beginning of 1962 to a maximum level of 628.2‰ at the beginning of 1966 due to the high level of atmospheric nuclear detonations in 1961–1962 (Figure 4). The Δ^{14} C level in corals increased from –29.2‰ in early 1962 to 95.5‰ in early 1968. This period saw a steep rise of bomb ¹⁴C in the surface ocean of the Great Barrier Reef. After 1966, although atmospheric Δ^{14} C decreased, the Δ^{14} C level in Great Barrier Reef corals still increased with a lower rate and reached a maximum of about 141‰ between 1976–1980. This occurred because there was a large amount of excess ¹⁴C in the atmosphere after the major bomb tests which was still being transferred to the oceans. After 1980, the Δ^{14} C level in the surface ocean of the Great Barrier Reef decreased.



Figure 7 ¹⁴C in tree rings compared with that in corals for southern mid-latitudes. Measured Δ^{14} C values for Armidale *Pinus radiata* are shown for the revised chronology (RC) only. Δ^{14} C values for corals are the average values of 3 different sites (Heron Island, Abraham Reef, and Lady Musgrave Island) from the Great Barrier Reef (Druffel and Griffin 1995). Error bars are too small to be shown.

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We have used a 1D box model to estimate the time for air-sea exchange of CO_2 for the mid-southern Pacific, with the assumption that only vertical transport in the oceans was responsible for the transfer of bomb ¹⁴C from the atmosphere to the oceans. The model consisted of a box diffusion ocean from Oeschger et al. (1975), including a homogenous surface-mixed layer of 75 m, and deep sea water divided into 36 boxes of 25 m and 5 boxes of 560 m. The transfer of ¹⁴CO₂ between the surface-mixed layer and deep sea water was parameterized by a constant vertical eddy diffusivity *K*. The transfer of bomb ¹⁴C from the atmosphere to the surface-mixed layer was parameterized by a constant vertical eddy diffusivity *K*. The transfer of bomb ¹⁴C from the atmosphere to the surface-mixed layer was parameterized by a constant exchange coefficient k_{am} , which is inversely proportional to the time for the air-sea exchange τ_{am} . If the time history of atmospheric ¹⁴C (the source of bomb ¹⁴C for the oceans) and the constant eddy *K* are known, one can estimate the air-sea exchange coefficient k_{am} for a particular region using the above model.

The source function of bomb ¹⁴C in the atmosphere was our measured Δ^{14} C data from Armidale tree rings (1953–1977). Because atmospheric CO_2 content was not constant but increased significantly (Etheridge et al. 1998) during the period of our study (the bomb pulse period), we had to include the 12 C species in our modelling. The source function of atmospheric CO₂ was the measured CO₂ data from Law Dome DE08 and DE08-2 ice cores from Antarctica (AD 1832-1977, Etheridge et al. 1998). The eddy diffusivity K for the ocean close to the Great Barrier Reef corals $(22-24^{\circ}S, 152-$ 153°E) was determined from GEOSECS Tritium data of Pacific stations 269 (23°57'S, 174°31'W) and 310 (26°57'S, 157°9'W) (see Figure 8 for locations of Armidale tree rings, corals from the Great Barrier Reef, and the 2 GEOSECS Pacific stations). The mean depth of tritium penetration in 1973 for the 2 stations was 360 m (370 m for station 269 and 350 m for station 310, Broecker et al. 1980), which was equivalent to an eddy diffusivity K of 4890 $m^{-2}y^{-1}$ (Broecker et al. 1980). The average pre-bomb Δ^{14} C value of Great Barrier Reef corals was about -50‰ (-49.6 ± 3.6‰ for Abraham Reef for 1800–1957, Druffel and Griffin 1993; $-49.8 \pm 3.8\%$ for Heron Island for 1849–1955, Druffel and Griffin 1999). The model was run from 1832 to 1977 and the initial Δ^{14} C value of the surface-mixed layer was chosen so that the average pre-bomb Δ^{14} C value of the surface waters for 1832–1955 calculated from the model was in agreement with that of the Great Barrier Reef corals of -50‰.

The model was then run with different values of k_{am} . The best k_{am} was determined when there was the best fit to the measured Δ^{14} C for the mixed layer (Δ^{14} C values from the Great Barrier Reef corals for 1953–1977, Druffel and Griffin 1995) and the measured Δ^{14} C for the deep ocean close to the Great Barrier Reef (Δ^{14} C values of deep ocean for stations 269 and 310 in 1974, Östlund and Stuiver 1980). The air-sea exchange coefficient k_{am} for mid-southern Pacific estimated by the model was 1/ 7.5 yr⁻¹, which was equivalent to a τ_{am} of 7.5 yr. Figures 9 and 10 show Δ^{14} C values calculated by the model versus experimental Δ^{14} C data for the surface-mixed layer and deep ocean for the best estimated value of k_{am} of 1/7.5 yr⁻¹, respectively. A good agreement between measured Δ^{14} C data for surface ocean derived from corals and those calculated from the model was found (Figure 9). However, for the deep ocean the agreement between experimental ¹⁴C data and those determined from the model were not very good for the depth between 100–600 m (Figure 10). This suggested that using only vertical transport (diffusion) in the oceans does not properly explain the transfer of bomb ¹⁴C to the deep sea for the mid-southern Pacific Ocean.

The corresponding flux of CO₂ (k_{am} of 1/7.5 yr⁻¹) from the atmosphere to the surface ocean for midsouthern Pacific for the 1970s (CO₂ mixing ratio of 330 ppm, Etheridge et al. 1998) was 21.5 moles m⁻²y⁻¹. Our estimated value is in agreement with the estimate of 22 moles m⁻²y⁻¹ for the CO₂ invasion rate for the south temperate region of the Pacific by Broecker et al. (1985). Quay and Stuiver (1980) determined the CO₂ gas exchange for the mid-southern Pacific. Their average value of CO₂







Figure 9 Δ^{14} C in corals from the Great Barrier Reef (average values of corals from 3 different sites as in Figure 7) compared to that calculated from the model for the case of best estimate k_{am} of 1/7.5 yr⁻¹.

gas exchange from 4 stations (322, 320, 317, and 324) located east of 150°W was 25 moles $m^{-2}y^{-1}$. Stuiver et al. (1981) estimated the average air-sea exchange rate of 26.5 moles $m^{-2}y^{-1}$ for the south Pacific from 10°S to 50°S. Our estimate is slightly lower than those from Quay and Stuiver (1980) and Stuiver et al. (1981). The difference between the 3 estimates might be due to the difference in study areas: 23–27°S, 152°E–158°W (this study); 23–43°S, 128–146°W (Quay and Stuiver 1980); south Pacific between 10–50°S (Stuiver et al. 1981).

CONCLUSION

This is the first time that a site in inland Australia has been used to examine the rise in atmospheric ¹⁴C due to atmospheric nuclear detonations in the late 1950s and early 1960s. Our AMS ¹⁴C results for single tree rings from Armidale 30°S (Australia, rings 1952–1976) revealed some interesting features of Southern Hemisphere bomb ¹⁴C and their implications for global atmospheric circulation. On average, the difference between Armidale and Tasmania in terms of ¹⁴C was negligible, implying a small latitudinal gradient for the Southern Hemisphere. This situation contrasts with that of the Northern Hemisphere, where there was a large latitudinal gradient of ¹⁴C during the bomb peak. However, small offset variations between Armidale and Tasmania were observed. This might suggest some indications about relative contributions of the 2 excess ¹⁴C sources (the northern troposphere and southern stratosphere) to the southern troposphere. Together with previously published ¹⁴C data from tree rings, ¹⁴C in Armidale *Pinus radiata* decreased exponentially, halving every 16 yr.





Figure 10 Oceanic Δ^{14} C for stations 269 and 310 in the South Pacific (values respectively for January and April 1974 during the GEOSECS expedition, Östlund and Stuiver 1980) compared to that calculated from the model for the case of the best estimate k_{am} of 1/7.5 yr⁻¹. The penetration of bomb ¹⁴C in the Pacific Ocean at the time of GEOSECS expedition in 1974 was less than 1000 m (Broecker et al. 1985); therefore, only oceanic ¹⁴C data from depths less than 1000 m were used for comparison.

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By using our measured ¹⁴C from Armidale *Pinus radiata* together with previously published ¹⁴C data from Great Barrier Reef corals (Druffel and Griffin 1995) and from 2 GEOSECS southwest Pacific stations (269 and 310, Östlund and Stuiver 1980), we estimated the time for air-sea exchange of CO₂ of ~7.5 yr for the mid-southern Pacific, which was equivalent to a CO₂ flux from the atmosphere to the surface ocean of 21.5 moles $m^{-2}y^{-1}$ for the 1970s. The results also showed that bomb ¹⁴C is a very useful tool to complement the standard techniques of dendrochronology in detecting misidentified rings when tree rings are analyzed by ¹⁴C in a way similar to our experiment—a series of consecutive annual rings during the bomb pulse period.

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FRESHWATER RESERVOIR EFFECT IN ¹⁴C DATES OF FOOD RESIDUE ON POTTERY

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ABSTRACT. Radiocarbon dates of food residue on pottery from northern European inland areas seem to be influenced significantly by the freshwater reservoir effect ("hardwater" effect) stemming from fish and mollusks cooked in the pots. Bones of freshwater fish from Stone Age Åmose, Denmark, are demonstrated to be 100 to 500 ¹⁴C yr older than their archaeological context. Likewise, food residues on cooking pots, seemingly used for the preparation of freshwater fish, are shown to have ¹⁴C age excesses of up to 300 yr. It is probable that age excesses of similar or even larger magnitude are involved in food residue dates from other periods and regions. Since this effect cannot, so far, be quantified and corrected for, ¹⁴C dating of food residue, which may potentially include material from freshwater ecosystems, should be treated with reserve.

BACKGROUND AND HYPOTHESIS

Radiocarbon dates of charred food remains on pottery have become very popular among archaeologists. In principle, this kind of material has the obvious advantage of indisputable chronological association with the very usage of the pottery, a category of artifacts of fundamental importance for the study of prehistoric cultural processes. In practice, however, it has recently become apparent that many ¹⁴C dates of food residue from northern Europe are up to several centuries older than expected from other kinds of evidence (Fischer 2002; cf. Koch 1998:96, 98, 101, 107; Persson 1999:86).

Some of these surprisingly old food residue dates are probably due to the marine reservoir effect, which applies to cases where the δ^{13} C values are greater (less negative) than about -26% (see below). This paper discusses the hypothesis that dates of food residue which do not contain material of marine origin may also have significant reservoir effects, in this case stemming from freshwater organisms such as fish and mollusks cooked in the pots. This hypothesis was formulated on the basis of the following observations and inferences:

- Many of the surprisingly old food residue dates from northern Europe derive from Stone Age pots which are found in inland regions, including the Åmose bog in eastern Denmark. Some of the most striking examples are marked in Figure 1.
- Examinations of Stone Age food residue on pottery found in the inland have revealed remains of bones and scales of freshwater fish, which apparently have been cooked in the vessels (Koch 1998:151).
- In the Åmose, which is a bog with very fine preservation conditions for food remains, bones and scales from freshwater fish and shells from freshwater mollusks (*Anodonta*) often constitute a major part of Stone Age culture layers. Consequently, freshwater food is expected to have been a frequent ingredient in the food prepared in the cooking vessels found in this bog and probably in cooking pots found in other wetlands as well, where faunal remains were not so well preserved.
- Present-day river water and freshwater fish and mollusks from other parts of northern Europe are reported to have reservoir ages in the order of several hundred to a few thousand yr (Lanting and van der Plicht 1996, 1998; Heinemeier et al. 1997; Heinemeier and Rud 1998; Cook et al. 2001). Similarly, several studies have reconstructed past reservoir ages, based on pre-bomb samples in freshwater systems (e.g. Heier-Nielsen et al. 1995; Geyh et al. 1998). Thus, it can be expected that freshwater organisms prepared in the cooking pots from Stone Age Åmose have

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significant apparent ages. This age offset can result from the hardwater effect and other varieties of reservoir effect.



Figure 1 Northern European Stone Age sites with ¹⁴C-dated food residue on pottery, some of which has produced surprisingly old dates. In the case of the coastal settlements (rectangular signatures), the age offsets probably derive primarily from hitherto unrecognized marine reservoir effect. The apparent age of food residues from inland settlements (round signatures) and votive pots (x signatures) can in most cases be explained by hitherto unrecognized freshwater reservoir effect.

FOOD RESIDUE

In this paper, the term "food residue" refers to charred, usually dark residues up to several mm thick, which adhere to the inner surface of cooking pottery (Figure 2). The color of this material varies from pot to pot from black to dark brown to brownish gray—probably reflecting differences in the original composition, as well as in the secondary decomposition of the residue. It is generally considered to be the remains of food, fixed to the vessels during the cooking process (e.g. Andersen and Malmros 1985; Koch 1987, 1998; Isaksson 1997; Persson 1997, 1999; Nakamura et al. 2001).



Figure 2 Food residue on the inner surface of a sherd of a cooking pot from the Åkonge site. On this sherd, major parts of the approximately 1-mm-thick layer have peeled off (scale in cm). Photo courtesy of John Lee, The National Museum of Denmark.

The same kind of residue is regularly seen on the upper parts of the outer surface of many cooking vessels, where it probably ended up as a result of boiling over (cf. Andersen and Malmros 1985; Koch 1987, 1998:117). On the upper parts of the outer surface of such pots, another, generally thinner and more glossy coating is often seen, too (Figure 3). The latter seems (primarily) to be deposits of soot from the cooking fire (cf. Koch 1998:117).

A study of hundreds of Neolithic wetland votive pots with well-preserved traces of use concludes that the vessels in question were used for boiling food (Koch 1998:117). The blistery inner structure, which is often seen in the organic residues on the inner surface of the vessels, has been interpreted



Figure 3 Potsherd with a thin layer of glossy, dark coating on its outer surface, probably mainly consisting of soot from the cooking fire (scale in cm). Photo courtesy of Geert Brovad, The Zoological Museum, Copenhagen.

as a result of intentional fermentation (Arrhenius 1984; Arrhenius and Lidén 1989; Isaksson 1997), but might also have resulted from boiling food. Observation of microscopic fragments of pottery, which apparently have entered such food residue as a result of stirring, may indicate that the food was soup or porridge (Isaksson 1997).

Chemical analyses have revealed a diversity of fats, proteins, and trace elements in food residue on northern European pottery (Arrhenius 1984; Arrhenius and Lidén 1989; Lidén 1990; Isaksson 1997; cf. Malainey et al. 1999). Microscopic examination has, furthermore, demonstrated stray fragments of plant material in a matrix lacking cellular structure (Arrhenius 1984; Andersen and Malmros 1985; Arrhenius and Lidén 1989; Isaksson 1997).

From the coastal Mesolithic site *Tybrind Vig*, food residues with clearly visible remains of vegetable matter as well as bones and scales of marine fish are reported (Andersen and Malmros 1985; cf. Koch 1998:305). Likewise, organic residues adhering to the inner surfaces of Stone Age cooking pots from inland bogs have been demonstrated to include scales and bones of freshwater fish (Koch 1998:151, 307, 320; cf. Koch 1998:321, 323, 339). An apple seed embedded in the food residue is also reported (Koch 1998:119).

Most of the dates of food residue presented in Table 3 and 4 were made at the AMS laboratory at the University of Aarhus, Denmark (labeled "AAR"). The samples were given a standard AAA treatment (1M HCl and NaOH at 80 °C for several hr prior to combustion and graphitization for dating). The ¹⁴C dates are reported in accordance with international convention (Stuiver and Polach 1977) and normalized to a δ^{13} C of –25‰ VPDB as described in Andersen et al. 1989. Table 3 also includes some dates produced by the AMS laboratory in Uppsala, Sweden (samples labeled "Ua"). To this are added a number of context dates produced by the former ¹⁴C laboratory in Copenhagen (labeled "K").

TEST DESIGN

The Åmose in eastern Denmark (Figure 1) stands out as a suitable case for testing the hypothesis on freshwater reservoir effect in food residue on pottery from inland areas. Among the numerous Stone Age sites from this bog, the kitchen midden at the Åkonge site (Fischer 1985, 1999, 2002) was selected as the primary source of data. It consists of 2 stratigraphic units, termed layer 3a (upper part of the midden) and layer 3b (lower part of the midden). Both of these layers include pottery with food residue, and both are rich in organic cultural remains of direct relevance, such as bones of freshwater fish and marrow-split bones of terrestrial mammals (Figure 4).



Figure 4 A 0.5×0.5 m square of the Åkonge inland kitchen midden during excavation, seen obliquely from above. The site belongs to the time immediately after the introduction of farming, when hunting and fishing still formed the primary subsistence base. Fragments of cooking pots are scattered in between food remains of terrestrial and freshwater origin. Bones of terrestrial mammals are the most conspicuous, but a closer view reveals numerous fragments of cracked hazelnut shells and scales and bones of freshwater fish. Due to leaching, the carbonate of the mollusk shells has disappeared in the upper part of the deposit. Photo courtesy of Peer Rievers.

A program for testing the hypothesis of freshwater reservoir effect in food residue dates was outlined in 1998. It included 4 experiments, which should provide the following kind of data:

- 1. A series of ¹⁴C dates of present-day fish and mollusks from the Åmose freshwater system.
- 2. Series of ¹⁴C dates from chronologically and stratigraphically well-defined Stone Age culture layers. These series should include samples of bones of freshwater fish as well as samples of terrestrial material of negligible lifespan, which could neither be suspected to be redeposited nor influenced by marine or freshwater reservoir effects.

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- 3. Series of ¹⁴C dates from stratigraphically and chronologically well-defined sediments including samples of food residue as well as samples of terrestrial material with negligible lifespan, which could neither be suspected of having been redeposited nor influenced by reservoir effects.
- 4. Combinations of food residue dates and dates on less problematic material (preferably terrestrial plant material of negligible lifespan) from individual potsherds.

Experiment 1

Live samples of relevant species of fish and mollusks were taken from present-day Lake Tissø in the Åmose river valley (Figure 1). Hydrologically and geologically, this lake is related to the former lakes in the Åmose basin in many ways, including its mix of groundwater and precipitation water (Høy and Dahl 1993; Noe-Nygaard 1995; Hedeselskabet 2000:13).

It was expected that any reservoir effect in prehistoric fish bones from the Åmose would primarily be the result of dissolved fossil carbonate in the groundwater. It would have seeped into the former lake from the surrounding hills with their calcareous underground, which is characteristic of most of north and east Denmark. Alternative—but in the specific case less probable—causes of a potential age offset could be water-absorbed CO_2 resulting from decay of old organic material in the lake and CO_2 with a high residence time in truly old groundwater seeping into the lake (cf. Tauber 1983).

In principle, the potential apparent age of the groundwater could be up to about 1 14 C half-life (about 5700 yr) due to a 50% dilution with CO₂ from fossil carbonate (Heier-Nielsen et al. 1995). It was uncertain, however, if the hardwater effect in the groundwater could be detected in present-day fish in Tissø, which are also influenced by the atomic bomb pulse.

Experiment 2

The Åkonge kitchen midden is very rich in bones and scales of freshwater fish (Figure 4). Of the larger fish bones, 5404 had already been determined to species (Enghoff 1995). The dominant categories were cyprinids (*Cyprinidae*) and pike (*Exox lucius*), with a relative representation of 49% and 35%, respectively. Among the cyprinids, tench (*Tinca tinca*) was most numerously represented.

A collection of tench and pike bones from the Åkonge kitchen midden was selected for ¹⁴C dating. It was decided to study these particular species for 2 reasons. First of all, because they apparently were the species most frequently consumed on this site, and secondly, because they represent different trophic levels. Tench feed on insect larvae (primarily mosquito), bivalves, snails, and slugs (Muus 1998). Pike of the size represented in the Åkonge sample almost exclusively feed on fish such as cyprinids, but may also occasionally eat ducklings and frogs (Muus 1998). If the hardwater effect was influencing the dates of these bones, it should be most pronounced in the tench samples since its food is generally more aquatic than that of the pike.

From the Åkonge kitchen midden, 6 ¹⁴C dates of red deer bone were already available and these were subsequently supplemented with dates on terrestrial plant and bone material. The same series of dates was used also in Experiment 3.

Experiment 3

The large collection of potsherds with well-preserved food residue from the Åkonge midden had been excavated and curated in such way that post-excavation pollution from dust, finger-grease, car combustion particles, etc. could be excluded.

Experiment 4

A detailed inspection of pottery from the Åkonge site had revealed a number of sherds from which could be taken a sample of food residue, as well as a sample of other material of a less problematic nature. These potential combinations of samples included terrestrial material of negligible lifespan that had been incorporated in the clay when the pottery was produced.

In the following, the complete set of dates from the test program is presented, with the exception of 1 fishbone sample which yielded too little collagen carbon (<0.2 mg) for a precise date.

Apparent Age in Present-Day Freshwater Fish

In Table 1, we list the result of dating a series of freshwater species caught live in Lake Tissø in May 2001 (mollusks) and February 2002 (fish). As can be seen, all individuals have unrealistic, positive ¹⁴C ages of, on average, about 300 BP. Due to the remains of the atmospheric ¹⁴C bomb pulse caused by nuclear bomb tests since the late 1950s, negative ¹⁴C ages of around –700 yr BP are expected for contemporaneous terrestrial samples (see e.g., Goodsite et al. 2001). By extrapolation of the dataset presented in this reference, the atmospheric ¹⁴C level around the time of collection is estimated at 109.4 percent modern carbon (pMC) and from the pMC ratio fish/atmosphere, estimated equivalent reservoir ages of the fish samples have been calculated in the last column of Table 1, averaging about 1000 yr. Since the atmospheric ¹⁴C level has been even higher in the preceding years (1963–2000), this value is probably underestimated, but it may be taken as indicative of local freshwater reservoir ages in the past having been considerably higher than the typical marine reservoir age of 400 yr.

Table 1 ¹⁴C dates on flesh from present-day fish and mollusks (*Anodonta*) from Lake Tissø in the Åmose Valley. From the ratio of the measured ¹⁴C level in the fish to the expected atmospheric ¹⁴C level of 109.4 pMC (percent modern carbon) around the time of collection (2001/2002), the apparent reservoir ages have been calculated in the last column. The average observed reservoir age is 1034 yr.

	Lab nr	¹⁴ C age	$\delta^{13}C$ ‰	Measured ¹⁴ C	pMC ratio fish/	Reservoir
Sample species	AAR-	BP	VPDB	level (pMC)	atmosphere	age (yr)
Pike	8369-1	209 ± 44	-26.4	97.4	0.891	931
Bream	8370-1	185 ± 55	-29.0	97.7	0.893	907
Pike-perch	8371-1	505 ± 36	-26.2	93.9	0.858	1226
Roach	8372-1	325 ± 60	-28.0	96.0	0.878	1049
Perch	8373-1	225 ± 80	-27.9	97.3	0.889	945
Freshwater mussel	8374	281 ± 43	-29.8	96.6	0.883	1003
Freshwater mussel	8375	315 ± 41	-32.0	96.2	0.879	1037
Freshwater mussel	8376	283 ± 36	-31.6	96.5	0.882	1005
Freshwater mussel	8377	417 ± 39	-31.2	94.9	0.868	1139
Freshwater mussel	8378	375 ± 34	-30.4	95.4	0.872	1097

A considerable part of the water in Tissø stems from groundwater. Some of it comes directly into the lake through its bottom. During the summers of 1998–2002, for instance, the average inflow of groundwater through the lake bottom was about 14% of the total inflow to the lake (Vestsjællands Amt 1999, 2000, 2001, 2002, 2003). A probably larger supply of groundwater arrives through the Åmose River and smaller streams from the hills surrounding the Åmose Valley (personal communication 2003 with Claus Koch, County Administration of West Zealand; cf. Hedeselskabet 2000:13).

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The moraine hills bordering the Åmose Valley are rich in grains of fossil carbonate, which is gradually dissolved in the groundwater and transported into the lakes. Here, its ¹⁴C-dead fossil carbon enters the aquatic food chain through photosynthesis.

Dates on Stone Age Fish Bones Versus Dates on Their Context

Table 2 presents the result of dating extracted collagen from 6 samples of freshwater fish bones from the Åkonge site in the Åmose. In one of these cases, the residual material—after extraction of collagen—has also been dated (AAR-4573), yielding the same age and δ^{13} C value within the measuring uncertainty. In the table the weighted average age of the collagen and of the residue from this sample is presented.

The context samples from the 2 layers of the Åkonge kitchen midden all represent cultural debris with well-documented find circumstances, which makes it reasonable to exclude the possibility that they were brought into the culture layer as a result of erosion or bioturbation. The zoological samples come from large, horizontally positioned bones of terrestrial mammals, the lifespan of which is of the order of 1–10 yr. The charred rootlet has a lifespan of less than 1 yr, and derives from a terrestrial tree.

The observed scatter in the ages of the terrestrial context samples is so small (70% of the statistically expected scatter) that all samples within each stratigraphic unit can be considered of the same 14 C age. In Table 2, this is expressed by the value *S*, the observed scatter (relative to the measuring uncertainty), which should be around 1 for a large number of samples assumed to be contemporaneous.

Table 2 Dates of bone of freshwater fish versus dates of context samples from 2 culture layers at the Åkonge site, Denmark. The dates of the contexts are based on terrestrial samples that have negligible lifespan and are not influenced by reservoir effects. It transpires that the ¹⁴C age of the fish bones are systematically older than the context samples. * = standard value assumed. S = observed scatter.

Stratigraphic	Sample		Nr of bones	¹⁴ C age	δ ¹³ C	* 1	Weighted average	Reservoir
unit	category	Material dated	in the sample	BP	‰	Lab nr	¹⁴ C age BP	¹⁴ C age
Layer 3b	Fish bone	Tench	2	5565 ± 40	-26.7	AAR-4576	5347 ± 19	480 ± 46
		Tench	2	5395 ± 40	-25.0	AAR-4574	(S = 3.0)	310 ± 46
		Pike	3	5245 ± 40	-23.1	AAR-4575		160 ± 46
		Pike	2	5238 ± 32	-21.2	AAR-4573		153 ± 39
	Context	Domestic ox bone	1	5120 ± 40	-21.8	AAR-4452	5085 ± 23	
		Charred rootlet	0	5095 ± 45	-26.6	AAR-5363	(S = 0.75)	
		Red deer bone	1	5070 ± 65	-20.9	K-4882		
		Red deer bone	1	5060 ± 65	-20.8	K-4881		
		Red deer bone	1	5010 ± 65	-21.4	K-4883		
Layer 3a	Fish bone	Tench	1	5315 ± 55	-20.9	AAR-4580	5229 ± 43	340 ± 66
		Pike	1	5090 ± 70	-24.6	AAR-4577	(S = 2.5)	115 ± 79
	Context	Red deer bone	1	4990 ± 65	-21.9	K-4886	4975 ± 36	
		Red deer bone	1	4990 ± 65	-21.6	K-4884	(S = 0.37)	
		Red deer bone	1	4950 ± 60	-22.6	K-4885		

The weighted average context ages of the 2 layers are used for calculating the reservoir age of each fish sample. All tench samples show highly significant reservoir ages of 310-480 ¹⁴C yr. The pike samples show much smaller reservoir ages, although significant for both layers, at about 115–160 ¹⁴C yr.

Present-day Åmose has a significant inflow of lime-rich groundwater from the surrounding hills (Hedeselskabet 2000:13). Due to differences in topography and water permeability of the under-

ground, some places in the basin now have a much higher influx of groundwater than others. Since the same general hydrological situation existed in the Stone Age, some branches of this former lake system probably had relatively high concentrations of groundwater, too. This may be the cause of the considerable variation in reservoir age within each of the 2 species of fish.

The results of experiments 1 and 2 are compatible and allow a clear conclusion: if the food residues in the pots from Åkonge are exclusively derived from the cooking of freshwater fish or mollusks, these residues would theoretically have apparent ages in the order of 100-500 ¹⁴C yr.

Dates of Food Residues Versus Dates of Their Context

In Table 3, we present results from the analysis of 3 small, chronologically and stratigraphically well-defined Stone Age inland sites: the Åkonge and Spangkonge sites in the Åmose, Denmark (Fischer 2002), and feature 8 from the Mossby site, Sweden (Larsson 1992), from each of which dates of food residue, as well as a number of dates on terrestrial context samples are available. All 3 sites belong to the initial part of the Neolithic, which in Denmark and southern Sweden began around 5150 BP (Fischer 2002).

Table 3 Examples of discrepancy between dates of food residue on the inner surface of pottery and their chronologically well-defined contexts. The dates of the contexts are based on samples of terrestrial material with a negligible lifespan. * = standard value assumed; S = observed scatter.

							Reservoir ¹ of food resi	⁴ C age idue
			¹⁴ C age	$\delta^{13}C$		Weighted	Individual	
Site	Provenance	Material	BP	‰	Lab nr	average BP	pot-sherds	Average
Åkonge,	Pottery	Food residue	5385 ± 40	-28.8	AAR-5108	5228 ± 21	300 ± 46	143 ± 31
Layer 3b		"Food" residue	5260 ± 70	-32.5	AAR-2678	(S = 2.5)	175 ± 74	
		Food residue	5185 ± 40	-28.0	AAR-5112		100 ± 46	
		Food residue	5150 ± 100	-27.0*	AAR-5110		65 ± 103	
		Food residue	5115 ± 40	-30.6	AAR-5107		30 ± 46	
	Context	Domestic ox bone	5120 ± 40	-21.8	AAR-4452	5085 ± 23		
		Charred rootlet	5095 ± 45	-26.6	AAR-5363	(S = 0.75)		
		Red deer bone	5070 ± 65	-20.9	K-4882			
		Red deer bone	5060 ± 65	-20.8	K-4881			
		Red deer bone	5010 ± 65	-21.4	K-4883			
Spangkonge	Pottery	Food residue	5180 ± 40	-26.7	AAR-4818	5180 ± 40	72 ± 52	72 ± 52
1 8 8	Context	Bone, red deer	5140 ± 65	-21.9	K-5044	5108 ± 33		
		Antler, red deer	5130 ± 65	-22.9	K-5043	(S = 0.62)		
		Bone, red deer	5110 ± 65	-22.6	K-5041	· /		
		Bone, red deer	5050 ± 65	-20.7	K-5042			
Mossby	Pottery	Food residue	5215 ± 120	-27.0*	Ua-429	5128 ± 60	295 ± 144	
Feature 8		Food residue	5170 ± 90	-27.0*	Ua-754	(S = 1.05)	250 ± 120	
		Food residue	4995 ± 110	-27.0*	Ua-430		75 ± 135	
	Context	Charred cereal grain	4925 ± 115	-25.0*	Ua-755	4920 ± 79		
		Charred hazelnut shell	4915 ± 110	-25.0*	Ua-753	(S = 0.06)		

In the table, we only include dates of food residue from the inner surface of pottery. It shall, furthermore, be noticed that 1 of these dates (AAR-2678) is from a so-called blubber lamp. The others are from larger, round-belly vessels of the cooking-pot type.

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The δ^{13} C value of the 3 food residue samples from the Mossby site is assumed to be -27.0‰. The choice of this value is based on the trend in the measured δ^{13} C values of northern European food residues on Stone Age cooking vessels from inland areas (Tables 3 and 4; Hallgren and Possnert 1997; Koch 1998; Persson 1999; Fischer 2002). We have applied a minor correction to the food residue dates from this site by subtraction of 15 yr from their originally published ages (Larsson 1992), which had been calculated on the basis of an estimated δ^{13} C value of -25.0‰.

The contextual dates from each of the 3 assemblages agree so closely (S \leq 1) that their weighted average values can be used as a base for comparison with the respective food residue dates.

The food residues in the individual cooking pots are most likely the remains of a somewhat different material. Some may primarily be sintered organic material from the cooking of freshwater fish or mollusks, others may derive mainly from the cooking of terrestrial plants or animals. Therefore, we cannot expect the food remains in different pots from one and the same site to have identical apparent age. This assumption agrees with the data in Table 3, which imply that the individual residues have significantly different age offsets, ranging between 30 and 300 yr.

Combinations of Dates from Individual Pot Sherds

Four cross-dates of cooking pots from the Åkonge site have been produced (Table 4). They consist of dates based on 3 different kinds of material:

- 1. Food residue from the inner surface of the vessels;
- Or coating from the outer surface of the vessels; Based on visual inspection, these coatings primarily consist of soot deposited during cooking on fire. In the case of AAR-5109 and AAR-5113, it cannot be excluded, though, that the samples include a minor proportion of the material which was cooked in the pots;
- 3. Or botanical material that was incorporated in the clay during the production of the vessels.

The latter group (3) of material includes the following 2 samples:

- *AAR-5363* is a charred rootlet of lime tree. Determined on the basis of its shape and preservation, the rootlet had its full strength and was probably alive when the clay was dug up. The absence of year-rings in the rootlet implies that its lifespan was less than 1 yr (report from Claus Malmros, The Danish National Museum). It, therefore, forms a solid basis for determination of the true age of the vessel from which it derives.
- *AAR-4817* is a small piece of charcoal of a deciduous tree of undeterminable species and lifespan, of which oak cannot be excluded (report from Kjeld Christensen, The Danish National Museum). The lifespan of the sample is estimated to about 20 yr or more, and potentially, up to several hundreds of yr.

Apparently, the dates of the coating of the outer sides of the vessels agree better with the actual time of production than those based on food residue from the inner surfaces.

The dates on food residue are consistently older than the dates on other types of material from the respective vessels. In 3 cases, this age excess is significant, being close to 2σ or more (Table 4). The 3 dates from the sherd Åkonge 49,5/77,0:26 (Figure 5) are especially informative, indicating (in agreement with Table 3) that the food residue in question has an apparent age of about 300 yr.

On the basis of the data in Table 4, we conclude that food residue, even of non-marine origin, can have a significant apparent age.

Table 4 Combinations of AMS dates from sherds of 4 cooking pots from the Åkonge site, Denmark. The age excess of the food residues is calculated in relation to the reference material from the respective sherds (rootlet, charcoal, coating on outer surface). These cross-dates indicate that the food remains dealt with have apparent ages of up to about 300 yr. * = standard value assumed. Rot sherd

identification		¹⁴ C age	¹⁴ C age	δ ¹³ C	
nr	Material dated	BP	excess	‰	Lab nr
49,5/77,0:26	Food residue, inner surface Coating, outer surface Charred rootlet, lifespan 0 yr	5385 ± 45 5195 ± 45 5095 ± 45	290 ± 64 100 ± 64 0	-28.8 -27.1 -26.6	AAR-5108 AAR-5109 AAR-5363
49,5/77,0:18	Coating, outer surface Charcoal, lifespan ≥ about 20 yr	5195 ± 40 5155 ± 40	> 40 ± 57 > 0	-27.0 -24.3	AAR-4816 AAR-4817
50,0/75,5:18	Food residue, inner surface Coating, outer surface	$\begin{array}{c} 5185\pm40\\ 5070\pm45\end{array}$	$\geq 115 \pm 60$ ≥ 0	-28.0 -26.5	AAR-5112 AAR-5113
49,5/77,5:10	Food residue, inner surface Coating, outer surface	5150 ± 100 5140 ± 40	$\geq 10 \pm 108$ ≥ 0	-27.0* -26.8	AAR-5110 AAR-5111

We suggest that the age discrepancies observed in food residue from the Åkonge site are (primarily) the result of hardwater effect in freshwater organisms that were cooked in the pots. We base this suggestion on the facts referred to above regarding: i) the remains of freshwater fish observed in Åmose food residues, ii) the high density of freshwater fish and mollusks observed in the Åmose kitchen middens, and iii) the groundwater chemistry and hydrology of this area.

We furthermore suggest that freshwater reservoir effect of the same or even greater scale applies to ¹⁴C dates of food residue on Stone Age pottery from many other northern European inland freshwater systems that appear to have had similar groundwater chemistry, hydrology, and food habits.

DISCUSSION

Considering the composition of food remains in the Early Neolithic Åkonge kitchen midden (Figure 4; cf. Enghoff 1995; Gotfredsen 1998), the food residue on cooking pots from this site must represent a diversity of ingredients, including terrestrial plants and animals as well as freshwater fish and mollusks. It is, therefore, no surprise that the δ^{13} C value and apparent age of food residue from different pots vary to some degree (Tables 3 and 4). We have the impression that very negative δ^{13} C values may in some cases be taken as a warning that the food residue in question may have a particularly high age offset (cf. Fischer et al., forthcoming *b*). There is, however, no clear correlation between the δ^{13} C values and the apparent ages presented in this paper. Consequently, we cannot presently point out a method for detecting and possibly correcting for freshwater reservoir effect in food residue dates.

The measurement of δ^{13} C in food residue has been one of the most popular ways of exploring what kind of food was prepared in Stone Age pottery. Knowledge about δ^{13} C values in human bone collagen has formed the basis for the interpretations in many such studies of German, Danish, Swedish, and Norwegian Stone Age food residues. It is typically assumed that humans who consume a 100%



terrestrial northern European diet have δ^{13} C values in the order of -21%. Less negative values imply that a proportion of the person's diet came from the sea, while values more negative than -21% are indicative of a proportion of freshwater food (cf. Fischer et al., forthcoming *a*,*b*).

The δ^{13} C values measured in northern European food residue on Stone Age pottery are generally more negative than -22% (Figure 6; cf. Persson 1997, 1999:Tables 24, 36; Fischer 2002:Table 22.3). On this basis it has frequently been assumed that these food remains do not include marine ingredients, even if most of them derive from archaeological cultures believed to have subsisted primarily on marine resources (Segerberg et al. 1991; Glørstad 1996; Østmo et al. 1996; Thomsen 1997; Hallgren and Possnert 1997; Edenmo et al. 1997; cf. Andersen and Malmros 1985). Results from the analysis of potsherds from the coastal Mesolithic site Tybrind Vig exemplify this paradox. In the food residue on these sherds, many indisputable remains of marine fish are recorded (Andersen and Malmros 1985) and yet they have ¹³C values of -22.1 to -26.6%.

As far as we can see, this paradox-debate is a result of misinterpretation of the existing data. It is a generally accepted and a solidly tested model that δ^{13} C values of bone collagen are in the order of 5‰ less negative than the δ^{13} C values of the food from which it derives (van der Merwe and Vogel 1978; van der Merwe 1982; Chisholm 1989; Ambrose 1993; Ambrose and Norr 1993; Schwarcz 2000). In northern Europe, where all indigenous terrestrial plants have a normal Calvin (C₃) photosynthesis, flesh of plant-eating mammals has δ^{13} C values in the order of -26%, and when consumed by carnivores, turns into bone collagen with a δ^{13} C value around -21%. Flesh from marine species has less negative δ^{13} C values.

The organic material on the inner surface of Stone Age pottery represents food, not bone collagen. Consequently, food remains having δ^{13} C values less negative than about -26% must include a proportion of marine food. This assumption is strongly supported by the many δ^{13} C values of food res-



Figure 6 The distribution of δ^{13} C values in food residue from coastal and inland sites from Stone Age northern Europe. δ^{13} C = -26‰ VPDB is the approximate value of terrestrial food, and some mixtures of marine and freshwater components. The δ^{13} C values from the coastal sites are generally less negative than those from the inland sites; this implies that marine species formed a substantial part of the food cooked in the pots at the coastal sites.

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idue available. The greatest value reported from Denmark so far is -17.2%, which has been found in a Neolithic pot from Tømmerup Mose (Rahbek and Lund Rasmussen 1996:313). If it derives from a mixture of marine and terrestrial material, approximately 80% of the food remains in this funnel beaker must thus have been of marine origin and the ¹⁴C date of the pot thus needs correction for a marine reservoir effect of about 320 yr. If it also includes freshwater substance, the marine content and the age offset may potentially be even greater.

In Figure 6, we present the scatter of δ^{13} C values of organic residues on pottery from a number of northern European Stone Age sites. The diagram includes settlements from where 2 or more $\delta^{13}C$ measurements of food residue are available (Andersen and Malmros 1985; Segerberg et al. 1991; Hallgren and Possnert 1997; Persson 1999: Tables 24, 36; Åstveit 1999; Lübke et al. 2000; Hartz et al. 2002; Lübke 2002, 2003; Østmo, personal communication 2003). Some of these sites we classify as "coastal" on the basis that they were originally located in a marine environment, close to the shoreline of their time. In those cases where faunal remains are preserved, these finds furthermore indicate a subsistence dependent on marine fish and mammals. Another group of sites we classify as "inland." They were originally located along freshwater systems several km from the seashore of their period. The fauna remains from these sites indicate a heavy reliance on terrestrial and/or freshwater food. The Neolithic settlement Skogsmossen in eastern Sweden we classify as intermediate ("coastal/inland") since it was originally located approximately 1 km from the coast and has a faunal assemblage with more than 10% seal bones (Halgreen et al. 1997). The illustration indicates that δ^{13} C values of food residue from the coastal sites are normally within the interval –19 to –28‰ (range -17.7 to -29.5). Values from the inland sites are within the range of -26.1 to -32.5%. Thus, contrary to what has been reported in many recent publications, marine organisms seem to have been prominent constituents of the food cooked in pots in northern European Stone Age coastal sites.

 14 C dates of food residue, which includes organic material of marine origin, will be influenced by a reservoir effect of up to about 400 yr. In principle, this effect can be detected and corrected for by means of δ^{13} C measurements. Based on the considerations above, we conclude that dates of samples with δ^{13} C values less negative than about -26% need to be corrected. Failure to apply such corrections has caused confusion among archaeologists and publication of a number of false chronological "sensations."

So far, we do not have a method which allows us to detect if a sample is influenced by freshwater reservoir effect. We are, thus, facing a major problem since the error may, in some regions, potentially be much larger that the marine reservoir effect. In the case of the Åmose bog, the organisms in question represent freshwater reservoir effect of a magnitude up to 500 yr. ¹⁴C dates of present-day river water and of freshwater species elsewhere in Europe have demonstrated even higher apparent ages (Lanting and van der Plicht 1996, 1998; Heinemeier and Rud 1998; cf. Cook et al. 2001). Consequently, food residues deriving from freshwater organisms from these waters may have apparent ages in the order of many hundred yr.

A number of ¹⁴C dates made on food residue on pottery have recently been presented as remarkably or inconceivably early appearances of various cultural phenomena in northern Germany (Hartz et al. 2000), Denmark (Koch 1998:96, 98, 101, 107, 321, 324, 331), Sweden (Segerberg et al. 1991; Hallgren and Possnert 1997; Persson 1997, 1999), and Norway (Østmo 1993; Glørstad 1996; Persson 1997, 1999). Based on the information presented above, these aberrant dates can now be explained as a result of marine or freshwater reservoir effect or a combination of both. It can, furthermore, be added that several other food residue dates from Danish votive pottery (Koch 1998),

which have not hitherto been considered dubious, are probably also influenced significantly by the freshwater reservoir effect.

Freshwater fish and mollusks usually have relatively negative δ^{13} C values. Furthermore, fish from lakes and rivers, as in the case of marine species, are characterized by relatively high δ^{15} N values due to the long food chains found in aquatic environments in general. Therefore, measuring both of these isotopes in food residues may be potentially indicative of samples which are to a high degree of freshwater origin and may, therefore, have significant excess ages.

CONCLUSION

Much is still to be found out about the materials and processes involved in the formation of food residues on northern European Stone Age pottery. It is, however, most likely that some of this organic material derives from preparation of aquatic organisms, such as freshwater fish and mollusks. This is very likely the case with the food residues seen in numerous Neolithic cooking pots found in the Danish bogs, where the well-preserved, contemporary food remains clearly point to the dietary importance of freshwater fish and mollusks. This paper demonstrates that ¹⁴C dates of fish bones from the Åmose have apparent ages in the order of 100–500 ¹⁴C yr.

The food residues seen in the pots from the Åmose are expected to derive from a combination of sources, including terrestrial plants, terrestrial mammals, and—not least—freshwater fish and mollusks. In accordance with this expectation, food residues from the Åmose are demonstrated to have apparent ages of varying magnitude up to about 300 ¹⁴C yr. So far, there is no method available either for detecting or correcting this error in ¹⁴C dates.

Although a larger volume of data would be desirable, the present study seems to justify a call for caution in the uncritical use of food residue as a dating material. Future measurements of stable isotopes, such as ¹⁵N and ³⁴S in charred food remains, may provide information of relevance for detecting which dates are significantly influenced by freshwater reservoir effect, and hopefully lead to a means of correcting these dates.

The apparent ages dealt with in this paper undoubtedly stem from fossil carbonate which is dissolved in groundwater and subsequently ends up as ¹⁴C-dead carbon in the aquatic food chain (hardwater effect). In areas other than dealt with here, freshwater reservoir effect in food residue dates may also, to some degree, originate from CO_2 absorbed in groundwater with residence times of thousands of yr before it ended up in the lake or river in question.

An apparent age of modern river water in the scale of up to 4000 yr indicates that even larger discrepancies than the 100-300 ¹⁴C yr seen in the Åmose material may be present in food residue dates from other inland regions around the world.

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14C AGES OF A VARVED LAST GLACIAL MAXIMUM SECTION OFF PAKISTAN

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ABSTRACT. In a core off Pakistan, we obtained 38 ¹⁴C analyses by accelerator mass spectrometry (AMS) from a 4.4-mthick, expanded, annually-laminated Last Glacial Maximum (LGM) section, bracketed by bioturbated intervals ascribed to the Heinrich-1 (H1) and Heinrich-2 (H2) equivalent events (52 ¹⁴C analyses between 24–15 kyr BP). A floating varve age scale, anchored to the oxygen isotope record of the layer-counted GISP2 ice core at the H2/LGM boundary, results in an annually dated record for the LGM from 23,450–17,900 cal BP. The floating varve scale of the LGM provides us with a tentative calibration of local marine AMS ¹⁴C age dates to calendar years.

INTRODUCTION

At the Last Glacial Maximum (LGM), an interval at $21,000 \pm 2000$ calendar years before present (yr BP; Mix et al. 2001), the chronology is mainly based on radiocarbon dates. During Marine Isotope Stage (MIS) 2–3, the conversion of ¹⁴C dates into calendar years is complicated because of strong variations which are hardly quantified (during MIS 2) in cosmogenic ¹⁴C production and in the relative size and rate of overturning of the various reservoirs of the carbon cycle (Beck et al. 2001). These changes also lead to considerable but unknown variations in the local reservoir age of seawater (Waelbroek et al. 2001; Sarnthein et al. 2001; Staubwasser et al. 2002). During MIS 3 and 2, beyond the range of dendrochronological calibration, ages are mostly tuned to the Greenland Ice Sheet Project 2 (GISP2) record, where annual layers were counted down to 50,000 yr BP (Alley et al. 1997; Meese et al. 1994; Voelker et al. 1998; Stuiver and Grootes 2000). For the LGM (late MIS 2), neither varved and dendrochronological records nor GISP2 signals are available for the precise monitoring of ¹⁴C age variations. Published terrestrial records and annually counted, pre-Holocene marine varve records (e.g. Cariaco Basin: Hughen et al. 1998) generally do not extend beyond 15,000 yr BP. However, some data are available from varved lakes—e.g., from Lake Suigetsu in Japan (Kitagawa and van der Plicht 1998, 2000) and from a Bahamian stalagmite (Beck et al. 2001).

The high-resolution laminated records from the oxygen minimum zone (OMZ) off Pakistan (Figure 1) offer an opportunity to fill this calibration gap using a floating varve chronology. Here we examine the laminated LGM sequence in core SO 130-261KL (abbreviated 261KL) (Figure 1) documenting about 5550 calendar yr (if corrected for erosional loss of varves). For comparison, the late Holocene varve record (about 5000 yr BP to Present) in nearby core SO 90-56KA (Figure 1) was studied by von Rad et al. (1999a) and Berger and von Rad (2002). The linear sedimentation rate of core 261KL (about 0.9 m/1000 yr) is almost 3 times higher than that of the thickest LGM sections at the continental slope off the Indus Delta (von Rad et al. 1999b). Hence, this expanded marine laminated LGM section (Figure 2) is unique for the Arabian Sea, and possibly also unique on a global scale.

The objective of this paper is to show the variability of ¹⁴C activity in the surface ocean over the LGM by means of varve counts, and to anchor this ¹⁴C time series to the GISP2 timescale. Our basic assumption for age control is that the bioturbated intervals in core 261 KL can be correlated with Heinrich events in the North Atlantic and with the corresponding major stadials in the Greenland ice record (Schulz et al. 1998, 2002). Our strategy is to develop a floating varve scale anchored to the

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Figure 1 Bathymetry of the continental slope west of Karachi with site SO130-261 KL at the continental margin of Pakistan (OMZ shaded). Inset (lower right): Generalized transect of water mass stratification (OMZ) and turbidite or plume fallout action in the northern Arabian Sea ambient to the core location.

GISP2 ice core scale at the H2/LGM boundary and counting back towards the end of the LGM, making allowances for core disturbance by turbidite erosion (Figure 3; Table 1).

SAMPLES AND METHODS

Samples

To avoid a strong influence by turbidite sedimentation and erosion (Figure 1), core SO 130-261 KL (abbreviated 261KL) was retrieved from the top of an isolated hill between 2 submarine canyons on the upper continental slope west of Karachi (24°46.2'N/65°49.2'E, 873 m water depth; von Rad and Doose 1998). Core 261KL has a total length of 17.86 m and reaches down to Interstadial (IS)-6 (about 34 kyr BP). This core contains a 4.4-m-thick, laminated section of the Last Glacial Maximum (LGM) between the H1 and H2 equivalent stadial events (Figure 2). Core SO 90-75KL (abbreviated 75KL), which contains the same LGM section, was taken from a position very close to core 261 KL. X-radiographs prove that both cores can be precisely correlated using 47 very distinctive coarse-grained marker layers, in part turbidites. No significant sections are missing between the correlated marker beds. Hence, we "spliced" the samples from 75 KL into the record of 261KL (Table 1) and supplemented 48 ¹⁴C dates in core 261KL by 4 ¹⁴C dates from core 75KL.



Figure 2 Core SO 130-261 KL (5.40–12.00 m below sea surface: m bsf): Lithology, varve thickness, conventional ¹⁴C dates in BP (corrected for a –400 yr reservoir effect) and δ^{18} O record of Globigerinoides ruber versus core depth. Bioturbated (light-colored) and laminated, dark-colored sediment sections (stippled) are marked: distinctly laminated intervals with denser pattern than less distinctly laminated ones. Coarse-grained marker beds include suspension fall-outs and genuine turbidites. Possibly erosive turbidites are indicated by thick lines. The laminated section between 11.65 and 11.08 m bsf is termed "IS pre-H2", whereas the bioturbated section below is called "pre-H2 stadial."



Figure 3 A) Oxygen isotope record of planktonic foraminifer *G ruber* versus age (cal yr BP) for core 261KL. B) ¹⁴C ages in BP from core SO 130-261 KL versus varve-based calendar ages, anchored to the GISP2 age scale 15.8–25 cal kyr BP. Open circles are TIMS ²³⁰Th-calibrated coral ¹⁴C ages (Bard et al. 1998; Stuiver et al. 1998). Calendar ages in H2 and H1 intervals are rough estimates, based on linear extrapolation of the varve scale assuming linear sedimentation rates. Horizontal and vertical error bars show varve-counting error and standard deviation (2 σ) of ¹⁴C ages (see Table 1). The laminated intervals (LGM and IS-pre-H2) are shaded. I = location of moderately thick turbidites (where 20–30 varves may be lost); II = location of major turbidite (7.64–7.70 m bsf) and reworked material, where up to 1000 varves are assumed to have been lost by erosion (see text).

Varve Chronology

Contact prints of X-radiographs of core SO 130-261KL served for fabric studies at the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in Hannover (von Rad et al. 1999a). For varve counts and measuring varve thickness, we used a tree ring measuring facility under a binocular microscope (Aniol 1983) at the Tree Ring Laboratory of the University of Göttingen. The varves of the LGM record of core 261KL were measured twice and by independent investigators (U von Rad and J Erbacher). The differences between these results were used to estimate the counting error between well-defined marker beds. The reproducibility within our varve chronology, which depends on the variable distinctness of the varves and the subjective interpretation, varies considerably from section to section. A conservative summary estimate of the error amounts to $\pm 7\%$ or ± 300 varve yr for the whole LGM section.

Counting errors resulting in a systematic under-counting of varve years can be linked to (1) amalgamation of varves due to compaction, (2) local erosion of varves below thick turbidites, and (3) local slumps. The excellent to moderate preservation of lamination shown in our X-radiographs suggests that the first error is unlikely. Erosion below thick turbidites cannot be fully discounted (see below). Local slumps have not been identified in our record, except for a 2–4 cm thick, very indistinctly laminated, sand-rich interval at 7.68–7.70 m below sea floor (bsf), consisting of reworked old material (about 6000 ¹⁴C yr older than the overlying and underlying strata, see Table 1). This interval was omitted from our interpretation.

For core 261KL we anchored the "floating varve chronology" at the H2/LGM boundary at 23,450 cal yr BP and tuned it to the annual-layer counted GISP2 timescale (age scale of Meese et al. 1994, employed in Stuiver and Grootes 2000). All age denotations in this paper are in "varve years" BP, which we interpret to be synonymous to "calendar years" BP (before 1950).

AMS ¹⁴C Dating

For the ¹⁴C calibration of the laminated LGM section in core 261KL, we determined 38 ¹⁴C ages by accelerator mass spectrometry (AMS) (Table 1). The spacing of samples in the LGM ranged from 10–25 cm, resulting in an average resolution of a few hundred calendar yr. These dates were supplemented by 14 AMS ¹⁴C ages from the underlying bioturbated layers, correlated to H2 and "pre-H2 stadial" and the laminated section in between H2A and H2 (termed "IS pre-H2"), as well as from the overlying H1 interval (Figure 2). The ¹⁴C activities were determined with the Leibniz Labor 3 MV HVEE Tandetron AMS system (Nadeau et al. 1997), mostly on monospecific planktonic foraminiferal samples (*Globigerinoides ruber* and/or *G. sacculifer*, depending on the availability of sufficient specimens in each sample; see Table 1). *G. ruber/G. sacculifer* dates from the same sample differ considerably (Table 1, nr 8/9, 11/12, 20/21, 22/23). This suggests that we are dealing with a somewhat noisy record with a scatter probably due to differential species habitats (since *G. sacculifer* produces its last chamber at up to 80 m water depth, it is being influenced by "older water"). A few replicate datings of the same sample (Table 1, nr 18/19, 37/38) give excellent agreement.

Local reservoir ages of 640 yr were estimated for Late Holocene (pre-bomb) sediments in the varved core SO90-56KA (von Rad et al. 1999a); reservoir ages ranging from 780 to >1000 yr were calculated by Staubwasser et al. (2002) for the period 6600-13,000 BP using ¹⁴C dates from a nearby core off Karachi. However, we cannot assess the variability of the paleo-¹⁴C reservoir effect during the LGM, a period which may have been sensitive to variations in the strength of the thermohaline circulation. We mainly rely on a reasonable fit with the coral data of Bard et al. (1998) between 24 and 20.5 kyr BP (see Figure 3b), and, thus, we apply in this paper the commonly used reservoir age estimate of 400 yr. The corrected ¹⁴C ages (-400 yr) were correlated with varve-counted calendar yr tuned to the GISP2 record (Table 1, Figure 3). Since we determined the ¹⁴C activity from *G. ruber* and *G. sacculifer* (which are species dwelling in the top 30–80 m of the ocean and mainly during non-upwelling seasons), the influence of differential advection of upwelled "old" deep-water masses may be low.

All varve thickness, ¹⁴C ages, and oxygen isotope data of cores SO 90-75 KL and SO 130-261KL were deposited in the PANGAEA data bank (www.pangaea.de/PangaVista?query=vonradu).

Tab yr E	le 1 ¹⁴ C ages r P. Note that at	neasured in core t a 7.67 m core d	SO 130-2 epth, we su	61 KL with calibrupplemented 1000	ation to GISP.) varves, assum	-controlled varve ned to be lost by	e yr (calenda turbidite ero	r yr) anchored a sion.	t the H2/LGM b	oundary at 23,450
Nr	Lab nr	Core 261KL depth interval (cm)	Average depth (cm)	Plankton Foramaminifer	Corrected ¹⁴ C activity pMC	Conventional ¹⁴ C age yr BP (uncorr.)	Standard deviation (±_yr)	Reservoir age (400 a) cor- rected ¹⁴ C age	Varve age (floating scale) cal yr BP	Comments/ stratigraphic unit ^a
1	KIA 13278	541-546	543.5	ruber + sacc.	17.91 ± 0.30	13,810	140	13,410	15,950	Bioturb.(H1)
7	KIA 13279	57–577	574.0	ruber + sacc.	17.48 ± 0.23	14,010	110	13,610	16,694	Bioturb.(H1)
б	KIA 13280	583-589	586.0	ruber + sacc.	16.10 ± 0.19	14,670	100	14,270	16,982	Bioturb.(?H1)
4	KIA 13281	616-621	618.5	ruber + sacc.	17.12 ± 0.23	14,180	110	13,780	17,750	Bioturb.(?H1)
5	KIA 6777	637–639	638.0	ruber + sacc.	15.08 ± 0.20	15,190	110	14,790	17,965	Lamin.LGM
9	KIA 6778	656–658	657.0	ruber + sacc.	14.54 ± 0.16	15,480	90	15,080	18,164	Lamin.LGM
7	KIA 3807* ^b	*66868	661.0	ruber + sacc.	14.46 ± 0.17	15,440	90	15,040	18,205	Lamin.LGM
8	KIA 10847	668–672	670.0	sacculifer	14.18 ± 0.13	15,690	70	15,290	18,307	Lamin.LGM
6	KIA 10846	668–672	670.0	ruber	15.67 ± 0.22	14,890	110	14,490	18,307	Lamin.LGM
10	KIA 10167	691–696	693.0	sacculifer	12.74 ± 0.15	16,550	90	16,150	18,590	Lamin.LGM
11	KIA 10849	700-702	701.0	sacculifer	13.37 ± 0.13	16,160	80	15,760	18,680	Lamin.LGM
12	KIA 10848	700-702	701.0	ruber	15.21 ± 0.22	15,130	120	14,730	18,680	Lamin.LGM
13	KIA 10850	708.5-712.5	710.5	ruber	13.01 ± 0.13	16,380	80	15,980	18,781	Lamin.LGM
14	KIA 10168	719–723	721.0	sacc. + ruber	13.28 ± 0.21	16,220	130	15,820	18,903	Lamin.LGM
15	KIA 12754	731-736	733.5	sacculifer	12.38 ± 0.14	16,780	90	16,380	19,182	Lamin.LGM
16	KIA 12755	742-746.5	744.3	sacculifer	12.10 ± 0.13	16,960	90	16,560	19,298	Lamin.LGM
17	KIA 3808*	*666-766	759.0	sacculifer	12.24 ± 0.15	16,870	100	16,470	19,300	Lamin.LGM
18	KIA 10851	761-765	763.0	sacculifer	11.94 ± 0.14	17,080	90	16,680	19,344	Lamin.LGM
19	KIA 10852	761-765	763.0	sacculifer	11.90 ± 0.12	17,100	80	16,700	19,344	Lamin.LGM
20	KIA 10169	768-770	769.0	sacculifer	5.28 ± 0.12	23,620	180	23,220	20,418	rework. mat./??
21	KIA 10179	768-770	769.0	ruber	5.48 ± 0.14	23,330	200	22,930	20,418	rework- mat./??
22	KIA 10853	773-776	774.5	ruber	11.63 ± 0.13	17,280	90	16,880	20,459	Lamin.LGM
23	KIA 10854	773-776	774.5	sacculifer	12.15 ± 0.13	16,930	90	16,530	20,459	Lamin.LGM
24	KIA 10170	790–794	792.0	ruber	11.44 ± 0.17	17,420	120	17,020	20,601	Lamin.LGM
25	KIA 10171	814-818	816.0	sacculifer	11.28 ± 0.18	17,530	130	17,130	20,806	Lamin.LGM
26	KIA 10172	852-856	854.0	sacculifer	10.41 ± 0.17	18,180	130	17,780	21,107	Lamin.LGM
27	KIA 6779	873-875	874.0	ruber + sacc.	10.20 ± 0.13	18,340	100	17,940	21,315	Lamin.LGM

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Table 1 ¹⁴ C ages m BP. Note that at 7.6	asured in core 7 m core depth,	SO 130-26 , we supple	I KL with call mented 1000	ibration to GISF varves, assumed	-controlled varve to be lost by tur	e yr (calenda bidite erosio	r yr) anchored at tl n. <i>(Continued)</i>	ne H2/LGM boun	dary at 23,450 yr
	Core 261KL depth interval	Average depth	Plankton	Corrected ¹⁴ C activity	Conventional ¹⁴ C age	Standard deviation	Reservoir age (400 a) corrected	Varve age (floating scale)	Comments/

		Core 261KL	Average		Corrected	Conventional	Standard	Reservoir age	Varve age	
;		depth interval	depth	Plankton	¹⁴ C activity	¹⁴ C age	deviation	(400 a) corrected	(floating scale)	Comments/
Nr	Lab nr	(cm)	(cm)	Foraminifer	pMC	yr BP (uncorr.)	$(\pm yr)$	¹⁴ C age	cal yr BP	stratigraphic unit ^a
28	KIA 10173	894–896	895.0	sacculifer	9.77 ± 0.16	18,690	130	18,290	21,580	Lamin.LGM
29	KIA 3809* ^b	1138 - 1140 *	912.0	sacculifer	9.80 ± 0.15	18,660	130	18,260	21,820	Lamin.LGM
30	KIA 12756	926–929	927.5	sacculifer	9.46 ± 0.13	18,940	110	18,540	22,000	Lamin.LGM
31	KIA 12757	944–947	945.5	sacculifer	9.39 ± 0.13	19,000	110	18,600	22,158	Lamin.LGM
32	KIA 10174	956–958	957.0	sacculifer	9.00 ± 0.16	19,350	140	18,950	22,283	Lamin.LGM
33	KIA 10175	973–975	974.0	sacculifer	8.45 ± 0.15	19,850	150	19,450	22,422	Lamin.LGM
34	KIA 10176	978–980	979.0	sacculifer	8.58 ± 0.16	19,720	150	19,320	22,485	Lamin.LGM
35	KIA 10177	993–996	994.5	sacculifer	8.54 ± 0.18	19,770	170	19,370	22,620	Lamin.LGM
36	KIA 10178	1020 - 1022	1021.0	sacculifer	7.81 ± 0.17	20,480	180	20,080	22,887	Lamin.LGM
37	KIA 11255a	1041 - 1046	1043.5	ruber	7.98 ± 0.16	20,310	160	19,910	23,165	Lamin.LGM
38	KIA 11255b	1041 - 1046	1043.5	ruber	7.80 ± 0.11	20,490	110	20,090	23,165	Lamin.LGM
39	KIA 11254	1054 - 1059	1056.5	sacc. + ruber	8.05 ± 0.12	20,240	120/110	19,840	23,321	Lamin.LGM
40	KIA 3810*	1248 - 1250 *	1057.0	sacculifer	7.99 ± 0.14	20,300	150	19,900	23,328	Lamin.LGM
41	KIA 6780	1063 - 1065	1064.0	ruber + sacc.	8.36 ± 0.12	19,940	120/110	19,540	23,430	Lamin.LGM
42	KIA 11253	1067 - 1070	1068.5	ruber + sacc.	9.02 ± 0.17	19,330	150	18,930	23,450	LGM/H-2 / ??
43	KIA 6781	1071-1073	1072.0	ruber + sacc.	7.75 ± 0.12	20,540	130	20,140	23,540	Bioturb. (H2)
44	KIA 13282	1074 - 1078	1076.0	ruber + sacc.	9.90 ± 9.16	18,580	130	18,180	23,620	Bioturb. (H2) / ??
45	KIA 13283	1088 - 1092	1090.0	ruber + sacc.	10.70 ± 0.17	17,960	130	17,560	23,925	Bioturb. (H2) / ??
46	KIA 6782	1112-1114	1113.0	ruber + sacc.	6.92 ± 0.11	21,450	130	21,050	24,348	Lam.(IS pre-H2)
47	KIA 11252	1121–1124	1122.5	ruber + sacc.	6.80 ± 0.11	21,590	130	21,190	24,458	Lam.(IS pre-H2)
48	KIA 11251	1141 - 1144	1142.5	ruber + sacc.	6.94 ± 0.12	21,430	140	21,030	24,653	Lam.(IS pre-H2)
49	KIA 11250	1181-1186	1183.5	ruber + sacc.	7.01 ± 0.15	21,350	180/170	20,950		pre-H2 stadial
50	KIA 6783	1201-1203	1202.0	ruber + sacc.	6.26 ± 0.11	22,260	150	21,860		pre-H2 stadial
51	KIA 6784	1433–1435	1434.0	ruber + sacc.	4.02 ± 0.12	25,810	240	25,410		pre-H2 stadial
52	KIA 6785	1456–1458	1457.0	ruber + sacc.	4.08 ± 0.12	25,700	240/230	25,300		Bioturb.(H2A)
a?? = a b* = 4 3808	apparent ¹⁴ C out dates in core SC 9.97–9.99 m. f	liers (see text).) 90-75KL with eq or K1A3809: 11.38	uivalent core 3–11.40 m. a	to 261KL depths (f pd for KIA 3810	or stacking meth	od, see Methods se	ction; the actu	al 75 KL core depths	are for KIA 3807:	8.97–8.99 m, for KIA
)))										

¹⁴C Ages of a Varved LGM Section Off Pakistan

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Stable Oxygen Isotopes

Two-hundred-forty samples were picked from selected depths and prepared for stable isotope and geochemical analysis. This led to a resolution of about 20–30 yr. Stable carbon and oxygen isotopes were analyzed from 10–15 specimens of the planktonic foraminifer *Globigerinoides ruber* (315–400 µm size fraction) by Dr Joachimski (University of Erlangen), using mass spectrometric standard methods. All values are reported in per mil (‰) relative to the PeeDee Belemnite (V-PDB) standard (Figure 3a). The stable isotope curve is also matched by the lightness and color values (measured with a GEOTEK color scanner), which in the Northern Arabian Sea cores have been successfully used as a stratigraphic tool to estimate organic carbon contents of the sediments (Schulz et al. 1998).

RESULTS AND DISCUSSION

Laminated Hemipelagic Sediments

On the basis of laminated and non-laminated sediment sections in many cores investigated off Pakistan (including core 261 KL), the paleoclimate and paleocirculation along the upper slope of the northeastern Arabian Sea fluctuated between the following 2 extremes:

- 1. Oxygen-deficient bottom water conditions (well-developed oxygen minimum zone, OMZ) were documented during the laminated (late) Holocene period, the Preboreal, the Bölling/ Alleröd warm spell, the LGM, and the Dansgaard-Oeschger Interstadials (IS 1–24).
- 2. Fully-oxygenated bottom water conditions occurred during the Younger Dryas and the Heinrich-equivalent stadials H1 to H7 (Schulz et al. 1998, 2002; von Rad et al. 1999b). The stadials H2 and H1 intervals are clearly reflected by δ^{18} O maxima of *G. ruber*, whereas the interstadials IS2 and IS pre-H2 are characterized by δ^{18} O minima. The middle part of the LGM (approximately 20,500–22,500 yr BP) shows more positive δ^{18} O values (Figure 3a). Sub-Milankovich climate changes were correlated peak-by-peak with the Dansgaard-Oeschger cycles and Heinrich events in the GISP2 δ^{18} O record (Dansgaard et al. 1993; Schulz et al. 1998, 2002).

The sediment laminae form couplets of light and dark laminae, in total approximately 0.4–0.8 mm thick (Figure 2). By comparison to a Holocene section in the nearby core SO 90-56KA (von Rad et al. 1999a), we regard the couplets as the result of seasonal variations in terrigenous and organic sediment supply, that is, as annual varves. In the central LGM section (9.5–8.7 m bsf), varve thickness has reached a minimum (suggesting reduced terrigenous river input due to more arid conditions in the Makran hinterland).

Plume Fallouts and Turbidites

The laminated sediments in core 261KL are interbedded with 47 silt- and/or sand-sized marker beds, which are a few mm up to a maximum of 30 mm thick. Whereas the thickest 10 beds are clearly graded (with mollusc/pteropod debris and large mud pebbles near the base and a sharp erosional contact to the underlying laminae), the majority of marker beds are ungraded (marked differently in Figure 2). Accordingly, we regard most of the latter beds as fallouts from turbid sediment plumes caught in the pycnocline on top of site 261 KL. In contrast, the thick, graded beds are interpreted as genuine turbidites which, in part, when thicker than 0.5 cm, may have been erosional, in total, possibly cutting out a few cm of laminated sediment, possibly up to 260 varves between 6.3 and 10.7 m core depth. Ten further thick turbidites, below which we assume an erosion perhaps reaching up to 30 varves, are also marked in Figures 2 and 3. Furthermore, we assume that up to 1000 varves were lost below the thick turbidite associated with a slump approximately 7.68–7.70 m bsf (see below).

Stratigraphic Correlation with GISP2 and Age Control

In core 261KL, the bioturbated pre-H2 stadial (or "H2A" interval) below 11.73 m bsf is overlain by a laminated interstadial (11.73–11.05 m bsf), named "IS pre-H2" in this paper (Figure 2). Although the lamination in this section is indistinct, we counted approximately 700 varves. This section has 3 ¹⁴C ages (Figure 3) around 21,500 ¹⁴C yr BP (24,900–24,200 cal yr BP, using reservoir ages between 400 and 1000 yr), which match the GISP2 age of this interstadial (H Schulz, personal communication 2003). The subsequent bioturbated section was assigned to H2, which has a midpoint age of 23,800 cal yr BP in GISP2. The H2 equivalent in core 261KL shows 2 peaks of heavy δ^{18} O values which fit to the "cool" peaks of 24,060 and 23,760 cal yr BP in GISP2. We assigned the top of this bioturbated H2 equivalent at 10.71 m bsf to the H2/LGM boundary with a GISP2 age of 23,450 yr BP (Meese et al. 1994; Stuiver and Grootes 2000) and employed this age as base of our new floating varved LGM timescale. On the basis of annual-layer counting, the uncertainty of the GISP2 timescale amounts to less than ±2%, down to an age of 39,852 yr BP (Meese et al. 1994).

Within the lowermost part of the laminated LGM section of core 261KL, we note 2 marked peaks of light ("warm") δ^{18} O values (Figures 2 and 3), which match the respective peaks in GISP2 of the IS2 interstadial at about 23,300 and 23,000 cal yr BP, respectively (H Schulz, personal communication 2003). The laminated LGM sediments were counted up to a core depth of 6.515 m bsf (varve age: 18,100 yr BP). Indistinct lamination, with a thickness of about 1 mm, continues up to a core depth of 6.30 m bsf (estimated varve age: 17,900 ± 300 yr BP), varves which were disturbed by subsequent bioturbation. In the overlying sediments, which are fully bioturbated, the δ^{18} O record shows a distinct change towards heavier values. We assigned this section overlying the laminated LGM to H1. In total, the laminated LGM record (10.71–6.30 m bsf) contains 4300 ± 300 varves. Further, 1250 varves may be lost by turbidite erosion, as outlined above. Accordingly, the section between H2 and H1 may originally have consisted of 5550 varves, which would result in a varve age of 17,900 yr BP for the base of H1. This age matches the approximate age of the LGM/H1 boundary at GISP2 (about 18,000 yr BP; Grootes and Stuiver 1997) and at various North Atlantic sediment cores (Sarnthein et al. 2001).

Distribution of ¹⁴C Ages

The 38 ¹⁴C age dates in the LGM section (Table 1) show a generally consistent pattern, where the ages increase with increasing core depth (Figure 2). Two ¹⁴C dates at 7.69 m bsf (Table 1: nr 20, 21), which are some 6000 yr too old, form obvious exceptions, a result of downslope sediment reworking (Figure 3). X-radiography indicates that these sediments consist of indistinctly-laminated, foraminifera-enriched sand, apparently stemming from the nearby upper slope or outer shelf. Furthermore, 3 apparent ¹⁴C outliers occur in the interval of H2 (Table 1, nr 42, 44, 45) dates that appear 1–3 kyr lower than expected, for unknown reasons.

Unfortunately, the strongly anoxic sediment section results in an early diagenetic alteration of magnetic mineral phases and does not produce any reliable geomagnetic record (N Nowaczyk, personal communication on the basis of about 280 geomagnetic measurements in core 261KL, November 2000). Hence, this evidence lacks for confirming or disproving any potential geomagnetic event in control of the cosmic ¹⁴C production, as achieved by the North Atlantic paleointensity stack since 75,000 yr BP (Laj et al. 2000).

CONCLUSIONS

We measured 38 AMS ¹⁴C ages from a 4.4-m-thick, expanded, annually-laminated marine sediment section of the LGM in core 261KL from the oxygen minimum zone off Pakistan. The section is
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bracketed by bioturbated sediment segments assumed equivalent to the H1 and H2 events. On the basis of varve counting and supplementing various varve segments lost by turbidite erosion, a floating age scale was constructed and anchored to the annual-layer counted age scale of the GISP2 ice core at the H2/LGM boundary. The new annually resolved varve record covers the LGM from 23,450 to approximately 17,900 BP at the base of H1, with a data gap possibly extending from 20,400–19,400 yr BP.

A close-up of the age-depth correlation (Figure 3b) reveals a number of ¹⁴C jumps and plateaus. In a future publication, we will attempt to compare the variability of the ¹⁴C concentration found in core 261KL from the northeastern Arabian Sea to ¹⁴C dates calibrated by coral ages (Bard et al. 1998) and by varve counts from the Lake Suigetsu record (Kitigawa and van der Plicht 1998, 2000). Further calibration efforts are required to expand the INTCAL 98 ¹⁴C timescale of Stuiver et al. (1998) further back across the last glacial stage.

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AMS DATING OF POLLEN CONCENTRATES—A METHODOLOGICAL STUDY OF LATE QUATERNARY SEDIMENTS FROM SOUTH WESTLAND, NEW ZEALAND

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ABSTRACT. A simple method for preparing pollen concentrates for ¹⁴C AMS dating is applied to organic and inorganic deposits from a peat bog in south Westland, New Zealand, from which preliminary AMS dating indicated age inversions and severe younger carbon contamination problems. The AMS ages of the pollen concentrates provided consistently older age estimates for each sample than ages derived from their respective organic residue or combined pollen and organic residue fractions. It is likely that the younger age estimates of the organic residue fractions result from the incorporation of younger plant material into the sample and possible contamination from younger humic acids percolating through the site.

INTRODUCTION

The advantages of radiocarbon dating concentrated pollen by accelerator mass spectrometry (AMS) from late Pleistocene and Holocene deposits have long been recognized (Brown et al. 1989, 1992; Regnell 1992) and the ability to obtain reliable ¹⁴C ages from pollen is well established (Mensing and Southon 1999). Studies have shown that AMS dating of pollen concentrates can eliminate many of the problems inherent with conventional ¹⁴C dating of lake, marine, and peat deposits (Long et al. 1992; Richardson and Hall 1994; Regnell and Everitt 1996). The application of AMS dating pollen concentrates to pollen analysis is of great importance, particularly where bulk samples are contaminated by either younger or older carbon. In these instances, AMS ages from pollen concentrates can provide more reliable chronologies and potentially reduce dating errors associated with short-lived paleoclimate events, including regional deglaciations, cooling, and tree species migration (Brown et al. 1992).

In the last decade, many techniques have been developed and improved to prepare relatively pure pollen concentrate samples for AMS dating. To date, pollen extraction procedures combine treatments including chemical digestion of organic matter using strong acids such as H_2SO_4 and fine sieving (Regnell 1992), microbiological degradation (Richardson and Hall 1994), centrifugation (Regnell and Everitt 1996), and manual separation with a micromanipulator (Long et al. 1992) or mouth pipette (Mensing and Southon 1999). Although clear improvements have resulted from some of these procedures, many are still not able to completely remove contaminants (Regnell 1992; Richardson and Hall 1994), or are limited to only concentrating large pollen grains from relatively large volume samples (Long et al. 1992; Mensing and Southon 1999).

Whereas these techniques have been generally successful when concentrating pollen from Holocene deposits or sediments containing large pollen grains, they become less efficient when attempting to concentrate pollen from:

- Sediments where pollen grain sizes are predominantly small (<50 μm), such as those associated with the Last Glacial Maximum (LGM) in New Zealand.
- Sediments where the volume of sediment available for dating a palynological event is limited.

A simple technique for preparing pollen concentrates for AMS dating using heavy liquid separation (Prior and Chester 2001) has previously been used to derive datable material from small volumes of

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Holocene sediment. This technique is considered to provide more accurate age estimates of greater precision than conventional ages from bulk sediment, particularly for dating vegetation changes interpreted from pollen analysis (Prior and Chester 2001; Horrocks et al. 2002). This paper tests the applicability of the method by attempting to produce more reliable ages from late Quaternary depositional environments in Westland, New Zealand, where severe ¹⁴C contamination problems have been reported previously (Grant-Taylor and Rafter 1971; Moar and Suggate 1979; Hammond et al. 1991). All ¹⁴C ages are reported in ¹⁴C years before present (yr BP), although where stated, calibrated years have been determined using INTCAL98 (Stuiver et al. 1998).

SITE INFORMATION AND ¹⁴C DATING PROBLEMS OF SOUTH WESTLAND, NEW ZEALAND

A 5-cm-diameter core was taken from a peat deposit (Okarito Pakihi) 70 m above sea level, near Okarito Lagoon in south Westland, New Zealand (43°14′50″S; 170°12′25″E; Figure 1), using a modified Russian D-section corer. Palynological and sedimentological analysis indicates that the site was formed as a lake impounded behind glacial terminal moraines that predate the LGM, but are close to the limits of LGM ice advances. The site became a peat bog after about 10 ka BP and provides a record of sediment and vegetation change that predates the LGM. The catchment around the site consists of non-carbonate lithologies (Warren 1967) and there are no indications of a "hardwater effect" in any previous ¹⁴C dating reported for this region.



Figure 1 Geologic and geomorphic map of the study area showing location of the study site at Okarito Pakihi, along with present and historic glacier extents (modified from Warren 1967).

An important feature in the development and maintenance of south Westland's landscape is the regional climate—in particular, rainfall. Precipitation is high, averaging 5000 mm yr⁻¹ at low altitudes in south Westland, and rises in the adjacent Southern Alps to as much as 15,000 mm yr⁻¹ (Chinn and Whitehouse 1980). The steep precipitation gradient is characteristic of New Zealand's Southern Alps, which have a strong orographic influence on the prevailing westerly and south westerly air streams. Consequently, dry periods are rare and lowland mean annual temperatures are around 15.3 °C in summer (January) and 6.7 °C in winter (July) (Garnier 1958; New Zealand Meteorological Service 1983).

Preliminary AMS ages of bulk sediment and wood macrofossils from Okarito Pakihi provide age estimates of $10,267 \pm 70$ BP, 9692 ± 65 BP, and 9758 ± 70 BP between 281-283 cm, and date the beginning of organic sedimentation and dominance of a tall Podocarp forest occurring at the onset of the Holocene (Table 1, Figure 2). Toward the base of the core, organic silts at 553-554 cm and 599-600 cm provide ages of $31,080 \pm 490$ BP and $35,630 \pm 430$ BP, respectively, and constrain the lowermost peak in all tree pollen (Figure 2). However, bulk AMS ages from the center of the core indicate an age inversion (Figure 2), where samples consisting of inorganic silty-sand bracket the peaks in herb pollen and yield AMS ages of $12,069 \pm 60$ BP (349-350 cm) and $11,228 \pm 90$ BP (390-391 cm), respectively.

Of the preliminary ages, all those that are older than about 10 ka BP are considered to be too young. The herb-dominated pollen assemblage, dated here by inverted ages of $12,069 \pm 60$ BP and $11,228 \pm 90$ BP, is generally interpreted to represent flora associated with the LGM between about 22-16 ka BP (Moar and Suggate 1996). Below this, the lowermost peak in tall tree pollen, dated here between $31,080 \pm 490$ BP and $35,630 \pm 430$ BP, is likely to represent flora older than 70 ka BP associated with Marine Oxygen Isotope Stage 5a.

The age inversions between 349–400 cm provide evidence that some of the AMS-dated samples were contaminated by younger or older carbon. An older ¹⁴C age may result from the inwash of older inorganic carbon residues into the site or the incorporation of dissolved carbonates into the tissue of aquatic organisms or the sediment (hardwater effect). A younger ¹⁴C age can result from root penetration through the profile, the percolation of humic acid through the deposit, or the downward movement of younger sediments through bioturbation from burrowing organisms.

The effect of root penetration has been previously noted in studies of south Westland soil sequences (Almond 1996) and it is considered to be an important contributing factor to the downward movement of tephra shards through root holes to below the horizon of initial deposition, particularly in soils with low accretion. The influence of younger carbon contamination has also been recognized in previous New Zealand studies by Grant-Taylor and Rafter (1971), Moar and Suggate (1979), and Hammond et al. (1991). These studies have demonstrated similar errors when peat and sediments are dated from the high rainfall, extreme leaching, and weathering environment of the west coast of the South Island. Through different acid/alkali pretreatments and by dating soluble (fulvic and humic acids) and insoluble fractions from bulk peat and sediment samples, these studies concluded that samples from loess, buried silt/sands, or peat older than 10 ka BP become significantly contaminated by younger carbon, particularly from humic and fulvic acids (Hammond et al. 1991).

To try to understand the nature and source of contamination in the bulk samples, 25 AMS age determinations were obtained from concentrated pollen, organic residue fractions, and macrofossils from a further 10 samples in the Okarito Pakihi core (Table 1). The pollen concentrates are defined as those that have a high pollen content, whereas the organic residue fractions contain a mix of organic matter or residue and pollen and are both sub-fractions of the sample <125 μ m. The fraction <125 μ m contains a mix of pollen and organic residue (Table 1), whereas the fraction >125 μ m contains large organic material.

Table 1 AM	S dates from Okarito Pa	akihi ^a						
Core depth		Fraction	Sample weight	¹⁴ C age	δ ¹³ C	NZA	Weight combusted	% Carbon
(cm)	Fraction	content	(gm)	yr BP	%00	nr	(mg)	yield
281-282	Wood *b	Wood		$10,267 \pm 70$	-27.7	10085/Wk-7155	-	
283	Bulk sediment *	Bulk sediment	$2.01 \Psi^{c}$	9692 ± 65	-27.4	10991	4.1	58.2
283	Bulk sediment *	Bulk sediment		9758 ± 70	-27.7	11103	12.4	68.9
283	Leaf: H. bidwillii	Leaf		9553 ± 60	-25.7	11605	1.77	63.7
283	Leaf: <i>Leptospermum</i>	Leaf		9591 ± 60	-26.2	11606	1.05	54.5
283	1.4 sg ^d	Organic residue		9565 ± 60	-26.5	11633	5.9	55.4
283	1.2 sg	Organic residue		9627 ± 60	-27.6	11634	6.1	65.6
283	1.15 sg	Pollen		9903 ± 65	-27.9	11635	11.5	70.8
300-301	>175	>175	7 8 4 6	11 215 + 65	-311	11200	1 95	87 5
300-301	1 20 58	Pollen	 0.1	11,975 + 65	-30.4	11076	11	64.1
300-301	1.255 sg	Pollen		$11,802 \pm 65$	-29.5	11075	1.6	46.5
302-303	<125 µm	<125 µm	8.75*	$12,231 \pm 60$	-29.3	11105	8.2	50.4
340–342	1.15 sg	Pollen	20.0*	$14,504 \pm 70$	-28.1	11199	1.7	66.5
340–342	1.20 sg	Pollen		$14,302 \pm 70$	-28.0	11197	3.7	63.4
340–342	1.25 sg	Organic residue		$13,340 \pm 110$	-27.8	11198	0.42	72.7
342–343	<125 µm (combined)	<125 µm	9.47*	$14,445 \pm 70$	-27.6	11104	8.9	21.4
349–350	Inorganic silty-sand *	Bulk sediment		$12,069\pm60$	-26.7	10082/Wk-7156		
390–391	Inorganic silty-sand *	Bulk sediment		$11,228 \pm 90$	-23.5	10090/Wk-7157		
400-403	1.50 and 1.4 sg	Organic residue	36.1*	9053 ± 85	-26.0	11201	<0.1	N/A ^f
400-403	1.30 sg	Organic residue		$14,689 \pm 85$	-26.7	11077	0.4	44.1
400-403	1.255 sg	Pollen		$19,330 \pm 120$	-26.7	11106	0.4	52.7
400-403	1.22 sg	Pollen		$20,110 \pm 120$	-27.2	11107	0.4	61.1
400-403	1.20 sg	Pollen		$19,500 \pm 170$	-27.2	11108	0.3	65.3
553-554	Organic silt *	Bulk sediment		$31,080 \pm 490$	-30.4	10091/Wk-7158	I	
554-555	1.15 sg	Pollen	7.36*	$42,200 \pm 1200$	-28.8	11202	3.9	68.5
554-555	1.20 sg	Pollen		$43,900 \pm 1500$	-28.7	11203	6.6	63.6
556-557	<125 µm	<125 µm	8.81*	>45,200	-29.0	11109	10.4	52.4
596-597	1.15 sg	Organic residue	3.95Y	>45,900	-30.0	11204	6.2	60.6
596-597	1.20 sg	Organic residue		>45,300	-29.3	11205	6.1	64.3
598-599 500 500	<125 µm	<125	2.97Ψ	$45,400 \pm 1800$	-29.5	11110	9.6	59.3
665-865	mµ c21<			$30, / /0 \pm 020$	-29.5 2002	01200	j.j	47.6
000-660	Organic silt *	Bulk sediment		$35,630 \pm 430$	-767-	8199	I	

^a Shading represents groups of dates from fractions in the same sample

 ^b * represents bulk sample, while other samples represent fraction from density separation
 ^c Y represents dry sample weight
 ^c A represents action the sample weight
 ^c A represents set sample weight
 ^c A represents set sample weight

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20 40 60 80 100

% pollen



Lithology

:::

Т.Х.

66

Fibrous Peat
 Compact Sedge Peat
 Brown Organic Silt Sand

Wood

Blue/Grey Silt Sand

Coarse Sand/Gravel

Light Brown Organic Sand

POLLEN CONCENTRATE PREPARATION

> 45300

> 45900

NZA 112045 45400±1800

36770±620

AMS Dates

Plain Text = Bulk AMS

= Macrofossil

Plain Text = Organic Residue

= Pollen Concentrate

35630±430

NZA 8199

One-cm-thick samples were taken from sections in the core associated with major changes in the pollen stratigraphy (Figure 2). Between 310–500 cm, where the weight of the pollen fractions was too low for combustion, up to 2 additional samples were taken adjacent to each sample point and combined with the first sample prior to dating. Sample weights ranged between 2–3.95 g dry weight and 7.36–36.1 g wet weight (Table 1).

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Chemical Treatment and Separation

The method for pollen separation and concentration previously described by Prior and Chester (2001) is also outlined below and illustrated in Figure 3. Extraneous matter was removed according to standard methods (Faegri and Iversen 1989), including the removal of carbonates using HCl, removal of humic acids using KOH, and the removal of silica using HF. Dilute nitric acid was used to aid in the removal of organic residue. The mesh sizes of the sieves (125 and 6 μ m) were selected to eliminate organic and inorganic matter both larger and smaller than most pollen (Figure 3). Sample separation by sieving is complemented by using Sodium Polytungstate (SPT) heavy liquid separation at a specific gravity (sg) of 2.1, to separate most of the inorganic material from the lighter organic matter and pollen fraction. Between each step, samples were washed in distilled H₂O, centrifuged, and decanted to remove any remaining residue from the previous procedures. The samples were then processed for pollen separation prior to AMS dating. The procedure for pollen separation is summarized below.



Figure 3 Summary flow chart of laboratory procedures used in preparation of pollen concentrates for AMS dating.

In each density separation cycle (Figure 3), SPT was thoroughly mixed with the sample, then centrifuged at 3500 rpm for 5 min. The supernatant was decanted and precipitates from each separation were saved as individual fractions and labelled with the density of the SPT used. For example, the pollen fraction dated at 283 cm precipitated at a specific gravity of 1.15 g cm⁻³ (Table 1). Sample material that floated in the supernatant was transferred to a clean centrifuge tube for the next separation. SPT was mixed to a specific gravity of 1.6 g cm⁻³ for the first separation and was decreased for each subsequent separation, repeating the cycle until all of the material in the sample had precipitated. For some samples, this was a density as low as 1.1 g cm⁻³. Microscope analysis of each separated fraction was undertaken to determine which fraction contained the highest concentration of pollen and the least concentration of organic residue. These pollen fractions were then preferentially selected for dating. Age estimates were also derived from fractions >125 µm and organic residue fractions separated by SPT. This was carried out in an attempt to identify which fractions were predominantly influenced by carbon contamination and to determine whether ages from combined fractions <125 µm provided considerably different ages to those obtained from the pollen fractions within the sample.

RESULTS AND DISCUSSION

Density Separation

Pollen analysis carried out on each sample (to identify types and calculate percent pollen composition) indicates that pollen of dryland taxa and spores of the aquatic plant *Isoetes* dominated the pollen concentrates. This analysis showed no evidence of redeposited or ancient pollen within the dated samples and it is therefore unlikely that they are influenced by older carbon from this source. The sieved fractions >125 um composed predominantly plant fragments and large organic residue and did not contain any recognizable pollen. The sieved fraction <125 µm contained a mix of pollen and finer organic residue. Density separation was carried out between 1.6 and 1.1 sg on the <125 µm samples and Figure 4a-f shows some of the typical results of the density separated fractions. Fractions separated at >1.3 sg contained predominantly organic residue and few pollen grains. The 1.3–1.15 sg fractions contained most of the separated pollen at varying concentrations between about 30–92%. These fractions always contained some component of organic residue. The separated fractions <1.15 sg contained some pollen, primarily small grains and fine organic residue. Most tree pollen and dryland shrub species were found to separate at 1.15 and 1.2 sg. The visual estimates of pollen content were supplemented by the percent carbon yield during combustion of the different fractions (Table 1). Percent carbon yields of 65–70% in fractions identified as pollen indicate a high sporopollenin content (Prior and Chester 2001).

The purest pollen concentrates were derived from inorganic sediments which inherently had less organic residue. However, these samples also provided the lowest weight of sample for combustion (Table 1). Pollen concentrates from organic rich samples contained more organic residue, but provided greater weight for combustion.

Dating

AMS age determinations on the Okarito Pakihi sediments, macrofossils, and microfossils are listed in Table 1 and calibrated ages are listed in Table 2 and displayed in Figure 5a–d. Six ages derived from bulk samples throughout the core ranged from about 9.6–35.6 ka BP and indicate age inversions in the sediment record.

The pollen concentrate age from the sample taken at 283 cm provides an older age estimate than those derived from the organic residue fractions, leaf macrofossils, or bulk sediments (Table 1). Although these conventional ages generally remain within 2 standard errors of each other, calibrated ages (Table 2) clearly show that the pollen concentrates provide older age estimates than the other fractions from the same depth at the 2 sigma range (Figure 5a). The results also indicate that the 2 organic residue samples separated at 1.2 and 1.4 sg provide similar age estimates to those derived from both bulk sediments and leaf macrofossils. In contrast, the age derived from wood taken above this sample between 281–282 cm provides an older age estimate than the other ages at 283 cm. It is not immediately obvious why the wood sample should provide an older age estimate for this depth than the samples below, but this may be an occurrence of the "old wood" problem. As most trees are long-lived species, their inner growth rings may be several hundred yr older than the time of death and deposition. Old-wood cores of large trees may survive processes of decomposition longer than the outer rings. Due to such potential ¹⁴C age offset between time of growth and the time of deposition, many researchers advise the selection of single-growth-yr sample materials (Bowman 1990).

At 300–301 cm, pollen concentrate ages provide older age estimates for the sample than the sieved organic residue >125 μ m from that depth (Table 1). When calibrated (Table 2), the pollen concen-

Table 2 Conve al. 1998). ^a	ntional (CRA) and calibrated ¹⁴ C	ages from Okarit	o Pakihi between 28	1–403 cm. Calibrations bas	sed on INTCAL98 (Stuiver et
Core depth				Calibrated age range,	Calibrated age range,
(cm)	Fraction	NZA nr	CRA	1 sigma interval	2 sigma interval
281–282	Wood *b	10085 (Wk-7155)	$10,267\pm70$	12,327–11,770	12,741–11,674
283	Bulk sediment *	10991	9692 ± 65	11,181 - 10,908	11.209 - 10.760
283	Bulk sediment *	11103	9758 ± 70	11,210–11,156	11,248-10,878
283	Leaf: H. bidwillii	11605	9553 ± 60	11,085–10,701	11,157-10,643
283	Leaf: <i>Leptospermum</i>	11606	9591 ± 60	11,124 - 10,732	11,167 - 10,692
283	1.4 sg	11633	9565 ± 60	11,092–10,706	11,160-10,679
283	1.2 sg	11634	9627 ± 60	11,159–10,767	11,178-10,701
283	1.15 sg	11635	9903 ± 65	11,327–11,211	11,551–11,185
300–301	>125 µm	11200	$11,215 \pm 65$	13,215-13,070	13,431–12,920
300-301	1.20 sg	11076	$11,975 \pm 65$	14,105 - 13,832	15,297 - 13,647
300-301	1.255 sg	11075	$11,802 \pm 65$	13,963–13,608	15,188 - 13,470
302–303	<125 µm	11105	$12,231 \pm 60$	15,228 - 14,120	15,425 - 13,876
340–342	1.15 sg	11199	$14,504 \pm 70$	17,636–17,117	17,917–16,874
340–342	1.20 sg	11197	$14,302\pm70$	17,398–16,889	17,672–16,650
340–342	1.25 sg	11198	$13,340 \pm 110$	16,287–15,778	16,552 - 15,082
342–343	<125 µm (combined)	11104	$14,445 \pm 70$	17,566–17,050	17,844 - 16,809
349–350	Inorganic silty-sand *	10082	$12,069 \pm 60$	15,042 - 13,876	15,144–13,671
		(WK-7/156)			
390–391	Inorganic silty-sand *	10090 (Wk-7157)	$11,228 \pm 90$	13,385–13,032	13,763–12,913
400-403	1.50 & 1.4 sg	11077	$14,689 \pm 85$	17,852–17,313	18,137–17,065
400-403	1.30 sg	11106	$19,330 \pm 120$	23,306–22,539	23,696–22,193
400-403	1.255 sg	11107	$20,110 \pm 120$	24,188–23,423	24,532–23,053
400-403	1.22 sg	11108	$19,500 \pm 170$	23,533–22,704	23,948–22,331
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 $^{\rm a}$ Shading represents groups of dates from fractions in the same sample $^{\rm b}$ * represents bulk sample, while other samples represent fraction from density separation







(B)





Figure 4 Examples of pollen concentrate and organic residue samples derived from density separation and AMS dated in this study. Pollen concentrates from 340-342 cm separated at 1.15 sg (a) and 1.2 sg (b) show little organic residue. Organic residue samples from 340-342 cm separated at 1.255 sg (c) and 1.4 sg (d): note increasing amounts of organic residue and lower pollen concentrations. The relative difference between a pollen concentrate (e) separated at 1.255 sg and organic residue sample (f) separated at 1.30 sg from 400-403 cm: note the greater presence of organic residue in f (scale bar = 200 mm).



Figure 5 Comparison of calibrated 14 C ages between 281–283 cm (a), 300–303 cm (b), 340–350 cm (c), and 390–403 cm (d) from Okarito Pakihi. Plots show global calibrated age ranges at 1 and 2 sigma.

trate ages are comparable to a combined pollen and organic residue sample <125 µm taken from below this sample at 302–303 cm (Figure 5b). Pollen concentrate ages from the sediment between 340–342 cm provide older age estimates than the organic residue fraction from the same depth, and age estimates that are comparable to the combined pollen and organic residue sample $<125 \mu m$ taken below this depth between 342–343 cm (Figure 5c). These ages also provide a convincingly older age estimate for this part of the sequence than the AMS age derived from a bulk sediment sample between 349–350 cm (Figures 2 and 5c). Ages from pollen concentrate and organic residue fractions between 400-403 cm also show marked differences, with the pollen concentrates providing age estimates that are approximately 4500 yr older. However, the youngest organic residue age (NZA-11201) was combusted from an extremely small sample weight (<0.1 mg) that did not produce a quantifiable percentage carbon yield (Table 1). Graphite produced from samples of less than 100 µg is easily contaminated with modern carbon and we consider this age estimate completely unreliable. The pollen concentrate ages from between 400–403 cm also provide a significantly older age estimate for this part of the sequence than the AMS age derived from a bulk sediment sample between 390-391 cm (Figure 5d). Pollen concentrate ages from between 554-555 cm provide closely conforming age estimates that are considerably older than the age derived from a bulk sediment sample between 553–554 cm. These ages are considered to be close to the limit of ¹⁴C dating as a combined pollen and organic residue sample <125 μ m taken directly below this depth provides an infinite age estimate. Ages from organic residue fractions between 596–597 cm also provide infinite age estimates for this depth and are comparable to the combined pollen and organic residue sample <125 μ m taken from between 598–599 cm. The sieved organic residue >125 μ m taken from the same sample between 598–599 cm provides a considerably younger and finite age estimate than the <125 μ m fraction from this depth. This age, however, is comparable to the age estimate derived from the original bulk sediment sample from between 599–600 cm (Table 1).

Sources of Error and Contamination

A review of the AMS ages presented herein indicates that pollen concentrate ages provide consistently older age estimates for each sample than ages derived from organic residue or combined pollen and organic residue fractions in the respective sample. Furthermore, the age estimates from the pollen and organic residue samples below 550 cm indicate that the base of the sequence is beyond the limit of ¹⁴C dating. It seems likely that the predominant source of error for the ages is in the organic residue and bulk organic fractions, and that at this particular site these fractions are prone to contamination by younger carbon. The most common form of contamination in high rainfall areas of New Zealand is by intrusion from younger plant material or humic acids (Hammond et al. 1991). It is likely that the younger age estimates reported here from the samples containing significant organic residues also results from the incorporation of younger plant material into the sample through root intrusion and possibly contamination from young humic acids percolating through the profile from the Holocene peat overlaying the deposit. The contaminating influence of humic acids has been previously noted (Head and Zhou 2000), where it was found to be incompletely removed from the sample by the standard acid/alkali/acid (AAA) pretreatment technique prior to dating. However, it is difficult to determine the specific contaminating agent from the results of this study.

The results from the ¹⁴C dating confirm that the ages derived from pollen fractions are less likely to be influenced by carbon contamination than organic residue and bulk organic fractions. Consequently, it is likely that these ages provide a more reliable age for the vegetation changes in the sequence. When the pollen concentrate ages are compared to the bulk sediment AMS ages from Okarito Pakihi, the pollen fraction ages show that the bulk sediment ages provide spuriously young ages for the sequence and should therefore be regarded with caution (Figure 5).

CONCLUSIONS

The present study indicates that density separation of late Quaternary sediments using SPT is an effective method for concentrating pollen for AMS dating from relatively small sediment volumes and from sediments that contain relatively small pollen grains. However, it remains unsuccessful in completely removing all the organic residue and plant fibers from most samples. The dating of the pollen and organic fractions from Okarito Pakihi suggest that younger carbon is the main contaminant in late Quaternary peat and sediment samples. The likely source of contamination is the organic residue, which either constitutes or carries the younger carbon from either younger plant material or possibly undissolved humic acids. These findings suggest that at this site and others in the region, any sediment samples, but particularly those older than about 10 ka BP that contain high concentrations of organic residue, may provide unreliable ages and should therefore be regarded with caution. The dating evidence indicates that the fractions containing high pollen ratios produced consistently

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older age estimates that are less likely to be influenced by contamination, and therefore, provide age estimates that are closer to the true age of the sample.

FUTURE RESEARCH

Although pollen fraction dating is used to overcome the dating inconsistencies in south Westland peat deposits older than about 10 ka BP, further dating of these deposits with independent time markers is needed to determine the reliability of the pollen fraction ages. The recent identification of a distinctive tephra layer in loess profiles and peat deposits within close proximity of the site (Almond 1996; Almond et al. 2001; Vandergoes and Newnham, unpublished data) may provide a distinctive isochronous benchmark for testing the accuracy and reliability of this method.

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IS THERE A FIFTH INTERNATIONAL RADIOCARBON INTERCOMPARISON (VIRI)?

E M Scott¹ • C Bryant² • G T Cook³ • P Naysmith³

ABSTRACT. The issue of comparability of measurements (and thus bias, accuracy, and precision of measurement) from diverse laboratories is one which has been the focus of some attention both within the radiocarbon community and the wider user communities. As a result, the ¹⁴C community has undertaken a widescale, far-reaching, and evolving program of intercomparisons, to the benefit of laboratories and users alike. The benefit to the users is, however, indirect, since the ¹⁴C intercomparisons have not been used to generate "league tables" of performance, but rather to allow individual laboratories to check procedures and modify them as required.

The historical progression of ¹⁴C laboratory intercomparisons from the Third (TIRI, completed in 1995, Gulliksen and Scott 1995) and Fourth (FIRI, completed in 2000, Scott 2003; Boaretto et al. 2000; Bryant et al. 2002) suggests that a Fifth (VIRI) should also be expected. We describe the plans for VIRI.

INTRODUCTION

Radiocarbon laboratories continue to routinely operate quality assurance (QA) procedures, within which intercomparisons such as the Fourth International Radiocarbon Intercomparison (FIRI) formed an integral part.

Users, however, continue to express a desire to see evidence of ¹⁴C measurement quality in general, and specifically, a hope for improvements in the precision of results allied to the ability to measure smaller and older samples. They often also wish to construct and make inferences based on assemblages of dates measured in different laboratories and possibly at different times.

Programs such as TIRI (the Third Radiocarbon Intercomparison) and FIRI operate in addition to any within-laboratory procedures for QA. They provide an independent check on the comparability of measurements and it is clear that, even with the increased availability of reference materials, laboratories still benefit from participation.

Criticisms of the design of TIRI and FIRI have included:

- The need for the measurements to be made over a relatively short period of time (hence, the workload within the laboratory is compromised);
- The fact that the intercomparisons provide only a snap-shot in time;
- That the samples are not anonymous but that laboratories are.

THE PAST (BRIEFLY)

Long and Kalin (1990) stressed that it was "incumbent on individual laboratories to engage in a formal programme of quality assurance." Polach (1989) noted that "internal checking needs suitable quality control and reference materials." The quality of the measurement is determined by the laboratory. Sound, reliable, precise, and accurate measurement requires traceability to ¹⁴C communityagreed reference materials

In the past laboratory intercomparisons, many of the samples have been natural samples, e.g. in 1982, International Study Group (ISG 1983), a floating chronology of 8 tree ring samples was used, with a date range of 4800–5200 BP. In 1990, in the International Collaborative Study (Scott et al.

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1990), both natural and artificial materials, including dendro-dated wood, the activities of which were less than 3 half-lives were used. In 1992, the International Atomic Energy Agency (Rozanski et al. 1992) created a set of secondary standards based on natural materials, the activities of which spanned background to modern. Finally in 1995 and 1999, TIRI and FIRI used natural materials, including dendro-dated wood, the activities of which spanned background to modern.

Typically, such studies have involved 10–20 analyses, often concentrated in a single year. FIRI required 10 analyses completed within one year; TIRI provided 6 core and 7 optional samples and a one-year window for core analyses; ICS had 3 experimental stages spread over 3 years, involving 4 samples in year 1, 6 samples in year 2, and 8 samples in year 3.

These intercomparisons showed evidence of broad comparability among laboratories but also some evidence of more variability than expected. Consensus values for the materials were derived and some reference materials were archived.

PLANS FOR A NEW INTERCOMPARISON PROGRAM

It is clear that there is a need for continuing "routine" QA checks using reference materials (indeed, users expect this). Thus, it is important that a program continue with identification and testing of new, appropriate ¹⁴C reference materials, as part of its QA role. The proposed design and organization for VIRI is intended to address some of the criticisms, while retaining some of the important features of TIRI and FIRI, namely using natural samples, previously homogenized and tested, and the anonymity of participating laboratories to ensure that league-tables of laboratories are not created.

The design issues which must be considered include the selection of materials, the inclusion of duplicates for a precision check, and the use of known-age material as an accuracy check.

Materials

We propose that the materials should be of natural origin and span the applied ¹⁴C timescale. Materials to be used include bone, wood, seeds, barley mash, shells, and peat (whole and humic acid extract). It is planned that for each material, several samples of different ¹⁴C activities will be provided.

Timescale

To avoid the spot-check nature of TIRI and FIRI, we propose that VIRI will be a 4-year project, starting in 2004. There will be a rolling measurement commitment, with samples distributed regularly throughout the 4-year period. Three or 4 samples would be distributed in each of years 1–3 and in year 4, a more general intercomparison would be organized, including duplicates and with up to 8 samples. Each year, a particular material would be the focus of testing. Some samples will only be available for AMS measurement.

At the end of each year, laboratories would receive a detailed report so that any operational corrections could be made and the final (intercomparison) phase would be tied into a major AMS/¹⁴C conference.

CONCLUSIONS

QA is of fundamental importance to laboratories and users and the program of intercomparisons is seen (within the ¹⁴C and user communities) as an important part of the QA process. A new laboratory intercomparison program (VIRI) will start in 2004. VIRI will be a rolling and ongoing program, with a small number of samples being dispatched to participating laboratories each year. The fre-

quency and number of samples in VIRI are still to be finalized after consultation with the community, but this short note summarizes the current plans.

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REPLY TO ISRAEL CARMI (2002): "ARE THE ¹⁴C DATES OF THE DEAD SEA SCROLLS AFFECTED BY CASTOR OIL CONTAMINATION?"

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INTRODUCTION

Carmi (2002) is a response to our study published in *Radiocarbon* 43(1) by Rasmussen et al. (2001). We noted widespread possible exposure to castor oil of the Dead Sea Scrolls (DSS) in the Rockefeller Museum in the 1950s and reported experiments showing that the AAA pretreatment used in the first 2 series of radiocarbon datings of the DSS (Bonani et al. [1992] and Jull et al. [1995]), "cannot be guaranteed to have removed all of the modern carbon in any samples if they had been contaminated with castor oil and hence could have produced some ¹⁴C dates that were younger than the texts' true ages." Carmi, a coauthor of the Bonani et al. (1992) study, criticizes our analysis on 4 grounds:

- 1. Carmi argues that "the extant [radiocarbon] dates of the Dead Sea Scrolls do not suggest a major deviation from their palaeographic or specific ages. There is thus no indication that the pretreatment was inadequate."
- 2. Carmi claims that our study, Rasmussen et al. (2001), "miscalculated the efficiency of their AAA treatment from the ¹⁴C data," and Carmi presents an alternative formula for calculation of the cleaning efficiency.
- 3. Carmi says the efficiency of the cleaning procedure of our experiments should have been calculated based on "the δ^{13} C values of the samples," and that when this is done, a dramatically different result is obtained.
- 4. Carmi claims that our "strategy of testing the validity of the dates of the Dead Sea Scrolls is wrong."

We believe that Carmi's response fundamentally misunderstands our paper and is in error on each of the 4 points.

ARGUMENT 1

Carmi argues that "evaluating whether or not the AAA treatment of the Dead Sea Scrolls was adequate can be done by comparing the ¹⁴C dates of the scrolls with ages assigned to them using palaeographic methods and with ages of explicitly dated scrolls." Here Carmi has the argument backwards. The aim of the original datings by Bonani et al. (1992) and Jull et al. (1995) as well as Rasmussen et al. (2001) was to establish independent data for dating the DSS; these then could function as a check upon the accuracy of the palaeographic dates. To state that the margin of error of the reported ¹⁴C dates in most cases do not deviate from the palaeographic dates by greater than 2.5 standard deviations is irrelevant to our experiments or point, and is not a sound justification for concluding

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that the "the pretreatment of the samples was adequate." In addition, Table 1 of Carmi (2002) contains significant mistakes in listing the data (at items #16, #31, and #33), which is probably why Carmi did not observe potential problems with castor oil contamination. Carmi's item 16 is incorrectly labeled "Community Rule(d)," when the ¹⁴C date at that item is actually that for 1QS. In additition, item 31 is incorrectly labeled "Community Rule," with the implication it is 1QS, and listed by Carmi as free from possible exposure to castor oil contamination (true for 1QS), when the ¹⁴C date at item 31 is actually that for 4QS(d), 1st sample, taken from the Rockefeller Museum, where there was possible exposure to castor oil. Also, Carmi's item 33 is incorrectly labeled as free of exposure to possible castor oil contamination, even though that text was edited by Milik, a user of castor oil, in the Rockefeller Museum.

ARGUMENT 2

There is no error in the calculations of Rasmussen et al. In fact, Carmi's Equation 1 is in complete accordance with our formulas—only in other units.

Carmi is proposing another formula for the percent of oil left in the parchment. In his formula the percent of oil left varies between 0 and 100%, corresponding to a variation from no retention to the saturated state. This is incompatible with the units used throughout the calculations of Rasmussen et al. We used weight percent of oil (e.g. 0.01 grams of oil/gram of sample) in the parchment in our Equations 1–4. Thus, in Rasmussen et al. no oil retention corresponds to PCT = 0% (as in Carmi's formula 1), but saturation does not correspond to PCT = 100%. In addition, Carmi incorrectly quotes our values in Table 2 (7, 12, 6, 8 wt%) as "retained", where it rightly says "removed." It is easily shown that the 2 calculations indeed are identical: e.g., take the number in column 5 in our Table 3, divide by the number in column 6, and multiply by 100, 15/22 * 100 = 68% [Carmi's value: 67.9%].

ARGUMENT 3

The reason that the oil removal values calculated by Carmi (2002) on the basis of the δ^{13} C measurements come out approximately similar to those he calculated from our ¹⁴a results is that (as noted above) Carmi used, in effect, the same formula that we did, except that Carmi's was based on absolute percentages. Had we calculated the oil removal percentages based on the δ^{13} C values using our formula we also would have come up with more or less the same results as those based on the ¹⁴a results. However, as stated very clearly in Rasmussen et al., we maintain as a methodological point that one should make the calculation on the basis of the ¹⁴a results rather than the δ^{13} C values, even though it would result in little difference in actual results either way.

ARGUMENT 4

It is not a shortcoming of the Rasmussen et al. testing strategy not to have dated saturated parchment samples without AAA pretreatment. It is essential to the experiment that all the samples have been subjected to the same pretreatments, i.e., that all the samples in one run have experienced identical AAA pretreatments, identical burning procedures, and identical graphitization procedures. The AAA procedure removes some (minute) parts of the samples as well as some of the contaminants. Therefore, the weight of the parchment will not necessarily be the same before and after the AAA cleaning, and it is not certain how much of the parchment was removed. If the AAA were applied to some samples and not to others, it would destroy the ability to calculate the oil retention accurately. This part of Carmi's comment is therefore irrelevant.

Carmi concludes that "it is clear that the AAA treatment removed less than 50% of the castor oil and old oil from the soaked parchments." And that is exactly what we concluded. Carmi accepts the results of our experiments showing that AAA is ineffective in removing castor oil from parchment samples, but asserts that this finding is irrelevant for dating the DSS ("the pretreatment of the samples was adequate"). We think it is relevant that the pretreatment used in the ¹⁴C datings of the DSS is incapable of removing a contaminant to which most of the Qumran texts have had known significant possible exposure. The reports of exposure come from the original team of editors working on the texts in the Rockefeller Museum, two of whom were coauthors of the Rasmussen et al. (2001) paper as well as the present reply. The description in Rasmussen et al. (2001) of potential exposure and risk, therefore, stands as an eyewitness account.

CONCLUSION

Points 2, 3, and 4 presented in the paper of Carmi (2002) are either erroneous or irrelevant. The Carmi paper is therefore reduced to a statement that constitutes a backwards argument, namely that all but four of the extant Bonani et al. and Jull et al. ¹⁴C dates are not in disagreement with the palaeographic dates, if 2 other cases among those 34 affected by unknown contaminants are ignored, and therefore there is no cause for concern that AAA pretreatment is incapable of completely removing castor oil. We reject this reasoning and conclude that nothing in the comment of Carmi (2002) gives cause to revise our original conclusion concerning castor oil contamination.

Finally, we note that inadequacy of AAA alone to remove contamination from parchment was also recently shown by Donahue et al. (2002).

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CHARACTERIZING THE ERROR IN THE ESTIMATED AGE-DEPTH RELATIONSHIP

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ABSTRACT. It is common practice to estimate the age of undated material extracted from a sediment core from radiocarbon or other radiometric dates of samples taken above and below the extracted material. This paper presents a simple expression for the variance of this estimated age. This variance accounts for both ¹⁴C dating error and error due to bioturbation.

INTRODUCTION

It is common practice to estimate the continuous age-depth relationship along a sediment core from radiocarbon or other radiometric dates of samples taken at discrete depths in the core. Such a relationship can then be used to estimate the age of undated material extracted at a known depth in the core. In doing so, it may be useful to have an idea of the magnitude of the error in the estimated age of the extracted material. For example, this would be important in assessing the significance of differences in the estimated timing of climatic events reconstructed by a geochemical analysis of material extracted from different cores. The purpose of this paper is to describe a simple model of this estimation error. The model, which appears to be the first of its kind, includes both ¹⁴C dating error and error due to vertical sediment mixing.

The remainder of the paper is organized in the following way. The basic model is developed in the next section. In the third section, this model is applied to a small data set. The final section contains some concluding remarks.

AN ERROR MODEL

The basic problem considered here is the estimation of the calendar age Y_0 of material extracted at nominal depth d_0 within a core. This paper focuses on the simple, but common, case where estimation is by linear interpolation between 2 control points at nominal depths d_1 and d_2 with $d_1 \le d_0 \le d_2$. In this case, the estimate of Y_0 is:

$$\hat{Y}_0 = w\hat{Y}_1 + (1 - w)\hat{Y}_2 \tag{1}$$

where \hat{Y}_1 and \hat{Y}_2 are the estimated calendar ages of material extracted at the control points and:

$$w = (d_2 - d_0) / (d_2 - d_1)$$
⁽²⁾

Linear interpolation is based on the assumption that, between control points, calendar age increases approximately linearly with depth.

The goal of this paper is to provide an expression for the variance of the estimation error $Y_0 - \hat{Y}_0$. Two sources of error contribute to this variance. First, as a result of bioturbation or other reworking of sediment, the true depositional depth of material extracted at the control and estimation points may differ from their nominal depths. This will be referred to as depth error. Second, the estimated calendar ages of the material extracted at the control points are subject to the usual dating errors. To proceed further, it is necessary to specify a statistical model of these errors and the way in which they interact.

Let the random variable Z(d) be the true depth of material collected at nominal depth d. Assume that:

$$Z(d) = d + \varepsilon \tag{3}$$

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where ε is a depth error with mean 0 and variance σ_{ε}^2 . A model of this variance is given below. Suppose that, as at the control points, the calendar age of this material is estimated by calibrating an estimate of its ¹⁴C age. Let:

$$\hat{R} = r[Z(d)] + \eta \tag{4}$$

be the estimated ¹⁴C age of this material where, in general, r(z) is the true ¹⁴C age of material at true depth z, and η is the ¹⁴C dating error with mean 0 and known variance σ_{η}^2 . Provided ε is small in relation to the scale of curvature of r(z):

$$\hat{R} \cong r(d) + r'(d)\varepsilon + \eta$$

$$= r(d) + e$$
(5)

where r' is the derivative of r(z) with respect to z. This derivative is essentially the reciprocal of the sedimentation rate. The combined error e has mean 0 and variance:

$$\sigma_e^2 = r'(d)^2 \sigma_\epsilon^2 + \sigma_\eta^2 \tag{6}$$

The estimated calendar age is given by:

$$\hat{Y} = c(\hat{R}) \tag{7}$$

where c(r) is a fixed calibration curve. Provided that e is small in relation to the curvature of c(r):

$$Y \cong c[r(d)] + c'[r(d)]e$$

$$= c[r(d)] + f$$
(8)

where c' is the derivative of c(r) with respect to r and f is the calendar age error with mean 0 and variance:

$$\sigma_{f}^{2} = c'[r(d)]^{2}[r'(d)^{2}\sigma_{\varepsilon}^{2} + \sigma_{\eta}^{2}]$$
(9)

The quantity c[r(d)] in (8) is the calibrated value of the true ¹⁴C age of material, of which the true depositional depth is equal to the nominal depth d. Thus, under this model, the estimated calendar age \hat{Y} is unbiased with variance given in (9). The mean of the true calendar age Y of material extracted at nominal depth d is also c[r(d)], but its variance is:

$$\sigma_Y^2 = c'[r(d)]^2 r'(d)^2 \sigma_\varepsilon^2 \tag{10}$$

The difference between (9) and (10) is due to the fact that Y (which is unobservable) involves no dating and, therefore, no dating error, while \hat{Y} (which is observable) does.

Returning to the main goal of this paper, it follows from these results that \hat{Y}_0 is an unbiased estimate of Y_0 . Under the assumption that the depth errors at the control and estimation points, and the dating errors at the control points, are independent, the variance of the estimation error $Y_0 - \hat{Y}_0$ is:

$$Var(Y_0 - \hat{Y}_0) = Var(Y_0) + w^2 Var(\hat{Y}_1) + (1 - w)^2 Var(\hat{Y}_2)$$
(11)

Finally, it follows from (9) and (10) that this variance is given by:

$$Var(Y_0 - \hat{Y}_0) = c'[r(d_0)]^2 r'(d_0)^2 \sigma_{\epsilon_0}^2 + w^2 c'[r(d_1)]^2 [r'(d_1)^2 \sigma_{\epsilon_1}^2 + \sigma_{\eta_1}^2] + (12)$$

(1 - w)^2 c'[r(d_2)]^2 [r'(d_2)^2 \sigma_{\epsilon_2}^2 + \sigma_{\eta_2}^2]

where $\sigma_{\epsilon_0}^2, \sigma_{\epsilon_1}^2$, and $\sigma_{\epsilon_2}^2$ are the variances of the depth errors at the estimation and control points and $\sigma_{\eta_1}^2$ and $\sigma_{\eta_2}^2$ are the variances of the ¹⁴C dates at the control points.

Before turning to a simple model of depth error, it is worth noting that the estimation variance in (11) depends through w on the relative location of the estimation point between the 2 control points. For example, if $Var(\hat{Y}_l) = Var(\hat{Y}_2)$, then $Var(Y_0 - \hat{Y}_0)$ is maximized when $d_0 = d_1$ or $d_0 = d_2$ (so that w = 1 or 0), and minimized when $d_0 = (d_1 + d_2) / 2$ (so that w = 1/2). Briefly, estimating Y_0 by averaging \hat{Y}_1 and \hat{Y}_2 reduces variance by averaging the errors in these estimated ages. When the estimation point is close to one of the control points, the estimate of Y_0 is dominated by the estimated age at that control point with little averaging of errors. In contrast, when the estimation point is midway between the control points, the estimated ages at the control points receive equal weight in \hat{Y}_0 with maximal averaging of errors.

The estimation error variance in (12) depends on the variance of the depth errors at the control and estimation points. A simple model of these depth errors is the following. The basic assumption is that the material collected at nominal depth *d* consists of *n* particles distributed at random within a sample volume of uniform height *h* centered at *d*. As a result of sediment reworking, between the time of deposition and the time of collection, each particle has undergone a random vertical movement of magnitude Δ with mean 0 and variance σ_{Δ}^2 . The variance of the true depth of a single such particle is the sum of the variance $h^2/12$ due to its random location within the sample volume and the variance σ_{Δ}^2 due to sediment reworking. The true depth *Z*(*d*) of the sample material can be approximated by the average of the true depths of *n* of these particles. This average has mean *d* and variance:

$$\sigma_{\varepsilon}^{2} = [\sigma_{\Delta}^{2} + (h^{2}/12)]/n \tag{13}$$

In many cases, $h << \sigma_{\Delta}$, so that $\sigma_{\varepsilon}^2 \cong \sigma_{\Delta}^2 / n$.

AN APPLICATION

Table 1 reports the depth, ¹⁴C age and error (σ_η), and calibrated calendar age of 12 samples of the planktonic foraminifer *Globigerinoides sacculifer* in a core taken near the Bahamas at 26°04′N, 78°03′W, in approximately 1000 m of water. These data and subsidiary information about them were kindly provided by William Curry. The continuous age-depth relationship for this core estimated by linear interpolation is shown in Figure 1. For these data, the calibration curve is essentially linear, with slope c'(r) = 1.128 for all values of *r*. The ¹⁴C age at each control point was based on $n \cong 100$ specimens, extracted from a sediment wedge of height h = 0.02 m. The bioturbation error σ_{Δ} is around 0.05 m. Thus, from (13), the standard deviation σ_{ε} of the depth error at each control point is approximately 0.005 m.

To illustrate the calculation of the variance in (12), consider estimating the age of a single particle extracted from a sediment wedge of height 0.02 m centered at depth $d_0 = 2.1$ m, based on the estimated calendar ages at the control points at $d_1 = 2.0$ m and $d_2 = 2.2$ m. It follows from (13) that the standard deviation σ_{ε_0} of the depth error at the estimation point is around 0.05 m. That this is an order of magnitude larger than σ_{ε} at each control point reflects the effect of averaging 100 particles at each control point. From (1) and (2), the estimated age \hat{Y}_0 is 38.7 kyr. To complete the calculation

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Depth (m)	Radiometric age $\pm \sigma_{\eta}$ (yr)	Calendar age (yr)	_
0.10	920 ± 35	510	
0.62	5290 ± 45	5640	
0.88	7630 ± 45	7930	
1.13	$11,000 \pm 50$	12,500	
1.21	$12,200 \pm 55$	13,800	
1.34	$17,100 \pm 100$	19,700	
1.51	$20,200 \pm 85$	23,400	
1.71	$25,900 \pm 120$	29,800	
2.00	$31,500 \pm 170$	35,800	
2.20	$37,400 \pm 360$	41,600	
2.40	$39,600 \pm 390$	43,300	
2.67	$45,700 \pm 500$	49,300	

Table 1 Depth, radiometric age and error, and calibrated calendar age for 12 samples of *G. sacculifer* picked from a sediment core.





in (12), it is necessary to estimate r'(d) at d_0 , d_1 , and d_2 . Under the assumption that the sedimentation rate is approximately constant between control points, a simple estimate is $[r(d_2) - r(d_1)] / (d_2 - d_1)$ or 29.5 kyr m⁻¹. Combining terms according to (12) yields $Var(Y_0 - \hat{Y}_0)^{1/2} = 1.69$ kyr.

In Figure 2, $Var(Y_0 - \hat{Y}_0)^{1/2}$ is plotted against d_0 the entire core. Although the standard deviation σ_n of the ¹⁴C dating error varies by a factor of nearly 15, the dominant source of variability in this figure is variability in r'(d). The reason is that the low sedimentation in relation to the level of bioturbation, combined with the absence of particle averaging at the estimation point, make $c'[r(d_0)] r'(d_0) \sigma_{\varepsilon_0}$ the dominant contributor to estimation error. The only part of this term that varies over the core is $r'(d_0)$.



Figure 2 Approximate standard deviation of estimation errors.

DISCUSSION

The purpose of this paper has been to describe and illustrate a way to characterize error in the agedepth relationship. This characterization appears to be the first of its kind. It is based on 2 assumptions of approximate local linearity: specifically, that the ¹⁴C age-depth relationship r(z) is approximately locally linear in depth z at the scale of the depth error ε and that the calibration curve c(r) is approximately locally linear in ¹⁴C age r at the scale of the total ¹⁴C age error e. Another key assumption is that, at each control point, the deviations of the true depths of the particles contained within the sampling volume from their common nominal depth are independent. This assumption would be violated if this material had been subjected to a large-scale disturbance that affected all of the particles in the same way. In a specific application, the reasonableness of these assumptions should be established before proceeding.

Beyond its use as a quantitative measure of estimation error, the error characterization presented here can provide useful qualitative information about the sources of this error. For example, in the application described in the previous section, it is clear that improving the ¹⁴C dating at the control points would have little benefit in estimating the age of undated material.

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Finally, it is possible to extend the error model described in this paper in at least 2 directions. First, this paper has focused on the simple (but common) case in which estimation is based on linear interpolation between 2 control points. It is straightforward to apply the error model to any other estimator that is a linear function of the calibrated ages of the control points. Such estimators include those based on regression and splines. Some details are provided in an appendix. Second, the model treats the calibration curve as fixed. It would also be possible to extend the model to include the effect of error in the calibration curve.

ACKNOWLEDGEMENTS

William Curry provided the data used in this paper. The helpful comments of an anonymous reviewer are acknowledged with gratitude.

APPENDIX

This appendix gives an expression for the error variance for a general linear estimate of the agedepth relationship. Let $\hat{Y} = (\hat{Y}_1 \hat{Y}_2 \dots \hat{Y}_n)^t$ be the vector of estimated calendar ages of material extracted at *n* control points. Here and below, the superscript *t* denotes the vector or matrix transpose. A general linear estimate of the calendar age Y_0 of undated material extracted at nominal depth d_0 has the form:

$$\hat{Y}_0 = \mathbf{w}^{\mathrm{t}} \hat{Y} \tag{A.1}$$

where $w = (w_1 w_2 \dots w_n)^t$ is a vector of weights. The variance of the error $Y_0 - \hat{Y}_0$ is:

$$Var(Y_0 - \hat{Y}_0) = Var(Y_0) + Var(\hat{Y}_0)$$
(A.2)

The first term on the righthand-side of (A.2) is given in Equation (10) in the paper. The second term is:

$$Var(\hat{Y}_0) = w^t \Sigma w \tag{A.3}$$

where Σ is the *n*-by-*n* diagonal matrix, with elements $Var(Y_1)$, $Var(Y_2)$,..., $Var(Y_n)$ along the diagonal. These variances are given in Equation (9) in the paper.

As a simple example, suppose that the age-depth model is estimated by fitting the line:

$$Y_i = \beta_0 + \beta_I d_j \tag{A.4}$$

by ordinary least squares, where d_j is the depth of control point *j*. The ordinary least squares estimate of $\beta = (\beta_0 \beta_l)^t$ is:

$$\hat{\boldsymbol{\beta}} = (\boldsymbol{X}^{t}\boldsymbol{X})^{-1}\boldsymbol{X}^{t}\boldsymbol{Y}$$
(A.5)

where X is the *n*-by-2 matrix whose first column has elements all equal to 1 and second column has elements $d_1, d_2, ..., d_n$. The estimate of Y_0 is given by:

$$\hat{Y}_0 = x_0^t \hat{\beta} \tag{A.6}$$

where $x_0 = (l \ d_0)^t$. From (A.5), this estimate can be written in the form (A.1) with:

$$w = x_0^t (X_t X)^{-1} X^t$$
 (A.7).

RADIOCARBON UPDATES

New AMS Laboratories

Two new AMS entries appear in our annual list of laboratories (starting on page 503).

- LTL Dr. Lucio Calcagnile University of Lecce AMS Radiocarbon Dating Facility Lecce Tandetron Laboratory Department of Engineering and Innovation Via Per Monteroni Lecce 73100 Italy Tel: +39 0831 507372; Fax: +39 0831 507408 Email: Lucio.calcagnile@unile.it http://gfa.unile.it/Itl
- MTC Hiroyuki Matsuzaki Research Center for Nuclear Science and Technology The University of Tokyo 21116 Yayoi, Bunkyo-ku 113-0032 Tokyo, Japan Tel: + 81 3 5841 2961; Fax: +81 3 5841 2950 Email: hmatsu@malt.renst.u-tokyo.ac.jp http://www.malt.renst.u-tokyo.ac.jp

Many other entries have been updated this year; please refer to the list for any new information *Radiocarbon* has received.

2006 International Radiocarbon Conference

At the business session of the 18th International Radiocarbon Conference held in Wellington in October of this year, it was agreed that the venue of the 2006 Conference would be decided by an email vote, according to rules set out in a posting to the ¹⁴C listserve on 11 September.

Two candidates made offers to host the 19th International Radiocarbon Conference: Oxford University, England, and Cheikh Anta Diop University, Dakar, Senegal.

Voting has now closed and the results are as follows:

Votes for Cheikh Anta Diop University, Senegal: 30

Votes for Oxford University, England: 38

Since a simple majority of votes cast was required to decide the issue, Oxford University was declared the successful candidate to host the 2006 Conference.

Congratulations to Oxford on their successful bid, and thanks to Cheikh Anta Diop University, as a relatively new laboratory, for being prepared to step forward and actively participate in the ¹⁴C conference series. The closeness of the vote is a testament to the quality of presentations by both candidates.

508 Updates

Upcoming Conference

8th International Conference on the Methods of Absolute Chronology

The GADAM Centre at the Silesian University of Technology, Polish Academy of Sciences, announces the 8th International Conference "Methods of Absolute Chronology", to be held 17–19th May 2004 in Ustroń, Poland. The Conference will concern the following subjects:

- 1. Methods of dating and their application in Quaternary geology.
- 2. Methods of dating and palaeoclimatic reconstructions.
- 3. Methods in research of paleo- and modern environment.
- 4. Methods and results of dating archaeological objects.

The Conference scientific program includes plenary and poster sessions on all the subjects above, and panel discussions on topics proposed by the participants. The working language of the Conference is English.

During the conference, a meeting of the Polish National Network of Absolute Dating is planned. Before the conference, the GADAM Centre is planning to hold:

- 5-day-long workshop titled, "Toward improved absolute chronology of Late Pleistocene and Holocene," the second of three workshops organized for young scientists by the GADAM Centre in years 2003–2005.
- 1-day-long GADAM Centre Advisory Board meeting.

The Local Organizing Committee chairperson is Anna Pazdur.

More information can be found at the conference web site, http://www.carbon14.pl/conference/2004may/.

35th International Symposium on Archaeometry

For the first time, the International Archaeometry Symposium will be held in Spain. The local organizing committee hopes to meet a large number of colleagues in Zaragoza, which will stimulate the further development of Archaeometry in Spain.

The meeting will be organized by the University of Zaragoza, in collaboration with the University of Barcelona and the Spanish Society of Archaeometry (SAPaC).

M J Aitken serves as president and M S Tite is the chairman of the committe. More information can be found at the conference web site, http://www.archaeometry2004.info.

RADIOCARBON LABORATORIES

This is *Radiocarbon*'s annual list of active radiocarbon laboratories and personnel known to us. Conventional beta-counting facilities are listed in Part I, and accelerator mass spectrometry (AMS) facilities in Part II. Laboratory code designations, used to identify published dates, are given to the left of the listing. (See p 533 ff. for a complete list of past and present lab codes.)

Please notify us of any changes in staff, addresses, or other contact information.

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510 Laboratories

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AC	Ingeis	Argentina	G*	Göteborg	Sweden
AECV	Alberta Environmental	Canada	GAK	Gakushuin University	Japan
	Center of Vegreville		Gd	Gliwice	Poland
AERIK*	Atomic Energy Res. Inst.	Korea	GD*	Gdansk	Poland
ALG*	Algiers	Algeria	Gif	Gif sur Yvette	France
ANL*	Argonne Nat. Lab., Ill.	USA	Gif A	Gif sur Yvette and Orsay	France
ANTW	Antwerp	Belgium	GIN	Geological Institute	Russia
ANU	Australian National	Australia	GL*	Geochronological Lab.	England
	University		Gro*	Groningen	The Netherlands
ANUA	ANU Accelerator	Australia	GrN	Groningen	The Netherlands
AU*	University of Alaska	USA	GrA	Groningen AMS	The Netherlands
В	Bern	Switzerland	GSC	Geological Survey	Canada
Ba	Bratislava	Slovakia	GU	Scottish Universities	Scotland
BC*	Brooklyn College	USA		Research & Reactor Cent	re
Beta	Beta Analytic	USA		(formerly Glasgow Unive	ersity)
BGS	Brock University	Canada	GX	Geochron Laboratories	USA
Birm	Birmingham	UK	H^*	Heidelberg	West Germany
Bln	Berlin	Germany	HAM	Hamburg	Germany
BM	British Museum	England	HAR*	Harwell	England
BONN*	Universität Bonn	Germany	Hd	Heidelberg	Germany
BS	Birbal Sahni Institute	India	Hel	Helsinki	Finland
C*	Chicago	USA	HIG* Hawaii Inst. of Geophys		USA
CAMS	Center for Accelerator	USA	HL	Second Institute of	China
CAM5	Mass Spectrometry	USA		Oceanography	
CAR*	Univ College Cardiff	Wales	HNS*	Hasleton-Nuclear,	USA
CENA	Centro Energia	Brazil		Palo Alto, California	
CLIVI	Nuclear na Agricultura	Diuzn	Hv	Hannover	Germany
CG	Institute of Geology	China	I	Teledyne Isotopes	USA
СН	Chemistry Laboratory	India	IAEA	International Atomic	Austria
CRCA	Cairo	Egypt	TATA	Energy Agency	Managa
CSIC	Geochronology Lab,	Spain	IAEA- MEI	L aboratory	Monaco
	IQFR-CSIC, Madrid	1	ICEN	Instituto Tecnológico	Portugal
CSM*	Cosmochemistry Lab.	USSR	ICEIV	e Nuclear	Tonugai
	USSR Academy of Scien	ces	IEMAE	Institute of Evolutionary	Russia
CT*	Caltech, Calif. Inst. Tech.	USA		Morphology and Animal	
CU	Charles University	Czech Republic		Ecology	
D*	Dublin, Trinity College	Ireland	IGAN	Institute of Geography	Russia
Dak*	Univ. de Dakar	République du	IGS*	Inst. of Geological Sci.,	Sweden
		Sénégal	II*	Isotopes, Inc., Palo Alto	USA
DAL*	Dalhousie University	Canada	IOAN	Institute of Oceano-	Russia
DE*	USGS, Denver	USA		graphy	
Deb	Debrecen	Hungary	IORAN	Institute of Oceanology	Russia
DEM	NCSR Demokritos	Greece	IRPA	Royal Institute of	Belgium
DIC*	Dicar Corp and Dicarb	USA	10.00*	Cultural Heritage	
	Radioisotope Company		ISGS*	Illinois State	USA
DRI*	Desert Research Institute	USA	IVAN	Institute of Valaanala	Ultraine
ENEA	ENEA, Bologna	Italy	IVAN	Corococ	Veneruele
ETH	ETH/AMS Facility	Switzerland		Caracas	venezuela
F	Florence	Italy	IWP	Problems	KUSSIA
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* Indicates laboratories that are closed, no longer measuring ¹⁴C, or operating under a different code designation.

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JUBR	Biren Roy Research Laboratory	India
Κ	National Museum	Denmark
KAERI*	Korean Atomic Energy Research Institute	Korea
КСР	National Cultural Property Research Institute	Korea
KEEA	Kyushu Environmental Evaluation Association	Japan
KI	Kiel	Germany
KIA	Kiel AMS	Germany
Ki (KIEV)	Institute of Radio- Geochemistry of the Environment	Ukraine
KN	Köln	Germany
KR	Krakow	Poland
KRIL	Krasnoyarsk Institute	Russia
KSU	Kyoto Sangyo University	Japan
L*	Lamont-Doherty	USA
LAR	Liège State University	Belgium
LE	St. Petersburg	Russia
LIH	NCSR Demokritos	Greece
LJ*	Scripps (UCSD) La Jolla	USA
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