Radiocarbon Dating by Accelerator Mass Spectrometry: Some Recent Results and Applications [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1987 **323**, 57-73
doi: 10.1098/rsta.1987.0072

Phil. Trans. R. Soc. Lond. A **323**, 57–73 (1987) [57]
Printed in Great Britain

Radiocarbon dating by accelerator mass spectrometry: some recent results and applications

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^{14}C differs from other nuclides measured by accelerator mass spectrometry (AMS) in that an extensive database of dates already exists. AMS dates should therefore have comparable accuracy, and the measurement of isotopic ratios to better than 1%, which was an important technical goal, has been reached. The main advantage of being able to date samples 1000 times smaller than previously lies in the extra selectivity that can be employed. This is reflected in the results and applications.

Selection can apply at several levels; from objects that formerly contained too little carbon, to the choice of archaeological material, to the extraction of specific chemical compounds from a complex environmental sample. This is particularly useful in removing uncertainty regarding the validity of a date, since a given sample may comprise carbon atoms from different sources each with their own ^{14}C 'age'. Examples from archaeological and environmental research illustrating these points are given.

^{14}C dating by AMS differs from conventional radiocarbon dating by having the potential to measure much lower levels of ^{14}C, and therefore should double the time span of the method. This potential has not yet been realized because of sample contamination effects, and work in progress to reduce these is described.

Introduction

The first successful demonstrations of cosmogenic nuclide abundance measurements by the method of AMS were made on ^{14}C (Bennet *et al.* 1977; Nelson *et al.* 1977). This was partly because ^{14}C is technically easier to detect at natural abundance levels than most long-lived nuclides, and also because a huge number of measurements by 'conventional' methods already existed. Consequently, a great deal is known both about the basic geochemistry of ^{14}C and about the application of radiocarbon dating to archaeological and geological chronologies (see, for example, Aitken 1974; Faure 1977, ch. 17). Now, eight years on, the field has developed in a rather predictable way. AMS has brought revolutionary changes to the study of those long-lived radionuclides (for example ^{10}Be and ^{36}Cl) whose measurement at natural abundance by the internal disintegration rate is extremely difficult; and technical interest in AMS has focused on those nuclides such as ^{26}Al and ^{41}Ca whose low signal:background presents a strong challenge (see Middleton & Klein; Henning, this symposium). By contrast, the development of ^{14}C dating by AMS has been largely determined by the pre-existing work in radiocarbon dating by 'conventional' methods. However, the accuracy of conventional dating has presented its own challenge for AMS techniques to match, whereas the thousandfold reduction in the sample-size requirements of AMS is inevitably making enormous changes in the practice of radiocarbon dating. A third development, that of pursuing radiocarbon dating back in time to double the effective range of dating (very roughly from 40 ka to 80 ka) remains still a hope rather than reality.

If the newer results from ^{14}C–AMS are to have a significant impact upon the very detailed existing radiocarbon database, they must match a set of technically demanding criteria that the 'conventional' (β-counting) method has already established. In this paper I aim to show how AMS methods as applied to radiocarbon dating are responding to this challenge.

Criteria set by conventional radiocarbon dating

The main features of conventional (β-ray counting) dating can be considered under the headings of sample size, accuracy, age range and throughput. Although many applications of AMS ^{14}C dating are unique, the majority of measurements are made in the context of the conventional radiocarbon database, and impose certain criteria for the performance of AMS dating, if such dating is to be worthwhile.

The reduction in sample size (from containing *ca.* 1 g of carbon to about 1 mg) is the outstanding feature of the newer (AMS) method. This allows a much greater degree of selectivity to be applied to the sampling process, and such selectivity can be practised at a wide range of levels. For example, sites may be selected that previously yielded inadequate samples (this applies particularly to open sites with shallow stratigraphy, and where organic preservation is poor); or the stratigraphic context within a site may be selected as being better related to the relevant archaeological event. Examples of these will be given later, as will cases where conventional radiocarbon dating is impractical because inordinately large samples are necessary (as for the dissolved organic content of ocean water). After selection of the sample from the field, further levels of selection within the field sample are often very valuable. In particular, the chemical discrimination between different sources (and, potentially, different ages) of carbon (e.g. contamination of a buried bone from mobile organic compounds in the surrounding soil; or terrigenous as well as autochthonous inputs into lake sediments) is very much easier and more effective for milligram samples. Such selectivity enables a radiocarbon measurement to be used to establish the radiocarbon date of the feature under study much more precisely and reliably, and much of the later part of this paper is written to illustrate this. An additional source of precision and reliability in dating a feature is the greater possibility of multiple sampling.

The other features relate more closely to the technical details of the measurement itself. Conventional dating typically achieves a statistical precision of better than 0.5% and an overall estimated error of between 0.5 and 1%. At its most accurate, on ideal material, an overall error of 0.2%, reproducible between laboratories, has been demonstrated (Pearson & Baillie 1983). For most applications the accuracy is likely to be limited by the homogeneity and relevance of the sample, and its value altered and error broadened after calibration to a calendrical date, but the figure of 0.5% remains a reasonable aim for AMS laboratories (Gillespie *et al.* 1983). In fact, establishing the reliability of dating is a difficulty in itself, because more than 90% of a dating laboratory's output is likely to be on material whose date is, in principle, unknown.

The number of existing radiocarbon dates is upwards of 50000. Therefore new dates are unlikely to have overwhelming impact, and need to be carefully selected. Furthermore, dating by radiocarbon is largely a cumulative process, and requires dedication and high volume production over a long term. AMS is well placed to provide a high throughput of measurements, because the time of measurement can be quite short, although its other advantages may be lost if equal attention is not paid to other aspects (e.g. of selection of material or context).

The low signal:background of the conventional method limits accurate dating to an age range of about 25 ka, and places a limit of about 40 ka for most samples. Although AMS has a greatly increased signal:background, the techniques for handling the smaller samples have not yet developed to the same extent, so that in practice a similar limit applies. However, in the range 25–30 ka, AMS methods show that the greater selectivity possible has a very clearly beneficial effect on the accuracy of the date.

Technical aspects of radiocarbon measurement by AMS

This subsection considers the performance of ^{14}C–AMS systems in relation to the criteria outlined above.

Accuracy

Achieving sufficient statistical precision when detecting ^{14}C nuclei is not a problem, except for very small and very old samples. In this context it should be recalled that a milligram of 'modern' carbon contains about 50 million atoms of ^{14}C. Up to 4% of the sample may be counted in the detector. Nor is there any difficulty in discriminating ^{14}C from other nuclides that are registered by the detector. The main problem lies in maintaining highly reproducible and at the same time maximum transmissions of ^{12}C, ^{13}C and ^{14}C through an extended mass spectrometer. Figure 1 shows a block diagram of the system as used at Oxford, some of which is common to all ^{14}C AMS laboratories. (A similar diagram, for comparison, is given by Litherland, this symposium.) Because some mass selection before acceleration is probably essential, yet it is also desirable to transmit the stable isotope beams through the system to reduce systematic errors in measuring the isotope ratio, the different isotope beams are injected in pulses, with a much longer pulse length for the ^{14}C isotope. The ^{14}C:^{12}C or ^{14}C:^{13}C isotope ratio for a sample is compared with that obtained from a standard, so that one is comparing ratios of beam transmissions of beams from two physically different samples. In this comparison, many systematic errors will cancel, and the final errors will be dominated by differences between the beams emitted from the sample and from the standard. Difficulties may arise principally at three levels: the sample in the source, the ion source 'target' (which is usually a solid), may be isotopically inhomogeneous due to fractionation; the beams emitted by each target may be different spatially or in isotopic fractionation; and different isotopes may be transmitted with different spatial distributions.

Differences in spatial isotopic composition because sample and standard account for less than 0.5% variance in the ^{14}C:^{13}C ratio measured at Oxford, for graphite targets deposited on wires from the cracking of C_2H_2. At Toronto, corrections for variable fractionation of about ±0.5% in the source are applied, which may be due to spatial inhomogeneities in the target, or to variation in fractionation in ion-beam formation (see below) (Beukens *et al.* 1986). Other laboratories (e.g. at Zürich and Arizona) report a precision of measurement that, without correction for fractionation, implies a variation of less than 0.5%. To some extent a solid target may be homogenized after preparation, but a gas target source would have considerable advantages in this respect.

The direction and intensity of a negative-ion beam produced by sputtering is sensitive to the local microtopography of the target as well as to that of the sputtering beam (Wehner &

Rosenberg 1960). Furthermore, Litherland has recently pointed out the sensitivity of isotopic fractionation in the sputtering process to several parameters that are difficult to control in the ion source (such as the target work functions, or the velocity distribution of sputtered atoms) (Litherland, this symposium). Suter has shown that accuracy of measurement depends upon the spatial configuration of different kinds of ion-source target (Suter *et al.* 1984). Significant differences in beam direction from different targets have been detected at Oxford, although measurements of source brightness for different targets have failed to show differences in the phase-space distribution that can be directly correlated with errors in the isotope ratio measurement. Nevertheless, the reproducibility of the spatial distribution of each isotope beam is fundamental to achieving high accuracy in the comparison of the measured isotope ratio. It is generally agreed that the least satisfactory stage in ^{14}C AMS from the point of view of accuracy is in the production of a negative-ion beam; and this stage is the one most deserving of attention in both understanding the detailed physics of operation and in developing new source designs.

The transport of the ion beam to the detectors offers many opportunities for isotopic fractionation. Electron-stripping cross sections are velocity dependent, (and therefore mass dependent for ions with equal energy), and substantial fractionation inevitably takes place both in the entrance tube and the stripper canal of the accelerator. Because an equilibrium charge-state distribution is sought, the effective fractionation is not necessarily linear with mass, and will depend on the terminal voltage. However, it is possible to operate in a régime where the control of stripper-gas pressure is adequate to render fractionation differences between sample beams insignificant. Potentially more serious are minor differences in the trajectories of each isotope, either caused by magnetic fields or by the optics of the isotope pulsing system. Such differences, which in the Tandetron accelerator tubes, for example, amount to more than 0.1 mm displacement due to the magnetic suppression system, are significant if the acceptance of the beam-transport system is less than the emittance of the beam to be transported. In such a case, some beam will be lost, and if the beam distribution varies from target to target, the loss will be isotopically dependent (with the ratio changing faster than the change in beam transmission). Therefore the two effects (variability in beam distribution from ion-source targets, and isotopically different trajectories) multiply together to give a variation in the isotopic ratio. The extent to which the beam transmission is limited by the system acceptance can be realized by plotting the beam transmission while varying one optical element. Figure 2 shows such a plot for a series of elements in which the transmission profile is seen to be reasonably flat-topped for the high-energy beam transport, but contains no region where the transmission is independent of slight beam displacements for the low-energy transport system. Such a situation is typical for most, if not all, operating AMS systems (see, Suter *et al.* 1984). Because it is difficult to increase the acceptance of the transport system (generally limited by the stripper-canal dimensions), one approach (taken especially by the Toronto laboratory), is to limit the emittance of the beam as near to the source as possible, although this necessarily increases the time of measurement.

Many types of isotope fractionation are approximately linear with mass, and so a correction can be applied by measuring the $^{13}C:^{12}C$ ratio at the same time as the $^{14}C:^{12}C$ or $^{14}C:^{13}C$ ratio (White 1981; Beukens *et al.* 1986). In any case, because it is known that substantial fractionation has taken place between atmospheric (reservoir) CO_2 and the sample (to about 2 % in $^{13}C:^{12}C$) depending somewhat on the metabolic pathways (Deines 1980), it is desirable to make an

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accurate $^{13}C:^{12}C$ measurement. Few laboratories do this (by AMS) at present, one difficulty being that several laboratories (Oxford, Arizona, Zürich) report variation in the $^{13}C:^{12}C$ ratio, which is beam-current dependent. The dependency is notably severe in the Oxford system (Gillespie *et al.* 1984), where it is independent of the ^{12}C pulse length, and can be plausibly explained as a space-charge effect, (although beam loading in the accelerator tube cannot be ruled out). Transverse momentum of ions in the beam increases as the integral of 1/radius along the beam, and calculations suggest that an increase in the effective emittance of up to 10% is possible for a 20 μA beam. The transmission curves (see figure 2) are generally significantly less flat-topped for ^{12}C beams than for ^{13}C beams.

Although most AMS groups with a developed laboratory for ^{14}C work claim a sample to sample reproducibility of *ca.* 0.5% in the ratio measurement, there is no general agreement as to how the evident differences between laboratories in beam production and transport may be compared, so that the observed differences may be fully explained. Demonstrating an overall accuracy of 0.5% or better is no easy matter (an ion beam of 10 μA from a modern standard and 5 ka old sample would take 21 h to reduce the statistical counting error of the result to 0.25%), and although the potential is there, it is likely to be some time before AMS laboratories are producing a significant fraction of dates with measurement errors of 0.5% or less. Even the present level of performance, for which quoted errors in the region of 1% or less are typical, is in any case vulnerable to the problems of maintaining complex and sensitive apparatus at the peak of performance.

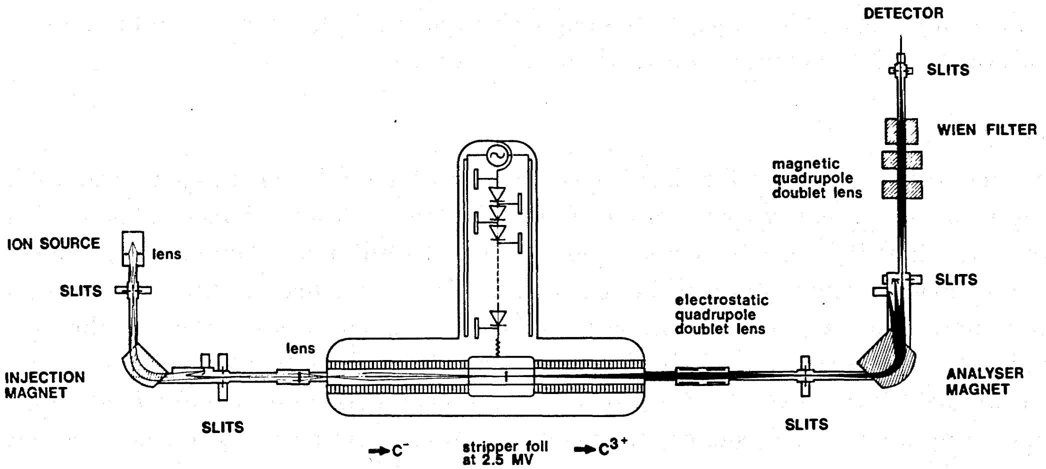

Figure 1. Block diagram showing basic scheme of AMS system for carbon dating. Negative ions from the ion source are magnetically selected and injected to the accelerator. Mass-12 or mass-13 ions are selected in short sequential pulses, followed by a longer pulse of mass-14 ions, at a duty cycle of about 10 Hz. After acceleration, $^{12}C^{3+}$ and $^{13}C^{3+}$ ions are measured following further magnetic selection, and $^{14}C^{3+}$ ions are counted in the detector after an additional velocity selection stage.

Throughput

Calculation shows the potential that AMS dating has for a high throughput. The time per sample is given by the available beam current (typically 10 μA), the age (or ^{14}C content) (typically $2\text{–}5 \times 10^{-13}$ times ^{12}C), and the required statistical precision (including time for measuring standards, backgrounds, controls, etc.). For most samples this amounts to less than 1 h. Therefore a high throughput is more concerned with managerial questions of continual

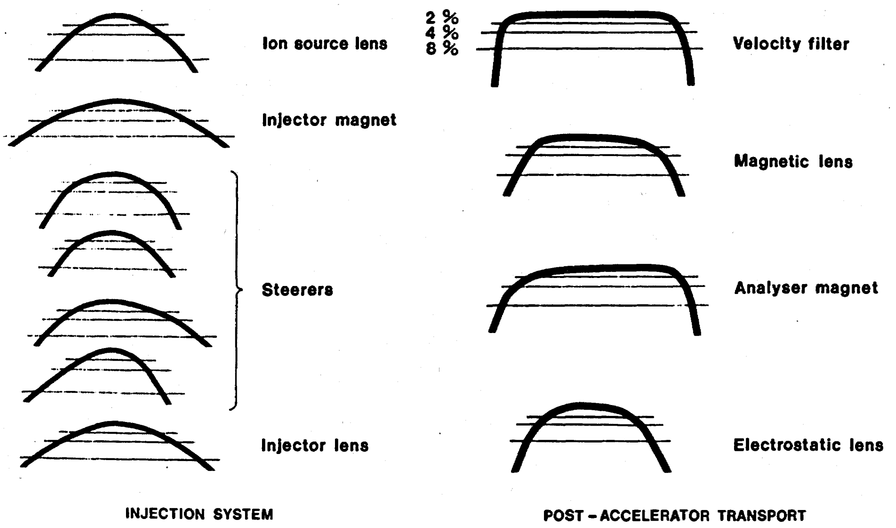

Figure 2. The variation of transmission of a beam at the detector as a function of varying the settings of the principal beam transport elements in order. Of most interest is the extent of 'flat-top' to the curve for variations of 2%, 4% and 8% in transmission.

accelerator operation, maintenance and research, the appropriate batch processing of samples, and the maintenance of adequate documentation. It is worth noting that, in some applications, samples can be treated in large batches (e.g. in oceanography), whereas in others, for example art history, careful individual consideration is essential.

Age range

As mentioned in the introduction, the challenge to extend the age range in practice has not yet been answered. In terms of the physics of AMS, the primary goal to detect ^{14}C at an abundance level of less than 10^{-15} has been easily met. In fact, the ultimate abundance level measurable is not known, because other effects dominate. These are, firstly, the existence of system contamination by ^{14}C, and contamination or memory effects from samples in the source. In practice, the Cs sputter source with graphite as a target is remarkably free from these effects. For example, for the present source used at Oxford the maximum age obtained on carefully cleaned graphite is 75 ka, whereas cross contamination between samples is less than one part in 20000. This is not true of the various attempts to use sources working from CO_2, but recent work by Middleton (1984) has suggested that a Cs sputter source with CO_2 as the target might have acceptably reduced levels of cross contamination, and our own work based on Middleton's source confirms this. That is to say, the system contamination is presently in the region of 45–50 ka, and cross contamination is less than 0.05% with a memory time constant of a few minutes. Moreover, the CO_2 source has the important merit that background levels can be measured before the gas is switched on so that a subtraction is possible for each target.

Contamination of the sample by 'modern' carbon either before or during its period in the source is by far the greatest problem to dating very old material. Because of this it is difficult to obtain ages greater than 60 ka (equivalent to about 1/2000 Modern) from geological graphite. Once the sample has been chemically processed, contamination at the level of 1/200 to 1/400 seems to be very common, even for a wide range of different target preparation methods (see, for example, §IV in Anderson & Picraux 1984).

The most suitable methods for target preparation are important in determining accuracy (i.e. the reproducibility of ion beam generated), throughput (i.e. the manpower required), and age (i.e. the degree of laboratory contamination introduced). There is now something of a common move towards a single method first advocated by Vogel (Vogel *et al.* 1984), in which CO_2 is reduced in the presence of iron, either by H_2 or Zn, to produce an iron–graphite mixture that has many desirable properties as an ion-source target. The method also gives among the lowest of introduced contamination levels, although CO_2 should be superior in this respect because less chemical processing is required (Klouda *et al.* 1984).

There is a further obstacle to extending the age range; contamination in the sample while in the field. However perfected laboratory techniques may be, an increase in age range of 6 ka will make the date twice as sensitive to the occurrence of traces of modern organic material. Because of the greater selectivity applicable to AMS-dated samples, it is easier to select material (e.g. through chemical purification) that is less liable to field contamination. An obvious and frequently cited example of such material is the amino acid hydroxyproline, which is very much more common in the protein collagen (as in bone) than elsewhere in Nature (Bender 1985), and can therefore be extracted. But in any case, ultimately, field contamination must remain the obstacle to complete fulfilment of the technical possibilities of increasing the age range of AMS dating.

Size

The theoretical required size of the ion-source target is given by the number of ^{14}C atoms to be counted, the overall transmission efficiency, and the age of the sample. Well under 1 mg of carbon is adequate for nearly all situations, and even 20 μg can give a useful accuracy in some circumstances. In practice, the sample size is limited by the chemical procedures for producing ion-source targets, and is generally about 1 mg. At Oxford, where most samples are archaeological, we standardize on 5 mg and only exceptionally treat samples smaller than 1 mg. The iron–CO_2 reduction method does, and the CO_2 source should, enable sub-milligram samples to be routinely measured; although the problems of contamination and sample integrity increase. Certain specialized samples, for which the outstanding example is CO_2 in ice cores, require special processing (and further research work) for accurate measurements to be made at the level of 50–100 μg (Andrée *et al.* 1986*a*).

Sample selectivity

The questions of sample selectivity are best included with an account of applications of AMS in radiocarbon dating. But they raise some important technical issues. At one end of the selection spectrum, the issues are largely to do with the context of the application, or the context of the sample. Even here, however, a great deal of feedback between the technical feasibility of AMS measurements and the potential application is most useful. At the other end of the spectrum lies the possibility of selection from the sample as submitted. This may be mechanical, for example the avoidance of rootlets, or the selection of macrofossils in sediments, or the discrimination between biogenic carbonate and recrystallized carbonate in shell; or it may be chemical, as in the selection of particular amino acids from bone protein, or specific ‘marker’ chemicals in organic sediments. Furthermore, it becomes possible to compare dates from different fractions, and so learn a great deal more about the processes that culminate in the heterogeneous material which provides evidence of the past.

Establishing AMS results in radiocarbon dating

Before illustrating the kind of applications where AMS is making a characteristic contribution, it is worthwhile to show how AMS results can first be established. That is to say, it is necessary to demonstrate convincingly and clearly that ^{14}C–AMS dates can corroborate radiocarbon chronologies developed by conventional ^{14}C dating where these chronologies are least open to doubt. For corroboration it is desirable for the following to be established.

1. That the isotope ratio measurement is sufficiently accurate (which can be checked from laboratory-prepared standards; for example, the Harwell benzene series (Otlet *et al.* 1980)).
2. That isotopic fractionation, if significant, between the atmospheric CO_2 and the submitted sample is accounted for.
3. That agreement between the most accurate β-counting measurements on the same or similar material is obtained.
4. That a range of different materials of the same age should give dates within statistical agreement.
5. That the dates obtained from different fractions of the same sample should agree, or be interpretable in the light of the relevant geochemical and environmental processes operating on the sample.
6. That samples obtained from a site, for which a 'conventional' radiocarbon chronology is believed to be securely established, should give dates in accord with the existing chronology.

Each of the separate processes involved needs to be scrutinized, but in practice it is the outcome of the whole chain that is significant. Figure 3 shows results obtained at the Oxford laboratory for the last two years on the dating of material of known age. Material of known age, in fact, can be surprisingly contentious when closely questioned, and we have limited our choice to a variety of different material from the destruction of Pompeii in A.D. 79, and from the sinking of the Mary Rose in A.D. 1546, and from dendrochronologically dated wood (Bristlecone Pine and Irish Oak). Each of these historical dates requires calibration to give the 'expected' radiocarbon age, but precise and reproducible calibration curves now exist (Stuiver 1982; Pearson *et al.* 1983). (See also the calibration issue of *Radiocarbon*, vol. 28, 2B (1986).) The figure shows remarkably good agreement, with, apart from one very aberrant point, an overall standard deviation hardly greater than the counting statistics that average ±45 years. Publication of dates from known age material by the Oxford laboratory is in Gowlett *et al.* 1986, and earlier datelists referenced therein. The aberrant value (of nearly four standard deviations away) came from a single target (we normally date from two duplicate targets), with somewhat anomalous beam characteristics. This experience does illustrate the potential accuracy of AMS dating and at the same time, the potential problems. Also it underscores our policy of duplicate measurements, even though they seem redundant in 98% of the cases.

A different example is given in figure 4, from dating different samples from the same object; in this case the recently discovered body (Lindow Man) that was preserved so well in a peat deposit that most of the internal organs were still intact after *ca.* 2 ka (Stead *et al.* 1986). Small samples were made available for dating, and a crucial question has been the degree of

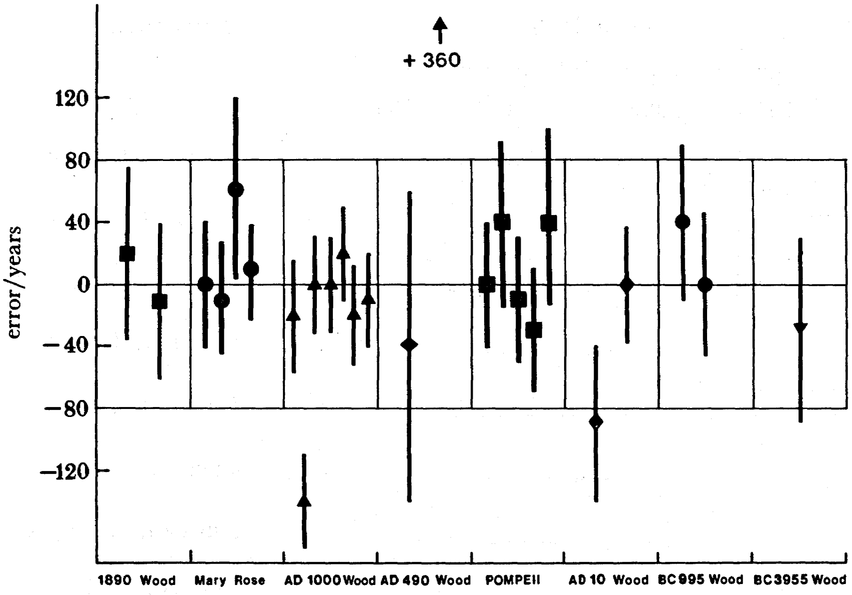

FIGURE 3. Results of measurements on material of known age. Vertical axis is the error in radiocarbon years from the calibrated age in radiocarbon years. An error of 80 years is equivalent to an overestimate of the $^{14}C^{-}$ content by 1%. The error bars here refer to errors from counting statistics only.

contamination of the samples through the 'tanning' action of the peat. Figure 4 shows the dates obtained at Oxford for a series of different extracted fractions, including a proline and hydroxyproline mixture purified from bone collagen. Because of a discrepancy with another laboratory (Stead *et al.* 1986) it was important to demonstrate both the consistency of dates obtainable from different materials (hair, muscle, bone, stomach contents), and the fact that the effect of environmental contamination on different fractions was minimal after pre-treatment. (Some of these results have been published in Stead *et al.* 1986; the remainder are planned for publication in *Archaeometry*.)

Two further examples illustrate the incorporation of AMS dates into the pre-existing structure of conventional dating. Figure 5 shows a series of stratigraphically ordered dates from the Giants' Hills long barrow (Evans & Simpson 1986). The accelerator dates, made on either very small charcoal fragments, or on human skulls too valuable to destroy, are seen to conform well with the conventional dates, and together provide evidence for three distinct phases of Neolithic activity on a site in which the environmental changes are well documented. Figure 6 shows a series of dates from bone from the Upper Palaeolithic rock shelter of Abri Pataud (Dordogne). Although all the implications cannot be considered here (Mellars & Bricker 1986), the following are apparent.

1. The accelerator dates on this site (and others) have produced a more-coherent group of dates than has generally been the case for this period of bone; (the Groningen laboratory dates are also recognized as being particularly coherent, and the Abri Pataud comparison was partly chosen because a useful set of dates was available).

2. The dates measured are in general agreement, or older than, the oldest dates obtained by conventional methods (including Groningen, although the difference here is small).

3. There appears to be evidence of modern contamination in some of the extracted material

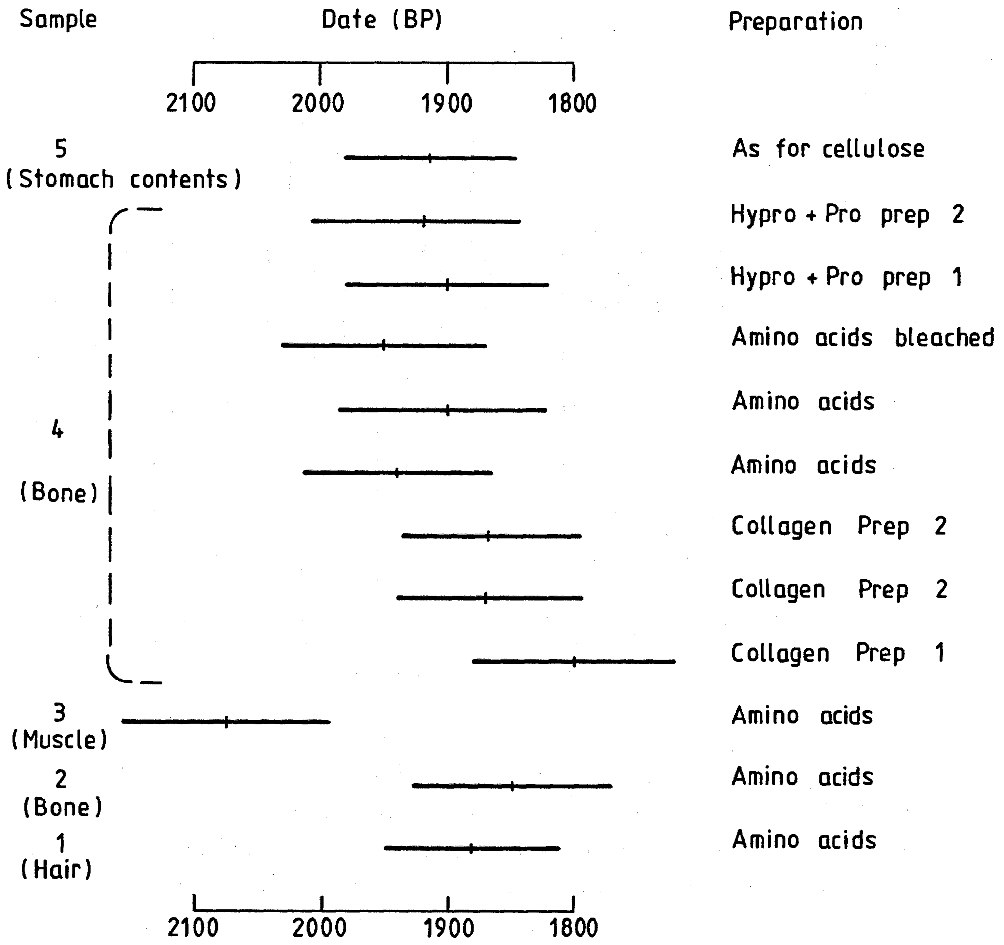

FIGURE 4. Results of measurements on different components and fractions of Lindow Man. The main group of dates refer to different fraction from the same bone. The length of the line is equal to the estimated total error (which is about 80 years).

from the samples, in that the resulting date is stratigraphically much too young. Only those bones for which less than 4% of the original collagen remains show this.

Although the comparison with the Groningen dates helps to establish the reliability of AMS dates in this context (and further results of this general pattern from the Upper Palaeolithic could be cited), the results also show that further research in understanding and eliminating the source of field contamination in bone is necessary before bone older than 35 ka can be reliably dated. For example, we have found that the extracted collagen (defined as proteinaceous material extracted from decalcified bone that is insoluble in 1 M HCl at room temperature) has the appropriate amino-acid composition even for bones with very low collagen preservation (1–2% of modern levels). It seems likely that methods of purifying the amino acids from hydrolysed collagen (Gillespie *et al.* 1986) do not sufficiently discriminate against potentially contaminating entities (such as amino sugars).

Before considering the wider applications of ^{14}C–AMS dating, it is worth making the point that dating in general allows very little opportunity for checking the validity of the result (or rather the validity of the interpretation of the results as a 'date'). This is especially true for a new technique like AMS where dating in novel contexts is likely. To some extent, a consistency argument can be supplied, but all too often this can develop into a circle, so that the validation is only apparent. Stratigraphic succession frequently can provide some check, but the site stratigraphy that is beyond question is rare indeed. Therefore in considering the steps required to establish where AMS dates can be relied upon, it is important to give a clear appreciation of the reliability of results in a given circumstance. The example above of low-collagen Upper Palaeolithic bone being liable to 'date' too young (because of insufficient removal of field contamination) is a case in point. This is fairly well recognized in this case, but other sites, with less-secure stratigraphies, may give no independent evidence to check the dates. It follows, therefore, that a continual effort to define those parameters (such as collagen content and perhaps soil chemistry) which determine the reliability of AMS 'date' is required. Many more model projects such as the example cited above, where checking of results is possible, need to be done.

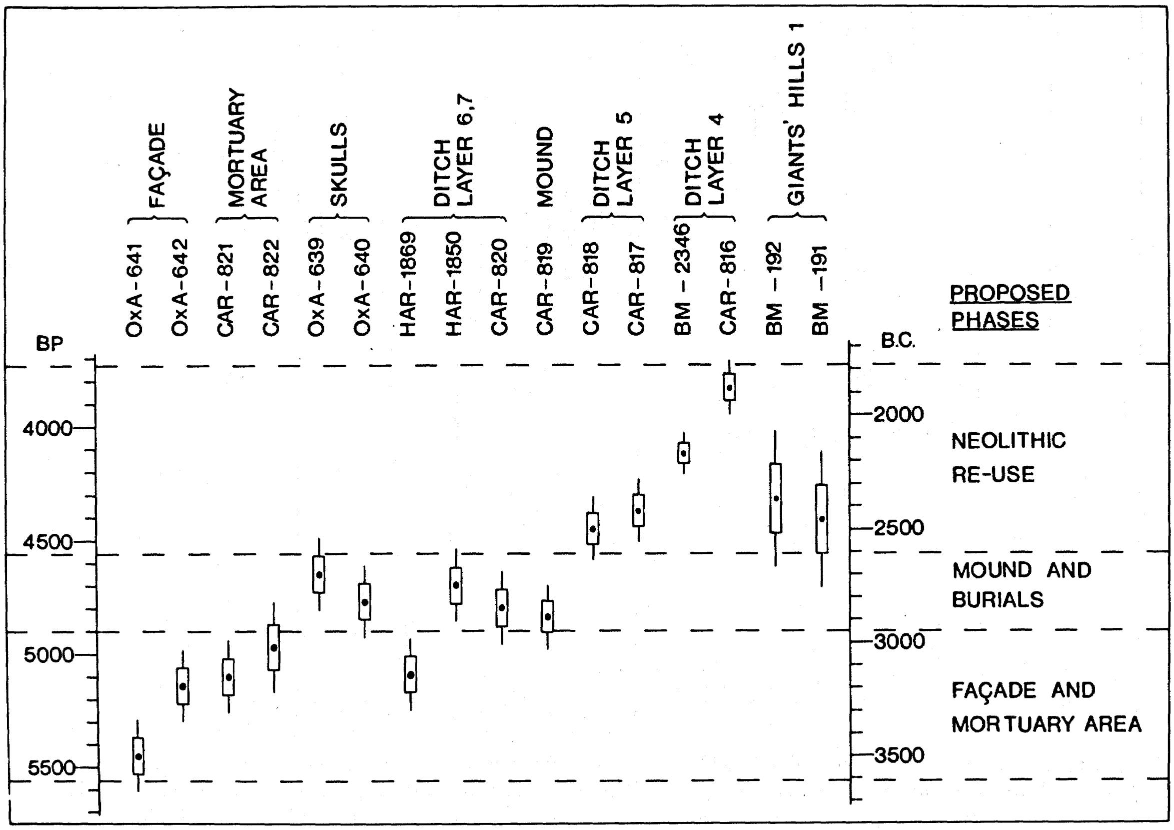

FIGURE 5. Radiocarbon dates at one and two standard deviations from Giant's Hills 1 (BM-191, BM-192) and Giants' Hills 2 as issued by the different radiocarbon-dating laboratories. The dates are arranged in stratigraphic order.

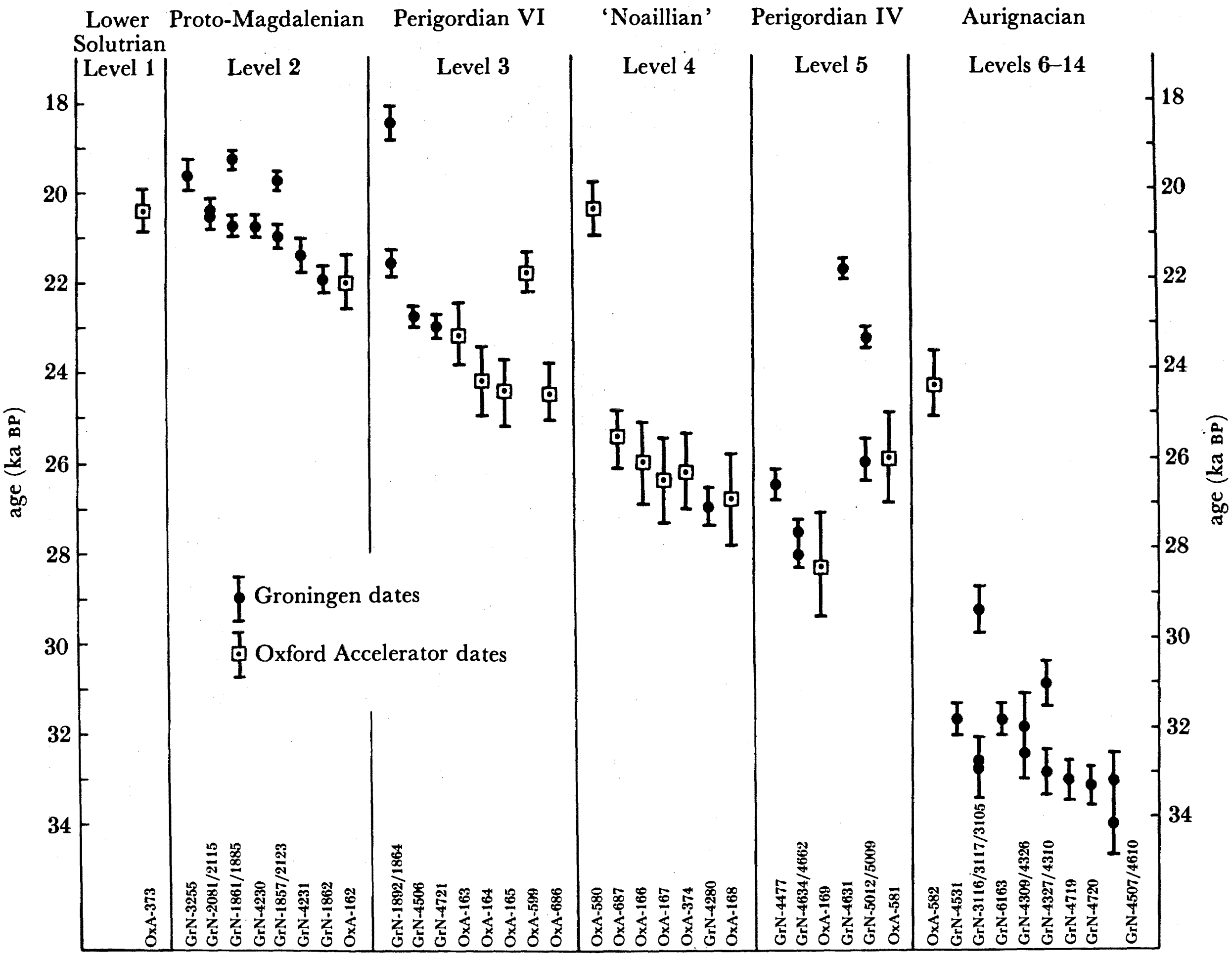

FIGURE 6. A comparison of dates obtained by Oxford (AMS) and Groningen (conventional ^{14}C) from bone from Upper Palaeolithic levels from the site of Abri Pataud. The sequence is in stratigraphic order. Note that several dates, from both series of laboratory measurements, are apparently too young. The errors for the Oxford dates are dominated by the estimate of the variation in laboratory-derived modern carbon contamination.

APPLICATIONS

Because the two preceding talks in this Discussion Meeting have dealt with applications to archaeology and Earth sciences more fully, only the briefest mentions can be made of the variety of applications. This may help to demonstrate the range of possibilities at the present state of development of radiocarbon dating by AMS.

The selectivity in sample size is well demonstrated in a programme to date a series (10–12) of bone points from Upper Palaeolithic–Mesolithic sites in England. Previously, the dating of these has been by often unreliable links of association. We have dated two such points from Sproughton (Cook & Barton 1986) that were in a stratigraphically complex context which suggested quite different ages for the points. In fact they turn out to have approximately the same age (about 10,800 BP; OxA-517, OxA-518). Bone points, although geographically somewhat distinct from harpoon finds, have been thought of as a later artefact, but our earliest date comes from an elk in which two such points were still embedded. The date for the elk is 12400 ± 300 (OxA-150), which is as early as any harpoon found so far. On the other hand, we also have a date of 9240 ± 160 (OxA-500) of a point from Earls Barton, so that the use of bone points continued for a very long period.

An illustration of the value of small-sample dating comes from a recently completed study of dates from a Neolithic chambered tomb (Gowlett *et al.* 1987). It was possible to date small charcoal fragments from the ground surface immediately below the tomb, and also samples from a number of separate disarticulated skeletons that, because of their disposition, formed an approximate 'horizontal' stratigraphy within the tomb. The aim was to find out for how long the tomb had been in use. The results are presented in figure 8, which shows the 20 radiocarbon dates both in units of years BP, and after calibration (in units of cal B.C.). With the error at one standard deviation of ±70 years, the distribution of dates is such as to be consistent with the use of the tomb being limited to a very short time span (i.e. less than 100 years), although it is apparent that the accuracy of the dating is just about sufficient to distinguish earlier and later samples. Although the results show that the period of occupation

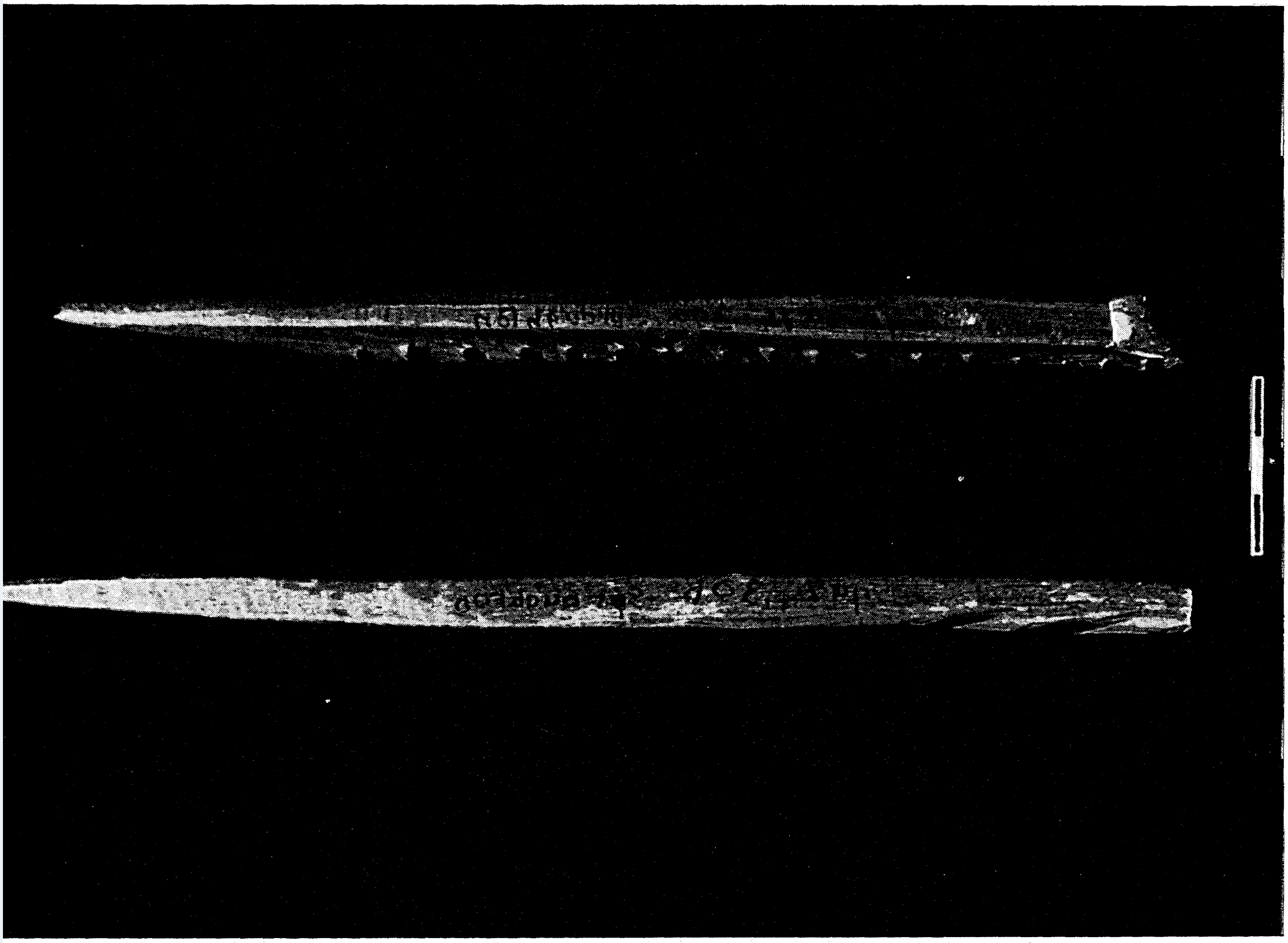

FIGURE 7. The two bone points from Sproughton, dated by AMS.

was almost certainly less than 400 years, and quite possibly no more than 100 years, it is clear that greater precision in the measurements is needed for the original question to be properly answered.

As an example of chemical selection, figure 9 shows results obtained from different organic components of a lake sediment (Fowler *et al.* 1986). Although it is not yet possible to date single molecular species, the molecular classes often reflect the different possible carbon sources that contribute to a lacustrine sediment. Of particular interest here is the very much older date obtained on the 'cellulose' fraction for the lower samples. This indicates a high proportion of carbon of much greater age that has been inorganically deposited before the re-establishment of vegetation following the deglaciation of the landscape. Many other examples, of different processes in lake sedimentation could be given. For example, the Zürich laboratory has made a study of dating the macrofossils found in lake sediments (Andrée *et al.* 1986*b*).

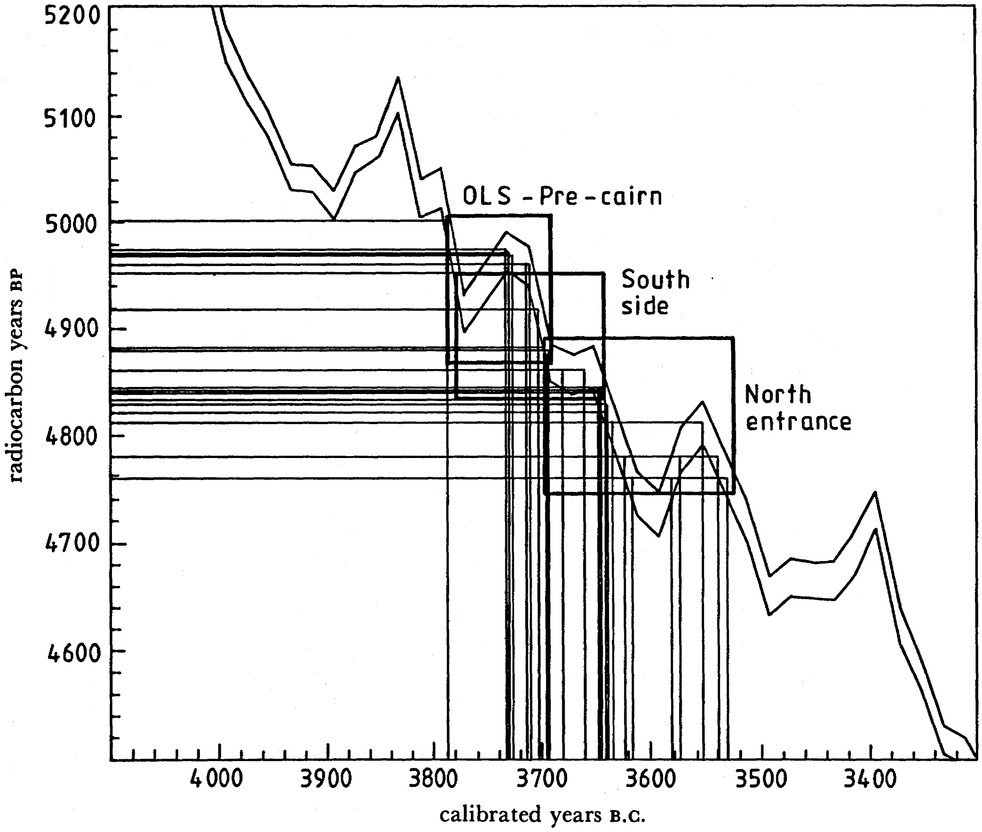

FIGURE 8. A series of dates obtained from the Neolithic chambered tomb of Hazleton in Gloucestershire, England. The vertical axis is in radiocarbon years, and the corresponding calibrated date is displayed along the horizontal axis. No error bars are shown, but the radiocarbon date error is generally ±70 years. The three boxes shown enclose the mean and two standard deviations for the pooled dates from material located in the three areas (OLS refers to the old land surface beneath the monument), and show a distinct separation between the earliest dates and the north entrance dates.

It is inevitable in a review of this kind that most examples are taken from the work that one knows best. The Oxford Radiocarbon Accelerator Laboratory has mainly specialized in archaeological work, but of course a great number of archaeological samples are being

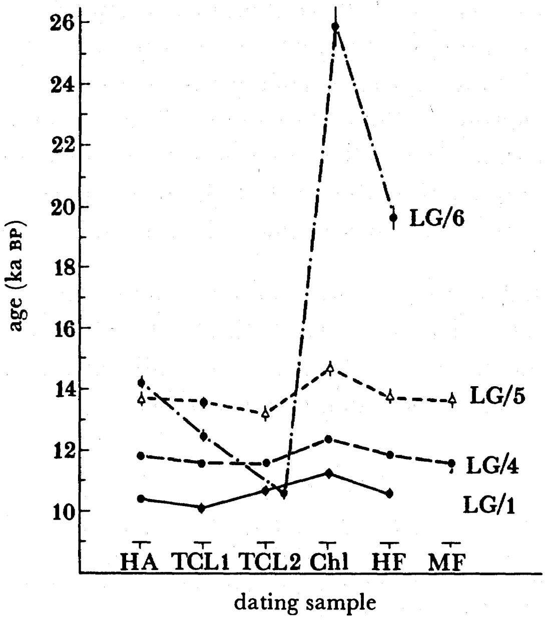

FIGURE 9. Dating of different components from four separate depths from a core obtained from Llyn Gwernan. There is a very striking difference in the age measured on the older fractions treated with sodium chlorite, where extensive reworked fossil carbon is present. The errors are comparable to the drawn size of the points. Abbreviations: HA, humic acid; TCL, polar lipid fractions; Chl, chlorite preparation; HF, extraction with hydrofluoric acid; MF, macrofossils.

measured in the 6–12 laboratories now active Worldwide in ^{14}C dating by AMS. A striking example of archaeological dating with small samples is that given by Nelson on the dating of what are believed to be blood residues on prehistoric stone tools. Material was extracted from two such tools, in one case providing only 50 μg of carbon. The results (1010 ± 90 BP (RIDDL-120) and 2180 ± 160 BP (RIDDL-121)) were in agreement with the expected archaeological age (Nelson *et al.* 1986). However, it is mainly in other fields where many of the applications of AMS ^{14}C dating are to be found.

The ability to select species-specific Foraminifera from deep-sea cores is an outstanding example of the power of the AMS method. Oeschger (this symposium) has described the work by the Zürich laboratory in comparing the ^{14}C content of planktonic and benthic Foraminifera of the same age, thus providing information on ocean ventilation rates in the past. To this work must be added the dating by the laboratory at Gif-sur-Yvette on selected Foraminifera from cores that contain the record of the last deglaciation, and so provides a direct dating for the melting of the Continental ice sheets (Duplessy *et al.* 1986).

Perhaps the most exotic example of biological specimens dated by radiocarbon is that made by the Tucson, Arizona, laboratory on mussels and worms (vestimentifera) from a hydrothermally supported abyssal community 3200 m deep in the Gulf of Mexico. This showed the predominant food source not to come from vented fossil methane, despite the indications of extreme values in the stable isotope ratios, but from available dissolved inorganic carbon in sea water (Paull *et al.* 1985). A second, quite different, application of AMS by this group has been to the measurement of ^{14}C concentration in Uranium ores, in which they sought evidence of production of ^{14}C by emission in the radioactive decay of ^{238}U, with an estimated branching ratio (relative to α production) of about 10^{-9} (Barker *et al.* 1985).

As a final example, the measurement of ^{14}C content in atmospheric methane is being carried out by the AMS laboratory (Institute of Nuclear Sciences, Lower Hutt) in New Zealand. This forms part of the effort to understand the causes of increase in atmospheric methane (at present about 2% per year), by estimating the biological-source fraction. Preliminary results suggest at least some atmospheric methane is of biological origin. What is clear is that the radiocarbon dating of an atmospheric component at the level of about one part per million (by volume) would not have been worth attempting before the arrival of AMS.

The work of the Oxford Laboratory reported here is equally the result of the efforts of my colleagues. They are J. A. J. Gowlett, E. T. Hall, E. Hendy, C. Perry, I. Law, C. R. Bronk, J. Foreman, M. Humm, A. Bowles and A. Stoker. The Radiocarbon Accelerator Laboratory is supported in part by the Science and Engineering Council.

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Discussion

W. D. Mook (*Groningen, The Netherlands*).

1. On the date Dr Hedges shows for the Hazleton burial chamber from 4700 to 5000 years BP, there is a very sharp drop in the calibration curve, so that what looks like 250 years BP is probably only 100 calibrated years.

2. On Abri Pataud, which we have been measuring at Groningen, the stratigraphy is quite complicated and difficult, and I think it is quite uncertain how the correlation between the profile at the front and the back of the cave is to be made. So even for a very good chemical treatment of the samples Dr Hedges may obtain the ages he quotes, which may in fact be the correct ages.

3. When Dr Hedges compares the AMS and conventional techniques, I think there is only one advantage for AMS; this is the smaller sample size. For example, at Groningen the age limit for conventional dating can be extended to 60 ka in a 50 l counter and two days of counting.

R. E. M. Hedges.

1. Certainly the calibration curve needs to be considered. Its effect is actually quite complicated to work out, and I think not as clear as Dr Mook suggests. (The calibrated dates are included in the published diagram.)

2. Concerning Abri Pataud, we have had some spirited arguments with the archaeologists involved about the stratigraphy. The site was chosen for its stratigraphic reliability, however, and whereas at first I thought our dates were probably correct, I am struck by the fact that the samples that seem to be too young are also those that are low in collagen. We need, however, to understand why those particular bones are low in collagen.

3. I take the point, but the fact remains that very few conventional dates of over 40 ka have been published. Whether or not in principle AMS has the advantage in age, in practice the advantage of much smaller samples enabling better chemical processing to be done means that many more samples over 40 ka can now be dated.

H. Margaritz (*Weizmann Institute, Rehovot, Israel*). After Dr Hedges work on different fractions in bone, has he reached a conclusion on the best method to use?

R. E. M. Hedges. Routinely we take collagen, hydrolyse it, and purify the mixture of amino acids by ion exchange and date the purified mixture. I should say we date about 80–90% of our bones that way, but we would not use a routine method where the collagen level of the bone is less than 5% or so of the modern value, and where the bone is beyond 20 ka or so. We still have to do more work before we know how to reliably date such bone.

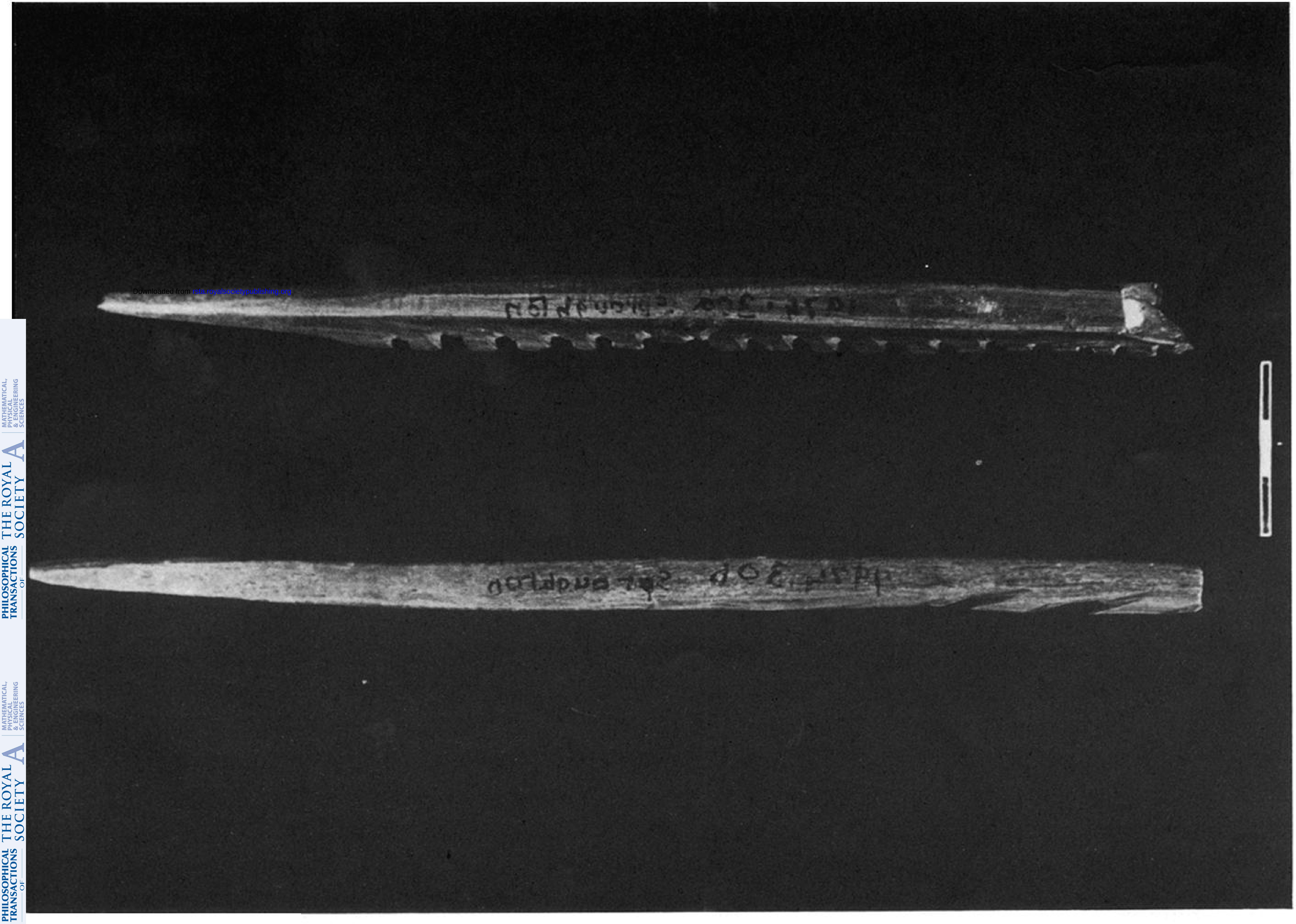

FIGURE 7. The two bone points from Sproughton, dated by AMS.