Some interesting and exotic applications of carbon-14 dating by accelerator mass spectrometry

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Abstract. There are many applications of \(^{14}\)C dating and other measurements using accelerator mass spectrometry (AMS). In particular, applications to dating of archaeological samples and interesting artifacts are discussed. Other applications, such as to extraterrestrial materials such as lunar samples and meteorites show the broad range of topics that can be addressed with \(^{14}\)C studies.

1. Introduction

Carbon-14 (or radiocarbon) is produced in the upper atmosphere by the action of secondary thermal neutrons on nitrogen, which has a relatively high cross section. It has a half-life of 5,730 years which means that amounts of \(^{14}\)C produced cover the time scale of approximately 50,000 years, which is also the period of interest to archaeology and many other fields. Radiocarbon dating relies on the basic assumption that organic or inorganic materials in equilibrium with the production of \(^{14}\)C in the atmosphere and its removal into the oceans, establish a consistent level of \(^{14}\)C. This relies on the well-established radioactive decay equation, where the decay rate is equivalent to the number of atoms:

\[
\frac{dN}{dt} = -\lambda N
\]  

(1)

Where \(N\) is the number of atoms, \(t\) is time and \(\lambda\) is the decay constant of the nuclide. When the animal or plant dies, it is removed from this equilibrium and so the level of \(^{14}\)C decays according to equally recognizable equation:

\[
\frac{N}{N_0} = e^{-\lambda t}
\]  

(2)

There are a vast number of applications of \(^{14}\)C and we can touch on only a few in this paper. Originally, \(^{14}\)C was counted by decay counting of the 156keV \(\beta\)-decay of the nuclide, however since 1977, this has been increasing supplanted by accelerator mass spectrometry (AMS), so that this now predominates. Indeed, AMS has become the method of choice for most measurements of longer-lived radionuclides, of which the most well-known is carbon-14 [1-4]. This method allowed much smaller samples of carbon to be measured than were previously possible using decay counting, because
instead of waiting for decays to be counted, we can count the atoms directly. In practice, the measurement of samples of carbon of 0.05 to 0.5mg is now possible [4].

For historical reasons, radiocarbon ages are quoted in “years before present” (yr. BP), where “present” is 1950AD. In practice, the production rate of $^{14}$C in the atmosphere has varied, so that it is important to calibrate raw radiocarbon ages derived from eqn. 2 to the “calendar age”. This is achieved by using a calibration of radiocarbon ages against true age from tree-ring records up to 12,700 before present. Beyond that time, calibration is achieved by cross-referencing $^{14}$C ages of corals to the U-Th ages of the same corals. This involves some assumptions about the constancy of the oceanic $^{14}$C record, but we now have a calibration for the last 50,000 years, basically the entire range of radiocarbon dating [5]. An example of a calibration is shown in figure 1.

Two other effects can change the $^{14}$C in the atmosphere. Fossil-fuel burning has raised the level of CO$_2$ in the atmosphere from 280ppm in the 18$^{th}$ century to almost 400ppm today. This $^{14}$C-free carbon added to the atmosphere dilutes the original signal. After 1950AD, we have an opposite effect on the radiocarbon curve. There is a large increase due to the atmospheric testing of nuclear weapons, which raised the atmospheric value in the northern hemisphere to 1.8 times the pre-bomb value. Since this testing mainly ceased after 1963, with some minor exceptions, the level in the atmosphere has now decreased to about 1.04 times the pre-bomb value. In this paper, we will review some of the basics of the method, and then give some examples of applications, that highlight the usefulness of these measurements to a wide variety of topics.

2. Basics of the AMS Method

1.1 Basic principles

The basic principles of AMS have been reviewed in many publications [1-4], so we will highlight only some brief examples here. For radiocarbon measurements, developments over the last 15 years have been reducing both the voltage and size requirements, so that nowadays, radiocarbon AMS may be conducted over a wide range of energies. However, the basic design of the machine remains the same.
The basic layout consists of the following components:

a. An ion source, that produces $^12C$ ions by sputtering with Cs$^+$ ions onto a target, which is usually graphite, but can also be onto a Ta frit through which CO$_2$ gas is released. The gas is then effectively converted to graphite, as well as being ionized. This is often a complex mechanical device, which requires constant maintenance. The amount of material required varies but in general is between about 0.05 to 0.5mg C. A photograph of the ion source on the Arizona 3MV machine is shown in figure 2.

Figure 2: The Cs-sputter ion source in the Arizona 3MV AMS machine.

Figure 3: Layout of the 3MV National Electrostatics Corporation machine at the University of Arizona. The ion source is on the left-hand side, and the diagram shows the location of the various components, including the injection magnet, accelerator (terminal voltage at 2.5MV), and electrostatic and magnetic analysis at the high-energy end. In this case, the ions exiting the machine are mainly in the 3+ charge state.
b. An injection magnet, which selects mass 14.

c. An electrostatic device (generally called the “bouncer”) attached to the injection magnet chamber to allow selection of masses 12, 13 and 14 by applying a retarding potential to the magnet chamber.

d. An accelerator which accelerates the C ions, passes them through a gas (or sometimes a solid) stripper, which changes the charge to positive due to electronic collisions. Generally, for higher-voltage machines, the 3+ charge state is selected. For machines operating below about 500kV, C+ is selected. If the singly-positive charged ions are used, care must be taken that molecular ions do not pass into the detector.

e. An analysing magnet at the high-energy end of the machine, that selects mass 14. Masses 12 and 13, if injected, are deflected more than mass 14 and hence are directed to Faraday cups, where the current can be measured.

f. An electrostatic analyser, which defines E/Q.

g. A detector, which can consist of a gas-filled cell, or a solid-state surface-barrier detector, where the 14C ions are stopped and generate an electric pulse. These pulses are counted in the computer system and analysed.

An example of a typical system is shown in figure 3. Current technology has developed to the point where a machine can operate at 200kV or less [6]. Machines of this design are closer in size to a conventional mass spectrometer than older designs, which filled a room. A picture of such a small machine, the 200kV MICADAS system in Debrecen is shown in figure 4.

1.2 Chemistry

As equal in importance as the AMS machine, is the sample-preparation chemistry. Samples such as wood and charcoal can be pretreated with a relative simple acid-alkali-acid treatment, but other samples such as bones and textiles require more complex pretreatments [8]. Bone samples are cleaned with acid, and then the collagen is extracted by a weak acid treatment. The remaining protein, or collagen, can then be either combusted directly or hydrolysed to its component amino acids. Textiles are often treated to a sequence of organic solvents, in order to remove any organic contaminants that might have been added to the sample, for example for conservation purposes. All samples are converted to CO2 by combustion, or in the case of carbonates by acid hydrolysis. The CO2 is converted to graphite over an Fe catalyst and pressed into a target holder for AMS analysis. In some laboratories, CO2 can be injected directly into the ion source.

Figure 4: The 200kV MICADAS accelerator mass spectrometer installed at ATOMKI in Debrecen [7]. In contrast to figure 3, this machine is about 2m across.
2. Some examples of dating and other radiocarbon measurements.

It would be a vast task to try to summarize all the uses of AMS radiocarbon dating, so we will highlight just a few, to give some idea of the range of applications.

2.1 Unusual documents and textiles.

Some of the most interesting applications to radiocarbon dating involve sometimes controversial archaeological finds, ancient documents and textiles. At the Arizona laboratory, we have undertaken many such measurements, including dating of the Shroud of Turin [9], Dead Sea Scrolls [10,11], the Vinland Map [12], the Gospel of Judas and most recently, an unusual document called the Voynich manuscript [13]. An interesting feature of all these studies was the high interest of some sections of the public in these measurements. The Shroud of Turin, for example, clearly dates to the 14th century, with a calibrated radiocarbon age of 1260-1390AD [9], yet controversy still surrounds this object.

3.1.1 Dead Sea Scrolls

A less controversial example is the study of the Dead Sea Scrolls. These interesting documents, written on parchment or papyrus, contain detailed copies of books of the Old Testament, other religious commentaries on books of the bible of an esoteric nature, as well as more mundane business documents, such as financial transactions. These documents date from the mid-2nd century BC, for example the Book of Isaiah shown in figure 4, to the first centuries AD.

3.1.2 Voynich Manuscript

The intriguing Voynich manuscript is currently in the possession of the Beineke Rare Books Library at Yale University in the USA. The document was known since about the 16th century, since it was at one time in the possession of the Holy Roman Emperor Rudolph II. It was acquired from the widow of Wilfred Voynich, who had apparently purchased the manuscript from the Jesuit College of Frascati, near Rome, about 1912. The document is enigmatic in that it is written in an indecipherable language, which is assumed to also be encrypted. Many have tried to decipher this code, but none have succeeded. The document consists of strange drawings of astronomical features, botanical drawings of unknown plants and ritual bathing. The purpose of the document remains unclear. Greg Hodgins at the University of Arizona worked with the Beineke Library to get the manuscript dated, which turned out to be in the 15th century, to 1404-1438AD [13].

2.2 Archaeology

The field of archaeology has relied heavily on radiocarbon dating since its inception in the early 1950’s. Many radiocarbon dates are produced which find their way into archaeological reports of various kinds. It would be difficult to narrow down to a few examples. Recently, Ramsey et al. [14] have attempted to correlate radiocarbon dates on known materials from the tombs of Egyptian pharaohs, which gave good agreement for the Middle and New Kingdoms, but the dates for the Old Kingdom were generally older than archaeological estimates. Similarly, Friedrich et al. [15] dated an olive branch found in the destruction layer of the eruption of Santorini, generally assumed to be about
1550BC, but their radiocarbon dates came almost a century older. The reasons for these offsets are not yet established.

In the New World, much interest is focused on the arrival of early humans, which is considered to be sometime during the last Ice Age period, which ended about 11,000 years ago. A famous site close to Tucson, Arizona, known as the Murray Springs site [16] is well dated to 10,900±50 radiocarbon years before present (BP). At this location, the layer dated overlies the last evidence for mammoths in this region at a site where humans clearly killed the mammoths. This is clear evidence for humans, since arrow points are found here, and also the interaction of humans with the mammoths, that became extinct at the end of the last Ice Age. When we do the calibration [5], as discussed earlier, this corresponds to an absolute age range of 12930-12820 years before present. Recently, there is some evidence that humans arrived before this time [17], but this is still an on-going controversy. Jull and Burr [18] summarize some recent studies on this subject.

2.3 Meteorites
Another completely different approach is to use $^{14}$C to study the times that meteorites have resided on the surface of the Earth. Most meteorites are stony-irons, they contain silicate and iron together. They are irradiated in space at approximately 1600 times the cosmic-ray exposure level at the surface of the Earth. The cosmic-ray exposure produces a cascade of secondary particles and $^{14}$C and other radionuclides are produced by spallation reactions. This is a different production mechanism than in the atmosphere of the Earth. After the meteorite falls to the ground, it is shielded from most (but not all) cosmic radiation, and so the $^{14}$C that has built up in space will decay with the characteristic half-life. We can then use this signal to estimate the residence time of the meteorites on the ground. Interestingly, the time-scale for the survival of meteorites in many desert locations is comparable to the radiocarbon time-scale [19]. This method has been used extensively to try to understand the infall rates of meteorites and their weathering in the terrestrial environment [19,20].

2.4 In situ $^{14}$C production in rocks
A new method which uses AMS measurements is the use of cosmogenic radionuclides produced in situ at the surface of the Earth by interactions of cosmic radiation with the silicate in surface rocks [21]. Measurements of radionuclides produced in situ in the surfaces of rocks, soils can be used to estimate exposure age and erosion rates. This is particularly true for the nuclides $^{10}$Be, $^{14}$C, $^{26}$Al and $^{36}$Cl. These methods can be applied to landscape evolution variability, such as weathering, sediment transport and soil development, retreat and advance of glaciers, tectonics, volcanic flows, meteorite impacts and other phenomena. One recent example using $^{14}$C is a study of rocks exposed by the recent retreat of the Rhone Glacier in Switzerland, that shows that these rocks were exposed for about 6,500 years within the last 10,000 years, even though they were covered by ice until recently [22]. This indicates that this glacier was small in the early Holocene period, which was warmer than current conditions.

2.5 $^{14}$C from solar flares or supernovae?
A final example of an interesting application of $^{14}$C is in tree rings. Although we use the tree ring chronology to establish a calibration curve [5], the fluctuations in the $^{14}$C in tree rings of different age also show variations from climatic events, changes in the CO$_2$ in the atmosphere and changes in cosmic-ray flux. We only discuss one very interesting event here, which was shown recently by Japanese scientists [23]. In this study, an increase in $^{14}$C in wood from AD 774-775 was discovered which does not have any explanation other than cosmic-ray effects. Hence, these authors proposed this signal is caused by intense solar flares or a nearby supernova. Further investigations from other sources of wood will determine if this is a global or local signal. In a completely different investigation, the effects of solar-cosmic rays on the surface of the Moon give us an excellent record of the integrated flux of solar radiation from integrating fluxes deduced from radionuclides of different half-life. From this record, it can be deduced that the solar flares could not have exceeded a total flux
of $\sim 5 \times 10^{13}$ p/cm$^2$ in the last 20,000 years. The tree-ring record over the last 7,000 years constrains this further to about $3 \times 10^{11}$ p/cm$^2$[24].

3. Conclusion
Carbon-14 is a very useful radionuclide which has extensive applications to dating of objects and as a tracer. This paper only presents a small aspect of the many diverse applications of this unique and versatile isotope.

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