THE FUTURE OF THE PAST[1]

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INTRODUCTION

For this opening presentation, a personal view of the future of radiocarbon dating was invited. Although the future and the past in some ways share a similar relationship to the present, predictions for the future can, eventually, be fully tested. The ability to retrodict the past, especially for the geological sciences, has relied, with varying emphasis, on two approaches, namely uniformitarianism and catastrophism—and these also are appropriate here. I have taken a strictly uniformitarian approach which in practice has meant that my view does not look very far forward at all. In hindsight, many of the important unexpected developments in radiocarbon dating in the last 20 years, for example the territory opened up by the accelerator mass spectronomy (AMS) method, or the detail and power of correlation with palaeoenvironmental signals preserved in ice cores, now seem predictable. While it is true that their potential importance was recognized early on in their development—nevertheless, it would have taken remarkable prescience to have foretold such major and abrupt shifts. What follows is therefore more of a consideration of the *state of motion* of the field, in the present, and I hope this summary will be useful to those looking for such a perspective. In fact some of the extrapolations into the future were subsequently immediately manifested during the Conference, as recorded in the Proceedings.

Radiocarbon dating is both a technique and an application, and it is clear to workers in the field that advances in each provide a positive feedback to the other. On the whole, it is probably technical advances that play the more important part, in opening up new, and perhaps unthought-of applications—the advent of AMS is a very clear example here. But the demands of applications themselves, which are often built on the results of previous applications by stretching them that bit further for greater achievement, do also stimulate efforts for increased technical competence. This positive feedback system is regulated, of course, often rather savagely, by the resources made available. So it is natural to consider the future in terms of both technical developments and the demands of different applications. The coverage here of these subjects is not comprehensively detailed—there is neither space nor justification to do so. I have emphasized archaeological applications, in part because of their importance in the work of the Oxford laboratory, but also because this millennial meeting is being held in a city whose claim to have one of the longest records of human occupation of any city gives it a special archaeological importance.

One prediction which I hope endures is that the practice of radiocarbon dating will continue to bring together scientists from a wide variety of fields, to produce a study which sees human history, or indeed the biosphere, indeed the entire planet, as an integrated whole.

TECHNICAL DEVELOPMENTS

Measuring instrumentation remains fundamental, and the AMS "revolution" is now a generation in the past. The aim to reduce the accelerator component in AMS to much lower voltages and thereby becoming much smaller is now beginning to bear fruit (Synal et al., this issue). This will alter the

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ecology of radiocarbon dating laboratories, and it will be interesting to see if the next generation of much smaller systems will occupy a new niche, or compete with and perhaps displace the larger installations. The advantages of smaller systems are mainly of capital cost, and to a lesser extent of running and maintenance costs; also, of course, they can be operated in a smaller space. This will be especially useful for biomedical work, where the costs of sample preparation are less closely coupled to the measurement costs, where large batches are required, and where high precision and low background are not usually paramount. But to challenge existing AMS systems, the small (< 1 MV) systems will have to equal the existing established technical specifications of count rate, reproducibility, sample size, and background. That they are coming close to this, at least in a dedicated research environment, is now being demonstrated—but only time will tell if they will take over the next generation of AMS laboratories. The issue does point up the need to consider separately the technical specifications of producing a radiocarbon date, which is considered next.

Sample Size

We are familiar with the effect the reduction by a thousand in sample size brought about by AMS has had on radiocarbon dating—but how much further can size be reduced?

A theoretical limit in dating is provided by the fact that a 1-nanogram carbon sample at one half-life old contains only 25 ^{14}C atoms. In practice, typically only ~1% of C atoms are detected, so that 100 ng C would give a statistical precision of about ± 1600 years. This is barely useful, and even at 1 or 5 µg, with a precision (at one half-life) of ± 500 or 250 years, the applications are necessarily limited to problems with low precision solutions.

Arguably, the sample size could be further reduced by a factor of 10, perhaps more. The detection efficiency of 1% comes from the product of transmission (25–35%), ion source conversion efficiency (5–10%) and sample handling efficiency (50–75%). All of these are capable of improvement, transmissions of 50% can be realized, with handling close to 100% for specifically designed systems. The greatest potential for improvement is for ion source development. For example, the CO_2 sputter source developed at Oxford is probably limited by most gas not forming a monolayer on the sputtering target—the efficiency of conversion to C$^-$ at the monolayer appears to be high (~50%). A program to optimize the source efficiency, as well as the other factors, which might cause compromises in beam current, etc., might well enable a factor of 10–20 decrease in sample size (or else improve precision by a factor of 3 or 4). While not dramatic, it could well compensate for the losses incurred by selecting only well characterized chemical compounds from samples (discussed later under chemistry).

Sample Handling

This remains one of the awkward areas in AMS ^{14}C dating, because C$^-$ is required (to avoid ^{14}N interference), and is only easily produced from graphite, whose preparation and handling is not trivial. CO_2 is a natural starting point, and the use of continuous flow combustion methods has brought about more reproducible batch processing, better monitoring (e.g. of combustion blanks), an inherently cleaner system and greater potential for scaling down in size. CO_2 as a sputter source target has been mainly used only by one group (Bronk and Hedges 1987), and the method has been slow to improve. Its potential, especially in biomedical applications, should see much more development in the future. The same can be said for the CO_2 discharge source in which C$^-$ is generated through charge exchange from C$^+$ (Schneider et al. 1997). These sources are likely to find their niche with small samples, or fast/cheap dates, but whether they will supplant graphite sources for most higher precision dating seems unlikely.

A gas source helps enormously in sample delivery to the source, and techniques similar to those used for stable isotopes (such as GC-C-IRMS) can be more or less directly applied (Hughey et al. 1997). However, an online dating operation is bound to be limited by counting statistics, so that applications are somewhat restricted, although will be quite novel. Such a GC-C-AMS, which has been described in principle (Eglinton et al. 1996), is suitable for sub-microgram samples. Larger samples, say up to 10 µg C, can be accumulated by repetitive trapping—in fact this method has been used to accumulate samples up to 1 mg C. The trap can contain either the purified compound, or its oxidized product (CO_2). Few of these methods are being exploited at present, and their future depends on the value of the applications they support. One advance, which would be of great importance in the bio-medical field, would be a successful interface between HPLC-separated compounds and an AMS system, but realistic designs have yet to be proposed.

Ultimate Age

From progress seen in AMS dating, the ultimate age that can be radiocarbon dated has increased by about 1000 years per year—but still has not equalled the isotope-enriched beta counting dates obtained from 70 ka BP peat cores (Grootes 1978). Indeed progress has been surprisingly slow and difficult. The reasons are partly to do with demand, and with the effort of verification; and partly with the difficulty of keeping absolute modern carbon contamination low enough. As an example, for a 1 mg sample, a background contamination level (e.g. in laboratory processing) of 1 ± 0.5 µg "modern" carbon (and this is typical) will give an absolute age limit of around 55 ka BP, even when all environmental contamination is eliminated. However, if there were strong economic reasons to date back to, say, 80 ka BP for adequately large samples, I should expect this could be developed over the next decade. Such a development would have useful implications, because it would necessitate intense study of deposits which may or may not be permanently compromised by various forms of environmental contamination. As an example, work on foraminifera sediments beyond 50 ka BP was described at the meeting (Grootes, this issue).

Accuracy and Precision

Beta counting labs probably can still claim, at their best, to generate dates with smaller errors than AMS labs (although the gap is closing quite fast)–but any further improvements in the future will surely be made by AMS labs.

Counting statistics, which limit precision, depend on sample size and on the economics of beam time. A (count statistics) precision of 2‰ implies $> 2.5 \times 10^5$ counts, or complete consumption of a 1 mg C sample at one half-life age (at 1% detection). It is hard to imagine this being much further improved, say to better than 1‰. In any case, improvement can be had, at the cost of beam-time, simply by making multiple measurements. The degree of measurement replication is also important, and is relatively easily tested in AMS operation. Replication of 2–3‰ (excluding counting statistical imprecision) is more or less standard, and 1‰ is talked of—and would indeed be necessary to justify higher count statistics per sample.

It is worth pointing out that, for a half-life old 1 mg C sample, dated to 2‰, the uncertainty in either a modern or old "blank" must be less than 2 µg or so—this can be achieved, but is difficult to test, especially for a dead blank.

As precision is improved, so the need to reduce, or identify, systematic errors becomes more urgent. In this context, it is extremely valuable to have the opportunity to compare high precision measurements from "conventional" (beta counting) labs with data measured on sample aliquots processed in

rather different ways and measured by AMS. Of course the main sources of systematic error in the *date* are more liable to be due to ^{14}C contamination and/or reservoir effects, and the future for these is discussed below.

Calibration Curve

An important consideration for accurate dating is the use and accuracy of the calibration curve. In one way it sets a sensible limit to the accuracy that is worthwhile for a single radiocarbon date (through both measurement errors of the curve, and ambiguities in the curve's structure). However, groups of dates, if linked by additional chronological information, can be calibrated as a whole, on the basis of Bayesian statistics (or related arguments) (Buck et al. 1992; Bronk Ramsey 1995, 1998). Deploying these methods will become more commonplace, and should form the starting point of any dating strategy. A particular familiar case is "wiggle matching", usually of annual tree rings. In the future we can expect far more use of this, perhaps relying on shorter time-spans, but with the aid of a much more accurate and defined short-term calibration curve. Also, just as multiple proxy records are recorded stratigraphically in ice cores, so other proxy records (such as stable isotope changes) are likely to become increasingly useful to reduce the statistical spread due to the calibration curve. This means the importance of refining the calibration curve will continue to be uppermost, not just in the newly explored regions from 10 ka to 30 ka BP, but also still in the Holocene (especially, for example, in examining short term [e.g. annual] fluctuations).

The Cost of Dating

The large-scale operation of AMS dating laboratories (each producing several thousand dates per year) potentially permits the cost of a dating measurement in the market place to be quite, perhaps very, low. Actually the cost of sample preparation, to say nothing of the costs of obtaining/selecting samples in the first place, will become the dominant cost in producing a date. This dichotomy leads to the recognition that there are two kinds of dating operation; one, in which the samples collected have no great intrinsic importance other than to test a particular hypothesis, and where most processing can be done in parallel (because the samples and their chemistry are all similar); or the other, in which the samples represent individually unique records, and require processing serially. In the first case, e.g. a biomedical field trial, the "dates" need last no longer than the project; in the second, (the obvious example is in archaeological samples), the dates become a permanent feature of a unique record.

So the future holds the possibility for much cheaper dates, but also the potential for a disastrous confusion in quality control. Part of the difficulty is due to the central part chemistry must play in selecting the material that is actually measured.

THE ROLE OF CHEMISTRY IN RADIOCARBON DATING

Whether ^{14}C is being measured as a tracer in a metabolic or geological system, or as a dating component from the biosphere, any sample needs both definition and separation from its environment, and nearly always a mechanical approach is insufficient. Chemistry aims to isolate only representative and relevant carbon atoms or measurement. Since the natural range of ^{14}C content is about 1000, and measurements can be accurate to 2‰, this implies definition/separation of, preferably, better than 0.1–0.2%. Achieving such high purity is very challenging even when the materials studied are straightforward, but the additional effect of chemical decomposition over time, aided by microbiological action, makes the deployment of chemistry almost entirely pragmatic. The issue is further complicated by the huge range of different materials which are measured for their radiocarbon con-

tent. However, perhaps 70% of all dates (excepting sediments) are made on either charcoal, wood, bone or shell.

Chemical Strategies to Remove Post-Depositional Environmental Contamination

Removal of Chemically Labile Minor (But Unidentified) Components

This is the famous acid-alkali-acid wash, which is undoubtedly frequently effective. The Longin process in bone collagen extraction is similar, as is the use of surface etching in carbonates (e.g. foraminifera), and the use of bleaching oxidation for wood.

Selective Extraction of the Most Significant Carbonaceous Material

Various strategies have been developed to distinguish various degrees of carbonization of woody material—such as oxidation by acid dichromate, oxidation in thermally distinct stages, and oxidation by a RF discharge in O_2. Sometimes whole lipid extracts are made for dating.

Attempts to Define Chemically Complex Material

Chemically simple samples (e.g. charcoal, carbonates) may easily be contaminated by the addition or exchange of molecularly similar material, which is then very difficult to distinguish. Complex material, such as degraded bone collagen, or soil "humic acid", is impossible to define properly. In the case of collagen, this has been treated as a protein (backed up with amino acid composition), as polypeptides following specific enzymic digests, as a set of amino acids, or as individual separated amino acids (such as hydroxyproline).

Purification of Specific Compounds

This becomes possible by combining improving methods of separation with better knowledge of environmental biomolecular diagenesis together with the ability to date smaller samples. Lipids in particular lend themselves to gas chromatographic separation and survive post-depositionally with relatively little diagenesis. Most small molecules are soluble and may be leached out unless polymerized. Breaking down polymers, e.g. cellulose to glucose, chitin to glucosamine, and insoluble proteins to amino acids, is a strategy that is scarcely used at present, and in any case needs to be specific (a general approach using hydrolysis is likely to produce more complicated products e.g. as the outcome of Maillard reactions). However, it is in this area that knowledge and capabilities are likely to increase on all three fronts.

It must be an important goal for radiocarbon dating to be able to be quite specific about the precise chemical nature of exactly what had been dated. This is rarely possible at present. Furthermore, the ability to use analytical methods to detect impurities depends on knowing what it is that can be contaminated.

Chemical Strategies for Investigating Multiple Carbon Sources

Post-depositional carbon sources can be separated intellectually, if not necessarily physically, from the potentially numerous carbon sources that may combine to constitute a particular sample material. Multiple carbon sources only matter, for radiocarbon dating, if they contain reservoir carbon. However, reservoir carbon, as in the marine ecosystem, or from dissolved geological carbonate in freshwater, or oxidized or mobilized soil organic matter, can pervade the foodweb, so that its influence can be quite subtle. In other cases, for example in sediments, or in pottery manufacture, multiple sources can be pre-supposed—but this does not necessarily suggest how they can be circum-

vented. For future progress we need much more information about the flow of nutrients through the relevant food chains, and for the mobility and transformations of soil organic matter. No doubt better chemical specificity will help–for example, radiocarbon and stable isotope analysis of essential and non-essential amino acids in bone collagen can help track down the different sources of nutrition (Beavan-Athfield, this issue). Research is underway to understand the degree to which cooking pot use accounts for the lipid composition that can be extracted from it (Stott et al. this issue). Perhaps lipids will become key to the study of sediments.

The notion that biospheric radiocarbon is well mixed is only good to a certain approximation, and as radiocarbon dating becomes more accurate, so this assumption becomes less exact.

Summary of the Role of Chemistry

Inevitably, the major systematic error in radiocarbon dating must be the uncertainty that the measured material contains representative or relevant carbon atoms. Much of the uncertainty is traditionally assessed by judging how well the chemical methods employed work on similar material. Unfortunately, this type of systematic error is essentially sample dependent, and so cannot be reliably estimated by appeal to data on other samples. Using chemistry to ensure that *well-defined compounds* are dated certainly helps to reduce some of the uncertainty, but single compounds, by themselves, do not necessarily define single chemical histories. This is an area requiring much more knowledge, which must surely grow since present development is quite immature. Using chemistry, also, to ensure that common environmental contaminant substances are not present is also likely to become much more sensitive and sophisticated—but the fundamental difficulty of being assured of the absence of contamination at, say, the 1% level, is daunting. Therefore, the possibility of significant systematic error will probably be with us for some while. In practice it seems that most contamination is not so different in radiocarbon age as to subvert most radiocarbon dates, and there are presumably good reasons to do with environmental chemistry that this is the case. But the uncertainty this brings is one which remains a major challenge for the future.

APPLICATIONS

The most immediate one is that of refining and extending the calibration curve, an operation which is well underway (Stein et al. this issue; Beck et al. this issue). It is now clear there is major structure in the 30–40 ka BP period, requiring an exacting precision, together with a wide-ranging set of calendrically dateable archives, for its unravelling. The next decade may well be seen as the time in which further calibration phenomena throw new light on global systems, as well as setting limits to the clarity of dating in this time-range. As measurement precision improves, so the present precision of the calibration curve will become less adequate—this is especially true of the early Holocene parts. Finer detail will help wiggle-match fitting, and perhaps other archival correlations. We can also expect to see much more emphasis on discovering and accurately dating marker horizons— tephra being the obvious one, but perhaps as yet unthought of possibilities here may change the scene dramatically.

Most archaeological applications are probably limited more by the archaeology than by radiocarbon dating, although an ability to date bone from hot environments, where most, or all, collagen has disappeared, would make a major advance. The themes of demographic movement are very much in the forefront of archaeological concerns, especially being stimulated by progress in the molecular genetics of both ancient DNA and modern human genomes. Dating is essential to such themes and the study of colonizations of the New World, of Australia, and of Europe by Modern Humans should be fully sorted out within the next generation. However, the complications revealed in the calibration

curve are also likely to put a brake on work, certainly on interpretation, on the Neanderthal/Anatomically Modern Human transition in Europe.

Other archaeology is likely to benefit from technical advances, such as the ability to date pottery reliably. One such would be the application of radiocarbon to organic traces, for example in cave paintings, or putative protein, lipid or carbohydrate deposits on tools. Identification of such material is notoriously difficult, and "authentication" by radiocarbon, perhaps on sub-microgram samples, would be very useful in the scientific development of this subject.

Most terrestrial dating applications are to dating sediments. It should become much more possible to dissect the taphonomic complexities of such deposits, as chemistry is used in a more selective way. We are still quite ignorant of the patterns of movement of organic materials in peats, or in soils, or in bacterially active sediments. Identifying re-worked material is hit-or-miss. The successful use of macrofossils will be–indeed is being–extended to smaller and smaller entities—pollen, phytoliths, diatoms….

In general, it seems to me that the future will bring increased emphasis on the *taphonomy* of sample formation—many of the important issues involved in this have already been mentioned here. It is worth recalling the questions of taphonomy which once, 10–20 years ago, dominated the then new possibilities of ocean and ice core dating—of foraminifera dissolution and bioturbation, and of *in situ* CO formation and gas bubble capture in ice cores. While such study is called for in order to understand the integrity of a radiocarbon date, in its own right a general understanding of the taphonomy of carbon leads to an appreciation of the individual processes which together constitute many of the global processes which will be so important throughout this new century. Soils, the oceans, and the atmosphere, as well as the biosphere, dominate the circulation of carbon on the planet. Possibly, ocean studies have by now reached a certain maturity, and the next generation perhaps will see growth in radiocarbon dating much more towards atmospheric and soil studies. In any case, radiocarbon will maintain its deep involvement, at various levels of detail, on the major processes of the planetary ecosystem.

In global systems, radiocarbon is partly used for dating, partly used as a tracer. The bomb curve has been especially effective for the study of soils (Jenkinson et al 1999; Harkness 1986), and perhaps less so in other biospheric applications (surprisingly little has been done to remove uncertainties in turnover times, for example in animal, especially human, bone—again (see Geyh, this issue). For full use as a tracer, radiocarbon must be administered experimentally, and a major area of growth has been, and will continue to be, in the biomedical field. This is well reviewed elsewhere (Buckholz et al. 1999), and there is little to add, except to make the point that biomedical applications, in which enormous dilutions via metabolism of an initially administered ^{14}C spike can be tracked, will also advance as radiocarbon techniques progress. This is true for the very efficient measurement of small samples, and especially true for sample handling methods. Much of biomedical chemical separation depends on HPLC, and an online HPLC-C-AMS system would add a very useful new tool, as would the ability to scan, in the ion source, a target surface on which the products of innumerable chemical reactions are deposited in a microscopic array.

CONCLUSION

A colleague recently remarked on how the Radiocarbon Conference managed to retain a vigorous sense of purpose, despite being about a single technique developed over 50 years ago. That single technique has undergone much evolution during this time, as well as at least one revolution. We now seem to be in for a period of quiescence, with general improvements in small steps, and with most

of the methodological interest taking place in the deployment of cleverer chemistry. But this complacent outlook could turn out to be completely wrong.

A second influence, that rejuvenates research in radiocarbon, is the nodal point that ^{14}C occupies in the global network of circulating materials. To follow any carbon atom about the planet must be to cover a vast number of different adventures, and most of these have important influences on the future of mankind. This portentous fact keeps the science of radiocarbon fresh, making its continued study vital for assessing our own future. It is an enjoyable irony that it is the same nuclide which is also so important for assessing our own past.

ACKNOWLEDGMENTS

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