

MISUNDERSTANDINGS CONCERNING THE SIGNIFICANCE OF AMS BACKGROUND ^{14}C MEASUREMENTS

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ABSTRACT. We consider one misconception of those who currently reject the general validity of radiocarbon (^{14}C) age determinations older than, at most, 10,000 BP. There is an allegation that the presence of ^{14}C reported by accelerator mass spectrometry (AMS) laboratories in their measurements of ^{14}C infinite age (>100,000 years) organics used to define background levels, support their point of view. This article has been written for a general audience, primarily for those who have questions about the validity of these arguments. However, they may not be familiar with the literature relevant to providing a clear response to the claims of these individuals. We conclude that, in our view, of all of the possible explanations for the reports of the presence of ^{14}C in these background samples, the *least probable* explanation has been advanced by those rejecting the validity of the ^{14}C time scale in excess of, at most, 10,000 BP.

KEYWORDS: ^{14}C , AMS, backgrounds.

PURPOSE OF ARTICLE

The purpose of this review is to provide a resource for non-specialists in radiocarbon (^{14}C)-based geochronology to refute allegations that ^{14}C values older than, at most, 10,000 BP are invalid. Those advancing such opinions argue that ^{14}C laboratories using accelerator mass spectrometry (AMS) technology reporting ^{14}C background values provide scientific support for their point of view. The specific question posed by these advocates typically takes a form similar to: “If organic samples purported to be hundreds of thousands to millions of years old and older are reported consistently to contain ^{14}C by AMS laboratories, does not such data demonstrate that the true ages of these materials must be measured in the range of thousands of years not millions and hundreds of millions of years?”

It is our view that such a statement reveals that these individuals misunderstand a number of features of AMS technology as currently applied to the measurement of natural levels of ^{14}C in samples. Such lack of knowledge extends to issues involving the requirements of sample processing and the inherent contamination of samples of infinite or near infinite ^{14}C age by exogenous modern or near modern carbon. Because of these and other misunderstandings, the implications of background data reported by AMS ^{14}C laboratories are misinterpreted.

In the following discussion, we would like to emphasize to general readers that all of the material presented here is well-known to those involved with the use of AMS instruments measuring natural level ^{14}C . The general principals involved are also well understood by those scientists measuring other rare nuclides at or close to background levels. Also, we need to note that we will include considerations of issues that are not usually addressed in current ^{14}C research papers, since general features of the various types of AMS ^{14}C systems have already been well described in the literature (For example, Kutcher 2005; Povinec et al. 2009; Chen et al. 2011; Litherland et al. 2011).

In addition, some explanations, definitions of terms, and general understandings assumed in contemporary research presentations may not be immediately obvious to a general reader or

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non-specialist. Because of this, these items will be restated here in much greater detail than it is in the contemporary standard research literature. If some readers wish to refresh their overall understanding of the general features of the ^{14}C dating method, the presentations in Taylor et al. (1992), Trumbore (2000), Jull and Burr (2014), and Taylor and Bar-Yosef (2014) contain helpful information.

NATURE OF THE MISUNDERSTANDINGS

In dealing with this topic, we suggest that the fundamental problem of those rejecting the validity of ^{14}C values in excess of, at most, 10,000 years, citing the objection stated above as a basis of their objection, is that they appear to lack a basic understanding of the nature of AMS technology used in the measurement of ^{14}C . Specifically, there are four areas where this lack of knowledge has led to erroneous statements when they comment on AMS-based ^{14}C measurements on various types of infinite age samples.

By *infinite age samples*, we mean organics for which it can be reasonably assumed that, due to the ~5700-year ^{14}C half-life, we can be confident that all of the cosmogenic (cosmic ray produced) ^{14}C originally contained in these samples has long decayed away. This is because, based on various lines of scientific evidence, the geological and/or paleontological ages of these samples are at least several hundred thousand years and, in many cases, many orders of magnitude older. In making this statement, we assume, of course, that any infinite age sample has not been contaminated by younger organics. As we will see, this assumption will need to be significantly nuanced later in this discussion.

The four areas where these individuals appear to exhibit particularly deficient knowledge are (1) the definition and implications of “backgrounds” and “sample blanks” employed in AMS-based ^{14}C measurements, (2) an understanding of the difference between finite and infinite ^{14}C age determinations, (3) the distinction between “machine-based backgrounds” and “sample-based backgrounds” in creating net background values unique for each AMS system measuring natural ^{14}C and, (4) the effects of trace amounts of modern or near modern contamination on measured ^{14}C values when dealing with infinite age samples.

We will begin by outlining the basis on which AMS-based ^{14}C measurements are obtained by first reviewing the general operational features and components of the majority of AMS systems currently measuring natural levels of ^{14}C . We will then focus attention on the definition, nature, sources, and implications of *backgrounds / sample blanks* in obtaining ^{14}C data. In commenting on the sources of AMS-based ^{14}C backgrounds, we will provide the basis for our view that, of all of the possible scientifically relevant explanations concerning the sources of ^{14}C when infinite age samples are being measured, those individuals holding the view stated above have elected to advocate the *least probable* explanation.

NATURAL ^{14}C DETECTION TECHNOLOGY AND TERMINOLOGY

From the very beginning of ^{14}C studies, researchers involved in instrument design for the measurement of natural ^{14}C activity were confronted with several physical realities which had to be addressed if routine measurements of natural or cosmogenic ^{14}C concentrations were to be accomplished at some reasonable level of accuracy and precision. In this discussion, *accuracy* addresses how close a ^{14}C -derived age determination comes to the actual or true age of a given sample. *Precision* refers to the magnitude of the time segment or interval that is assigned to a ^{14}C age value based on some clearly defined criteria. For ^{14}C measurements, that time envelope is largely, but not entirely, dependent on the counting statistics associated with

the measurement of the ^{14}C content of a given sample and the various standards used in calculating ^{14}C ages.

One of the principal challenges in obtaining natural level ^{14}C measurements is the result of the very low concentration of natural ^{14}C in organic samples at the level of about 1 ^{14}C atom for every 10^{12} ^{12}C atoms in modern organics. There is also artificial “bomb” ^{14}C , which was produced during the detonation and testing primarily of thermonuclear weapons in the atmosphere beginning in the mid-1950s and accelerating in the early 1960s. The potential implications of the existence of bomb ^{14}C for our topic will be discussed below.

Any type of technology designed to measure natural ^{14}C levels at a reasonable level of accuracy and precision is confronted with the task of identifying and measuring pulses—typically in an electronic circuit—which usually indicate the presence of ^{14}C in a sample. In AMS technology, the signals from non- ^{14}C mass 14 particles such as the most plentiful isotope of nitrogen, ^{14}N , or mass 14 molecules such as $^{12}\text{CH}_2$, would be multiple orders of magnitude more prevalent than ^{14}C if it was not for a fortunate circumstance that will be explained below. Clearly, natural level ^{14}C measurement technologies used for dating applications must deal with highly disadvantageous “signal to noise” isotopic ratios.

It is critical to an understanding of the issues raised in this paper to realize that all AMS systems measuring ^{14}C concentrations, together with all other analytical instruments designed to obtain precise quantitative measurements of physical entities such as isotopes, elements, or molecules, share a well-known characteristic. This characteristic is referred to by somewhat different terms depending on the specific technologies employed. In the case of the methods used to measure natural level ^{14}C concentrations, that term is *background*. In some contexts, the term *blank* as in “machine blank” or “sample blank” is also used. In an instrument system designed to measure natural levels of ^{14}C , a background or blank is the product of some pulse or signal appearing in an electronic circuit which typically indicates the presence of ^{14}C when, in fact, *indigenous* ^{14}C contained in a given sample can be reasonably assumed *not* to be present.

So that the point just made will not be passed over quickly, let us reiterate the statement made at the end of the previous paragraph. *Every sensitive modern analytical instrument of which we are aware, no matter what type of physical entity such an instrument has been designed to measure, exhibits some type of background or sample / machine blank signal. There is, as far as we know, no exception to this statement.* In the remainder of this discussion, we will use the term *background* to encompass all of these types of signals.

In ^{14}C studies, a sample used for background measurements would be an organic of sufficient geological or paleontological age so that it can be reasonably assumed that, given the ^{14}C half-life of ~5700 years, all of that sample’s *original* ^{14}C content should have been reduced to zero. Examples of the types of organics used in the measurement of ^{14}C as infinite age or background samples would be fossil organics of various types such as coal, natural gas, and petroleum products, as well as geological graphite and Mesozoic age limestone. We might here note that questions have been raised regarding the use of coal samples which have been contaminated with organics of more recent origin as the result of the presence of various types of *in situ* microorganisms to serve as background samples (Lowe 1989; Vorres 1989; Chapelle et al. 2002). Others report that if adequate chemical pretreatment methods are rigorously and consistently employed, the problems reported with coal can be resolved (Santos 2011).

These types of organic samples are sometimes referred to informally as “dead” from a ^{14}C perspective. Obviously, if such a sample has been contaminated in some manner by younger organics, the assumption of essentially zero ^{14}C content would be invalidated. Unfortunately, as we will see, the effects on background samples of several types of trace ^{14}C contamination from modern organics, even at the level of less than 100 parts per million, can be most dramatic. Using the definition stated here of the term *background* in ^{14}C measurements, we can now consider the distinction between *finite* and *infinite* ^{14}C ages.

Finite ^{14}C Ages: *A finite ^{14}C measurement and the age determination based on this measurement is one in which the measured ^{14}C content in a sample can be distinguished at some explicitly defined level of statistical confidence from that exhibited in a background sample in the same detector operating under a common set of experimental conditions (see Figure 4). Most published ^{14}C “dates” are finite ^{14}C ages. In AMS systems, the difference between the net mean measured $^{14}\text{C}/^{12}\text{C}$ ratio of a sample of unknown ^{14}C age and that of the background material compared with the net mean $^{14}\text{C}/^{12}\text{C}$ ratio of a sample of known ^{14}C content defining the activity of a sample of zero ^{14}C age—a modern reference standard—is used in the calculation of a finite ^{14}C age of the sample.*

A finite ^{14}C -based age measurement is indicated when the results of a measurement are cited in conjunction with a numerical value that expresses the experimental uncertainty associated with the calculated finite age value. By general agreement within the ^{14}C research community, that experimental uncertainty is typically expressed in terms of a value which is dominated by *counting statistics* expressed at the ± 1 sigma ($\pm 1\sigma$) level which is equivalent to 68.3% of the age distribution. In some cases, an additional consideration of non-random scatter in the counting data is also included in the calculation. A definition and review of the concept of a statistically based standard deviation, as expressed in terms of “sigma” variations, can be found in any standard statistics reference text. Reviews and illustrations of how these statistical concepts are applied in expressing ^{14}C ages can be found in Taylor and Bar-Yosef (2014:121–129) and the literature cited in that work.

A finite ^{14}C age expression takes the form: [^{14}C age in ^{14}C years BP (Before Present)] \pm [$\pm 1\sigma$ -based measurement uncertainty expressed in ^{14}C years]. Therefore, a ^{14}C age value expressed as, for example, 2450 \pm 20 BP is a finite ^{14}C age. In this expression, the units (years) are assumed and “BP” can be understood initially as indicating “Before Present” although “Present” for technical reasons has a special meaning in ^{14}C studies (Stuiver and Polach 1977). Because of this, it was suggested early in the history of ^{14}C studies that “BP” should be referred to as an abbreviation for “Before Physics.” It might also be helpful here to explain that the finite ^{14}C “date” cited above represents a short hand expression that defines a probability-based age range. A more detailed explanation of the special meaning of “BP,” the statistics associated with the expression of conventional ^{14}C -based age expressions, as well as details explaining how finite ^{14}C ages are calculated can be found in Taylor and Bar-Yosef (2014:144–149) and references cited there.

Infinite ^{14}C ages: *An infinite ^{14}C measurement and the age based on such a measurement is assigned to a sample when its measured ^{14}C content cannot be distinguished at some stated level of statistical confidence from that exhibited in a background sample. It should be made clear that infinite ^{14}C measurements only define lower age limits. There is no upper age limit indicated when an infinite age ^{14}C age determination is cited. In the case of, for example, an expression of “> [greater than] 60,000 BP” (again “years” are assumed as the units) indicates that, on the basis of its ^{14}C concentration, the true age of the sample could range from 60,001 years (ignoring for a moment statistical considerations) to literally the age of the universe. From the*

perspective of the ^{14}C measurement obtained on that sample, it is not possible to determine an upper limit.

Infinite ^{14}C values are indicated when the age expression takes the form: “>” followed by a value calculated based on a comparison with the background values measured by the same instrument, calculated following explicitly stipulated statistical protocols. For a general explanation of how infinite ^{14}C ages are calculated, interested readers may consult Stuiver and Polach (1977) and Taylor and Bar-Yosef (2014:121–129).

AMS ^{14}C TECHNOLOGY: MEASUREMENT ELEMENTS, PROCEDURES, AND BACKGROUNDS

With these general points in hand, we will now proceed to the explanation of the specific nature of the misinterpretations of the published background ^{14}C values obtained on infinite age/background samples measured by AMS technology. To do this, we need to first provide a very brief overview of the essential components of a typical AMS system currently being used in the measurement of natural levels of ^{14}C in sample materials. This will provide a context for a discussion of the most probable set of explanations for the presence of electronic pulses in detector circuitry indicating the presence of ^{14}C from samples reasonably assumed to contain no measureable cosmogenic ^{14}C . We will also define a few terms as applied specifically to ^{14}C detection in the context of how these terms relate to the measurement of ^{14}C backgrounds in AMS systems.

Although the first AMS-based ^{14}C measurements were obtained on a cyclotron particle accelerator (Muller 1977), the current generation of AMS instruments used for routine natural level ^{14}C measurements, are, with a few exceptions, *electrostatic accelerators* (Tuniz et al. 1998; Tuniz and Norton 2008). It is data from these types of AMS instruments which have been most often cited and misunderstood by current critics. As indicated by the term itself, AMS systems combine the technical capabilities of a mass spectrometer with that of a particle accelerator.

Mass Spectrometer: A *mass spectrometer* is an instrument that can measure the ratios or relative concentrations of selected isotopes, elements, or molecules exhibiting different physical masses, weights or concentrations. In the case of AMS systems used in obtaining ^{14}C ages, the relevant values being measured to provide the basis of calculating ^{14}C ages are the *ratios* of the atomic mass of the naturally occurring carbon isotopes, ^{12}C , ^{13}C , and ^{14}C , as represented by $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ values.

$^{14}\text{C}/^{12}\text{C}$ ratios measured in samples are the values used to infer the age of a sample using standardized algorithms and protocols. $^{13}\text{C}/^{12}\text{C}$ ratios (usually expressed as $\delta^{13}\text{C}$ values) measure stable carbon isotope *fractionation* effects caused by several factors. Natural carbon isotope fractionation occurs, for example, depending from which carbon reservoir (e.g., terrestrial or marine) a given carbonaceous sample was derived. Also carbon isotopes in natural materials will exhibit different fractionation effects depending on which type of photosynthetic biochemical pathways are followed in different species and genera of plants.

Fractionation can also be introduced during an AMS-based measurement of a sample due to several aspects of the operating characteristics of a particle accelerator. Fortunately, in the calculation of a conventional ^{14}C age, measured variations in the $\delta^{13}\text{C}$ values will have a relatively small effect on the $^{14}\text{C}/^{12}\text{C}$ ratios exhibited in samples. However, to obtain the most precise determination of an inferred ^{14}C age, adjustments or *normalization* of the $^{14}\text{C}/^{12}\text{C}$ ratios in terms of variations in the $\delta^{13}\text{C}$ values are necessary to express a *conventional* ^{14}C age. Stuiver and

Polach (1977) and Taylor and Bar-Yosef (2014:26–27;124–127) explicitly define *conventional* ^{14}C ages and provide an explanation of how and why $^{14}\text{C}/^{12}\text{C}$ ratios are adjusted using $\delta^{13}\text{C}$ values so that all such ^{14}C age determinations are normalized to a common $\delta^{13}\text{C}$ value.

Particle Accelerator: A *particle accelerator* is what the name indicates. It accelerates a beam of particles within a confined space under a set of specified conditions. The specific functions of various components of an AMS instrument in obtaining AMS-based ^{14}C ages will be described after a consideration of the types of ^{14}C backgrounds that are encountered in AMS systems and how certain required sample conversion procedures contribute to background levels.

Types of AMS Systems ^{14}C Backgrounds: There are two major sources of ^{14}C backgrounds registered in AMS systems: *sample based* and *instrument based*. *Sample-based sources* reflect the effects of (1) exogenous ^{14}C contamination not removed by the application of appropriate *sample physical and chemical pretreatment* protocols and/or (2) ^{14}C added during or after the application of *sample conversion* protocols that renders pretreated samples into a form required by the measurement technology. *Instrument-based sources* reflect backgrounds produced by the characteristics of how an AMS instrument operates in its measurement of natural carbon isotopic ratios. Both of these background types have multiple sources that can be operating in unique ways depending on sample processing protocols and instrument component configurations employed in different AMS laboratories at different times.

AMS Sample Preparation: With few exceptions, organic samples for which an AMS-based ^{14}C age is desired must be subjected first, to *pretreatment* requirements and second, to *conversion* procedures.

Pretreatment procedures isolate by chemical and physical means a specific target carbon sample as free as possible from contaminating organics. Contaminating organics are those carbonaceous materials which were not present when a target organic ceased to exchange carbon with its environment. Typically, this occurs on the death of the organism from which the target organic was obtained. *Conversion procedures* employ various steps which will transform the isolated target carbon sample into a form that will allow the measurement of its ^{14}C content to be undertaken as efficiently and accurately as possible in an AMS instrument using current technologies.

Pretreatment Procedures: The types of samples for which ^{14}C -based age measurements are desired have typically been buried for lengthy periods of time within a variety of subsurface depositional environments which can contain many types of carbon-containing substances sometimes exhibiting a wide range of ^{14}C concentrations. The goal of any ^{14}C pretreatment approach is to remove all non-indigenous organics from a targeted sample, i.e., remove all organics which were *not* contained within that specified organic at the time of its death or withdrawal from whatever carbon reservoir it is derived. That is the goal. The reality is that with most natural materials, removing absolutely all, i.e., exactly 100.0%, of the carbon containing contaminants is, in many cases, not a routinely achievable goal.

Over the more than six-decade history of ^{14}C dating, a variety of sample-specific chemical and physical pretreatment protocols have been developed. Some of these strategies are straightforward while others involve an extended series of chemical steps. Some samples, such as wood and charcoal, typically present the fewest problems in removing a very high percentage of post-death contaminating organics. Others, such as bone, have presented more challenging problems and a variety of procedures have been applied with the goal of removing as much

contamination as possible on a routine basis. For a more detailed discussion of the issues and problems involved in sample preparation for ^{14}C analyses, interested readers can refer to Chapter 3 in Taylor and Bar-Yosef (2014).

One of the points noted above needs to be reiterated. Although sample pretreatment strategies have become very efficient in removing contamination from many types of samples, it would be presumptuous of ^{14}C laboratories to state that these techniques always, or even most of the time, remove 100.0% of the contamination mixed into or absorbed/adsorbed into samples. Thus, no research laboratory of which we are aware makes such a claim. What can be stated with a high degree of confidence is that if standardized sample pretreatment protocols have been carefully followed for standard samples such as charcoal and wood, it is highly likely that these standard methods will have, in the vast majority of cases, removed all but, at most, a few tenths of percent of contaminating organics.

For the majority of samples which have been dated by the ^{14}C method to less than 10,000 BP, this proviso is usually not of major concern because the very small trace amounts of contamination remaining after standard pretreatment methodologies are applied would adjust the ^{14}C content of a sample much less than the expected age range reflecting the analytical or measurement precision. However, when dealing with samples expected to exhibit ^{14}C ages >30,000 years, and especially those exhibiting ^{14}C contents at or close to background levels (>50,000 years), the effects of a few tens of percent or even at levels of 20–30 parts per million of modern organic contaminants will have significant measurable effects as will be reviewed in the next section.

An excellent example of the challenge of entirely removing contamination from a sample of infinite or close to infinite ^{14}C age, which are generally considered most amenable to standard pretreatment approaches, is illustrated from an examination of the results of applying various chemical pretreatment modalities to samples of Kauri wood (*Agathis australis*). The samples used in these studies are late Pleistocene in age which have been preserved in various peat swamp deposits located in New Zealand. The Kauri wood samples in Table 1 are assumed to be ^{14}C “dead,” i.e., >65,000 years, based on several lines of evidence. Table 1, Part A, illustrates the varying apparent ^{14}C ages of three compounds isolated from this sample, while Part B illustrates the increasing finite ages that are obtained depending on what types of pretreatment methodologies are employed.

For a more detailed discussion of the many issues and problems involved in applying various physical and chemical pretreatment modalities to various categories of sample types employed in ^{14}C studies, the materials contained in Gillespie (1984), Stuiver and Polach (1977) and Chapters 3 and 5 of Taylor and Bar-Yosef (2014) provide a number of examples.

Conversion Procedures: Following the completion of appropriate pretreatment steps, in all AMS systems currently measuring ^{14}C on a routine basis, a sample must first be converted into an appropriate physical form. The initial step in this process involves for samples such as wood, charcoal, or bone, is *combustion*. In the case of, for example, shell or other carbonate samples, the process involves *acidification*.

In a typical situation in the case of combustion, the chemically pretreated sample plus copper oxide to provide oxygen for the reaction, and silver to react with and thus remove non-carbon combustion products such as sulfur or nitrogen oxides, are placed in a quartz tube. This tube is evacuated to remove atmospheric gases which contain modern CO_2 , then sealed,

Table 1 Radiocarbon measurements of various fractions Kauri wood from New South Wales, Australia, assumed to be of infinite age. Adapted from Taylor and Bar-Yosef (2014: Table 3.1).

Sample nr	Component/ pretreatment	Fraction (°C)	¹⁴ C age (BP)
A. Components			
ANU-918[A]	Resin	—	11,100 ± 880 ^a
ANU-918[B]	Humics and Fulvics	—	15,900 ± 180 ^a
ANU-918[D]	Holocellulose	—	35,200 ^{+2000/-1500} ^a
B. Pretreatments			
ANU-918[C]	None	—	22,290 ± 560 ^a
ANUA-14118	ABA-SC ^c	910°	41,580 ^{+620/-580} ^b
ANUA-14114	ABOX-SC ^d	910°	48,000 ^{+1830/-1490} ^b
ANUA-15513	CE-SC ^e	910°	52,290 ^{+1560/-1310} ^b

^aDecay counting (Chappell et al. 1996).

^bAMS counting (Santos et al. 2001).

^cABA-SC = acid/base/acid + stepped combustion.

^dABOX-SC = acid/base/oxidant (dichromate) + stepped combustion.

^eCE-SC = cellulose-extraction (Loader et al 1997) + stepped combustion.

and the contents heated to 900°C. For acidification, the chemically leached carbonate sample is placed in a reaction tube, the tube is evacuated to remove atmospheric gases including CO₂, and an acid is introduced. In both cases, the desired reaction product of either combustion or acidification is the same, carbon dioxide (CO₂). Even though there is much focus on obtaining and processing materials such as copper oxide and silver used in the conversion of a sample into CO₂ to be carbon free, minute traces of exogenous carbon inevitably remain in these reactants.

While a few AMS instruments can employ CO₂ directly in their ion sources, in the majority of systems currently routinely operating, the CO₂ is subjected to an additional set of chemical processes whose final end product is a form of *filamentous graphite*. This term is used to distinguish this type of *synthesized* graphite from naturally occurring *geological graphite*. Today, in most operational AMS laboratories, this graphitic form is produced by reducing the CO₂ obtained from sample combustions/acidifications on iron acting as a catalyst in the presence of hydrogen or zinc at a temperature of about 500°C (Santos et al. 2007). The amounts of this synthetic graphite typically employed in AMS systems range from a few *milligrams* (mg) down into the 10–20 *microgram* (µg) range where 1000 µg = 1 mg. The effects on ¹⁴C measurements as a function of using microgram amounts of this synthesized graphite below about 300 µg to obtain a AMS-based ¹⁴C measurement is illustrated in Figure 6.

AMS Instrument Characteristics: We now turn to a brief description and operational purposes of the major components of a typical AMS instrument designed to measure as accurately and precisely as possible natural levels of ¹⁴C contained in a sample. Figure 1 is a simplified schematic representation of the major components of the AMS instrument currently operating at the Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) Laboratory located in the Department of Earth System Science, University of California, Irvine (Southon et al. 2004). The major components it incorporates are generally representative of those which are included in what is typically referred to as a “compact” AMS system. These AMS systems have been specifically designed to undertake natural level ¹⁴C/¹²C ratio measurements.

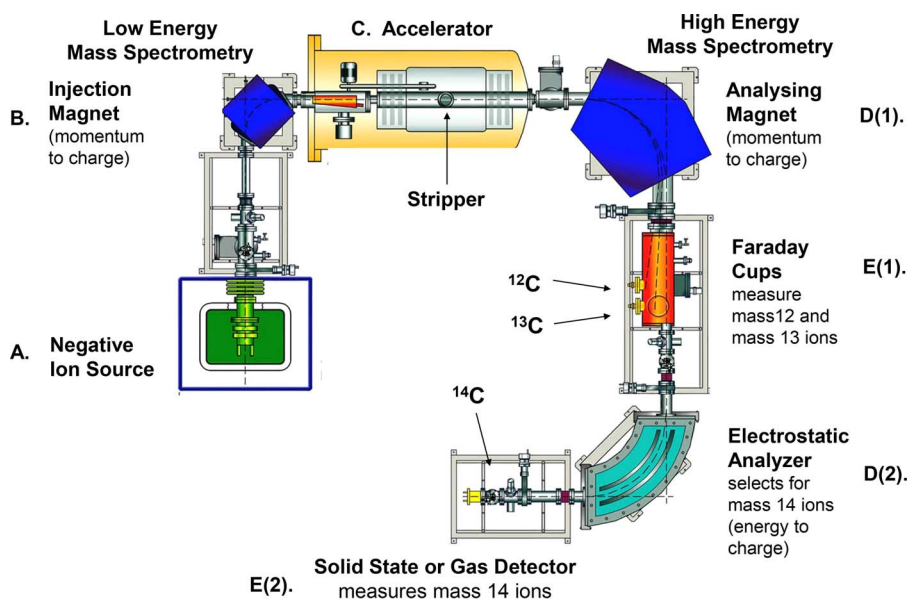


Figure 1 Simplified representation of major components of an Accelerator Mass Spectrometer (AMS) instrument measuring natural level ^{14}C at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) Laboratory, Department of Earth System Science, University of California, Irvine. The letters (A to E) refer to the components listed in Table 1. *Source:* This figure is adapted from Figure 4.6 in Taylor and Bar-Yosef (2014).

In this type of AMS instrument, there are five major components (Figure 1, Components A through E) in addition to a control and data analysis system. These components include a (A) negative ion source, (B) injection magnet, (C) accelerator, (D) analyzing magnet, and (E) ^{12}C , ^{13}C , and ^{14}C ion detectors. (The paragraph following the next one defines *ions*.)

The essential functions of and physical processes involved in each of the major components of an AMS system are briefly summarized in Table 2. We have already noted the preparation of a form of graphitic carbon synthesized from CO_2 produced from either the combustion or acidification of a sample. Up to about 1 mg of this synthesized graphitic carbon from each sample is pressed into a small sample holder which, in the UCI AMS instrument, is then inserted into a wheel assembly holding 60 samples (Figure 2). This sample wheel is then mounted on a component (Figure 1, Component A) of the AMS system *ion source* (Figure 3). This component with the sample wheel attached can then be mated to the main body of the ion source and a high vacuum obtained. Once an appropriate vacuum is achieved, the ion source is opened to the beam line of the AMS system leading to the Injection Magnet (Figure 1, Component B).

The function of the ion source is exactly what its name implies, the production of ions. *An ion is an atom or molecule to which electrons have been added to or removed causing it to become a charged (either negative or positive) particle and thus rendered susceptible to the effects of electromagnet fields.* Currently, for most AMS instruments designed to measure natural level $^{14}\text{C}/^{12}\text{C}$ ratios, the ion source is designed to produce *negative ions*. The reason for this is stated below. Some investigators have recently suggested that there would be certain advantages if initially, positive ions are produced from samples. These positive ions then would be immediately converted to, and accelerated as, negative ions (Freeman 2017; Paul 2017).

Table 2 Accelerator mass spectrometer: major components, functions and processes for measurement of ^{14}C (Tuniz et al. 1998; Southon et al. 2004; Taylor and Bar-Yosef 2014).

Component	Principal function	Physical processes
A. Ion source	Produce and accelerate ions from sample	Cesium ionized and focused on sample surface, resulting interaction causes ions to be produced permitting these particles to be influenced by electromagnetic fields and thus being capable of being accelerated in vacuum
B. Injection magnet	Low energy mass spectrometry	Mass selection utilizing differences in bending radii of particles with different momentum to charge ratios in a magnetic field
C. Accelerator	Disassociate molecules	Particles in beam pass through solid or gas stripper changing negative ions to positive ions and dissociating molecules
D. Analyzing system	(1) High energy mass spectrometry (2) Electrostatic analyzer	Mass selection separating ^{12}C , ^{13}C , ^{14}C ions momentum to charge ratios (same as mass selection in low energy mass spectrometry) Mass selection selects for mass 14 ions using energy to charge ratio
E. Ion detection sensors	(1) Measures ^{12}C and ^{13}C ions (2) Measures ^{14}C ions	Currents of ^{12}C and ^{13}C ions measured in Faraday Cups Silicon diode or gas counter detects individual mass 14 particles and measures energy
F. Control and data analysis system	Monitors and controls AMS system hardware	Based on data input, calculates $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios

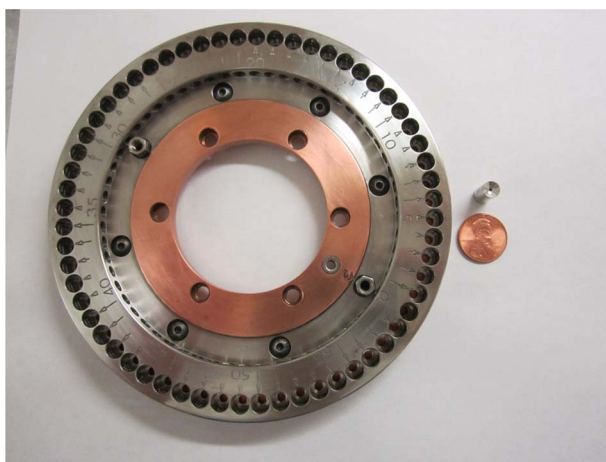


Figure 2 Photograph of KCCAMS MC-SNICS ion source sample wheel which can accommodate 60 sample holders (cathodes). To the right of the sample wheel is a sample holder with its size indicated by reference to a United States one-cent piece. The hole into which the sample synthesized graphite (see text) is packed is 1 mm in diameter and has a depth of 4 mm.

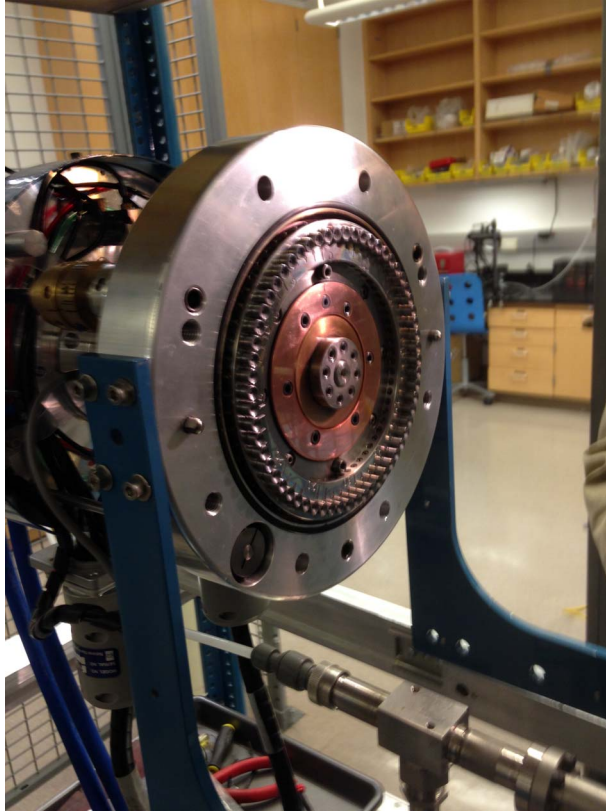


Figure 3 Photograph of the KCCAMS MC-SNICS ion source sample wheel (Figure 2) with 60 samples mounted on a movable assembly which will be mated to the body of the ion source (on the right out of the photograph), a vacuum established, and a valve opened into the beam line. See text for details.

Over the more than four-decade development of AMS technology, the ion source components of a typical AMS system have been the focus of almost constant technical evolution. The most important aim of modifications have been design changes which can enhance the efficiency by which ions are produced from graphitized samples. The principal purpose of these design changes is to increase the intensity of the beam current. One consequence of improvements made in the strength of the beam current is to allow more samples to be measured during a single measurement run of the same duration without compromising the precision of individual sample measurements.

A design feature of most ion sources contributes to the possibility of what is informally termed “cross talk” between samples can occur. Cross talk refers to trace amounts carbon from one sample being deposited on another sample during measurement or on the surface of components of the ion source itself. Figures 2 and 3 illustrate the close physical proximity of different samples in the wheel assembly. For the vast majority of finite age samples exhibiting ages less than about 40,000 years, such trace contamination can introduce very slight changes in $^{14}\text{C}/^{12}\text{C}$ ratios which is almost always assumed to be subsumed within the measurement precision. However, for samples of infinite or near infinite ^{14}C age, the effects are measurable and contribute to the level of the backgrounds exhibited in such samples.

The ionization process causes particles to exhibit either a negative (electrons added) or positive (electrons removed) charge. In most AMS systems currently measuring ^{14}C on a routine basis, the ion source is designed to add electrons which yields *negatively charged ions*. Since the movements of these negatively charged ions can now be influenced by electromagnetic fields, these particles can be accelerated and focused as a beam within a tube maintained at a high vacuum to greatly reduce (but not totally eliminate) the chances of collisions with other particles.

In a typical, currently routinely operating, compact AMS system, an injection magnet (Figure 1, Component B) directs the negatively charged ions exiting the ion source into a particle accelerator (Figure 1, Component C). In an AMS system measuring ^{14}C , one of the major problems of identifying and measuring ^{14}C ions is that, in addition to these ions, there are other mass 14 particles produced in the ion source. Normally, most of these mass 14 particles would be ions of ordinary nitrogen (^{14}N) which are multiple orders of magnitude more prevalent than ^{14}C ions. However, employing *negative* nitrogen ions, the major problem that would have been caused by the presence of nitrogen ions of mass 14 can be avoided because of a very fortunate circumstance.

That circumstance is that nitrogen either does not form a negative ion or, if a negative ^{14}N ion is actually formed, it has a lifetime much shorter than the few microseconds (where 1 microsecond = 1/10,000 of a second) transit time of particles traveling from the exit point of an ion source to a detector at the opposite end of the beam line of the spectrometer [Figure 1, Component E(2)]. *Thus when a negative ion source is employed in an AMS system, the result is that ^{14}N is almost completely (but not entirely) eliminated from the beam of particles exiting the ion source.*

However, even with the elimination of almost all ^{14}N ions, several other types of mass 14 ions will remain. There will be mass 14 *molecules* which include carbon atoms, such as $^{13}\text{CH}^-$ and $^{12}\text{CH}_2^-$, as well as molecules of other elements, such as lithium, exhibiting mass 14 signatures. These mass 14 *molecular* species are almost entirely eliminated because of a major design feature in most AMS systems. This is a component of many accelerators typically referred to as a “stripper” (Figure 1, Component C). This is a gas-filled tube (in some AMS systems it is a very thin foil) which functions to remove electrons (or “strip” electrons) from the negatively charged ions as they pass through the gas (or a foil) with the result that the negative ions entering the accelerator are changed to positively charged ions. *The important effect of this “stripping” process for ^{14}C AMS technology is that molecules are split apart into their constituent isotopic species.*

In the majority of AMS instruments, the acceleration of particles is accomplished in a two-step or tandem mode in which the negative ions exiting the ion source are first directed into the accelerator by the injector magnet (Figure 1, Component B), and then “pulled toward” a positively charged high voltage terminal near the stripper. After passing through the stripper, because these ions are now positively charged, they are “pushed away” from the positively charged terminal. In a few AMS instruments, only single stage acceleration is employed.

These now positively charged particles then enter an analyzing magnet [Figure 1, Component D(1)] which separates them into mass 12, mass 13, and mass 14 ions. Mass 12 and mass 13 ions are directed to separate ion collection devices known as “Faraday cups” [Figure 1, Component E(1)]. These devices convert the impinging mass 12 and 13 ions into a current which can be calibrated so that the output from each cup accurately represents the number of ions impinging on it.

The final step of the measurement process involves passing the particle beam through an electrostatic analyzer [Figure 1, Component D(2)] which will only pass mass 14 ions and then direct these ions into a gas counter (some AMS systems employ a solid state device) where the number of

individual mass 14 ions and their energies can be measured [Figure 1, Component E(2)]. The computerized instrument component controls and data analysis systems (Table 1, Component F) integrates the signals coming from the ^{12}C , ^{13}C , and ^{14}C ion collection devices and, using appropriate algorithms, computes $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios of the sample being measured.

Background Measurement Characteristics: It might be helpful to gain an appreciation of the nature of ^{14}C background measurements in a typical AMS system in relationship to measurements obtained on other samples. Figures 4A and 4B provide examples of a portion of the set of data needed to calculate an AMS-based ^{14}C age for two samples. The data illustrated in these plots are typical of that currently being obtained on the AMS system described in Figure 1 and Table 1 operating at the KCCAMS laboratory at the University of California, Irvine (Southon et al. 2004; Santos et al. 2007).

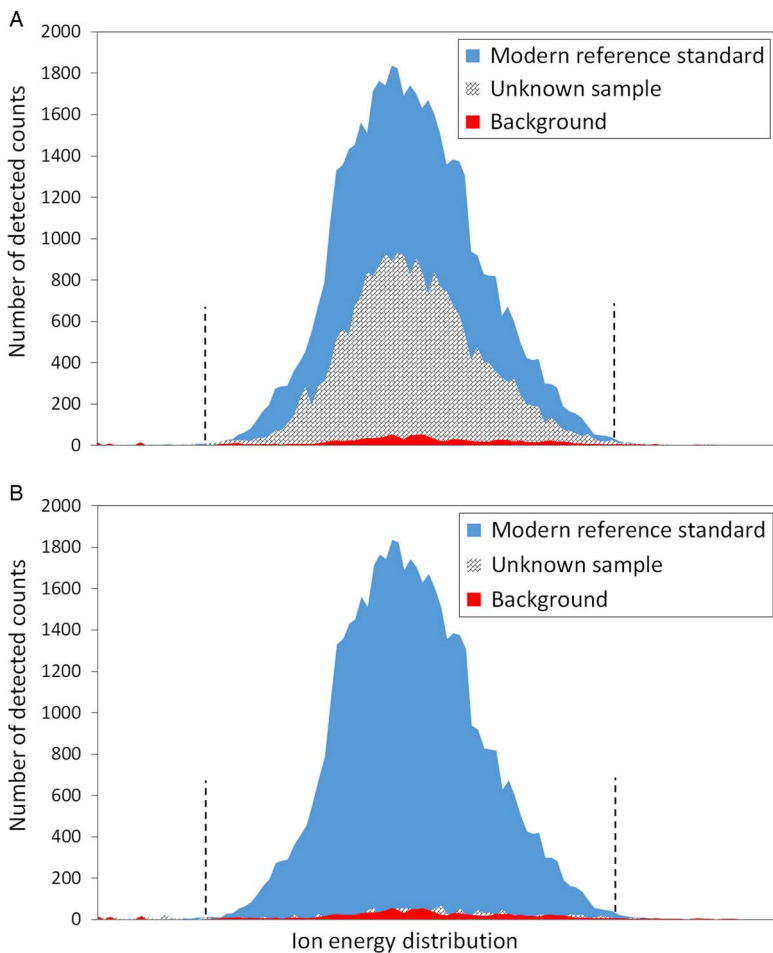


Figure 4 Plots of the relationship between number of detected counts and increasing mass 14 energy channels within an energy window delimited by left and right vertical dotted lines for three types of samples: (1) a modern reference standard, (2) an unknown age, and (3) infinite ^{14}C age background. Figure 4A represents unknown age sample exhibiting a mass 14 ion energy profile approximately half of that of the modern reference standard. Figure 4B represents an unknown age sample exhibiting a mass 14 ion energy profile which appears to be undistinguishable from the background energy profile.

Each plot represents the relationship between the number of detected ions on the y -axis and the energy of these ions falling into a series of energy channels that record each ion's relative energy on the x -axis (with the energy of the ions increasing from left to right) for three types of samples. More than 99% of the ions detected in the energy window defined by the two vertical dotted lines are mass 14 ions and, of these mass 14 ions, more than 99% are ^{14}C ions. In both figures, the data of three types of samples plotted are (1) a modern reference standard, (2) an unknown age sample and, (3) an infinite ^{14}C age background sample.

The data represented in each plot has been collected over a period of 2.5 minutes. Data obtained during at least 8, 2.5-minute counting cycles, will typically be employed in the measurement of a $^{14}\text{C}/^{12}\text{C}$ ratio for each sample which is the principal basis of a calculation of a ^{14}C age. The additional data required for each ^{14}C age calculation is that obtained from two Faraday cup detectors (Component E(1) in Figure 1 and Table 1). They provide data that allows the number of ^{12}C and ^{13}C ions to be measured for each counting interval for each sample. Using the data received from the ^{12}C , ^{13}C , and ^{14}C detectors and by employing appropriate algorithms, $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios can be calculated for each sample and conventional ^{14}C ages computed.

By simple visual inspection of the data plotted in Figure 4A, we note that the number of ions which are primarily ^{14}C ions detected for the unknown age sample is approximately half of that recorded for the modern reference standard. We would then provisionally conclude that the age of this sample is about one ^{14}C half-life old. Because of a convention adopted by members of the ^{14}C research community that stipulates which ^{14}C half-life should be used in computing a *conventional* ^{14}C age, the ^{14}C age cited for this sample would be ~ 5570 years, even though the most likely ^{14}C half-life value is nearer to ~ 5700 years. The discussion in Stuiver and Polach (1977) provides an explanation of why the most likely ^{14}C half-life is *not* used in the calculation of *conventional* ^{14}C dates.

The plot in Figure 4B reveals that the number of mass 14 counts of the second unknown age sample appear, on the basis of visual inspection, to be indistinguishable from those attributable to the infinite ^{14}C age background sample. When all of the measurement data for this sample is recorded, a standard statistical analysis of that data is undertaken. If it is determined that it is not possible to distinguish, at some defined measure of statistical confidence, the mean $^{14}\text{C}/^{12}\text{C}$ ratio exhibited by the unknown age sample and the mean $^{14}\text{C}/^{12}\text{C}$ ratio of the infinite ^{14}C age background sample, an infinite ^{14}C age would be calculated for this unknown age sample. The definition of and stipulations used in the calculation of infinite ^{14}C ages are enumerated and discussed in Taylor and Bar-Yosef (2014:127–129), based on information in Stuiver and Polach (1977).

AMS ^{14}C TECHNOLOGY: SOURCES OF BACKGROUND ACTIVITY

The summary contained in the two previous sections briefly reviewed sample pretreatment and preparation steps together with basic features and operational characteristics of AMS instruments undertaking measurements of natural level $^{14}\text{C}/^{12}\text{C}$ ratios. That discussion provides a context where we are able now to consider the most likely causes of the backgrounds reported by AMS laboratories.

In Table 3, we list 16 potential sources of ^{14}C signals from carbon samples of assumed infinite ^{14}C age in AMS instruments. Reflecting the two categories already identified in a previous section, the potential sources of AMS system backgrounds have been divided into two types: *sample based and instrument based*. Obviously, we do not include backgrounds that can be traced to equipment malfunction or non-standard operating conditions. Also, we

should emphasize that we do not suggest that each potential source of contamination listed in Table 3 contributes *equally* to the magnitude of the measured ^{14}C backgrounds in different AMS systems. That certainly would not be correct. The factors that separately and in

Table 3 Potential sources of ^{14}C signal in AMS-based ^{14}C measurements from samples of infinite ^{14}C age (Adapted from Taylor and Southon 2007).

I. Sample Based

A. Pseudo ^{14}C -free sample background: ^{14}C is present in carboniferous material used as background or sample blank that should not contain ^{14}C because of its geologic age.

- (1) *Non- ^{14}C -free sample:* Sample material erroneously assumed to contain no detectable *in situ* ^{14}C .
- (2) *Contaminated sample:* ^{14}C introduced into the ^{14}C -free sample material during chemical or physical pretreatment.

B. Combustion/acidification background: ^{14}C introduced during production of CO_2 from sample.

- (3) *Materials contamination:* ^{14}C introduced from materials in combustion/acidification tube other than sample (e.g., adsorbed CO_2 on oxidizer).
- (4) *Tube contamination:* ^{14}C introduced from walls of combustion/acidification tube (e.g., adsorbed CO_2).
- (5) *Tube leakage:* ^{14}C introduced from leakage of atmospheric CO_2 into combustion/acidification tube.

C. Graphitization background: ^{14}C introduced during graphitization process.

- (6) *Materials contamination:* ^{14}C introduced from materials in reaction tube (e.g., from Fe or Co powder as graphitization catalyst).
- (7) *Tube contamination:* ^{14}C introduced from walls of reaction tube.
- (8) *Vacuum line contamination:* ^{14}C introduced during CO_2 transfer in vacuum line.

D. Transfer background: ^{14}C introduced during graphite transfer to sample holder.

- (9) *Target / cathode contamination:* ^{14}C introduced from sample holder.
- (10) *Manipulation contamination:* ^{14}C introduced during physical transfer/packing of synthesized graphite into sample holder.

E. Storage background: ^{14}C introduced at any point in the sample processing sequence from any containment vessel.

- (11) *Particulate contamination:* ^{14}C physically introduced from carbon-containing particulates derived from storage containers.
- (12) *Atmospheric contamination:* ^{14}C introduced from CO_2 in air or from outgasing from storage container.

II. Instrument Based

A. Beam line anomaly: ^{14}C derived from some internal component of beam line reaches detector.

- (13) *Ion Source:* ^{14}C ions or other mass 14 particles ions introduced from memory effects from previous samples in ion source.
- (14) *Other beam line component:* ^{14}C ions or other mass 14 particles contributed from some other component of beam line.

B. (15) Ion identification anomaly: Mass 14 particle which is not ^{14}C reaches detector and is misidentified as ^{14}C .

C. (16) Detector anomaly: Pseudo- ^{14}C pulse registered when no ion of mass 14 is present at the detector (e.g., electronic noise).

combination contribute their background signals in AMS systems will be expressed in different levels in different instruments, although it would appear that the causes of the largest percentage of backgrounds which are reported may be very similar.

Sample-Based Sources: Twelve of the 16 possible sources of contamination listed in Table 3 would add carbon containing ^{14}C of varying age in different concentrations to the infinite ^{14}C age samples used for monitoring background levels in AMS ion sources. To provide a context that will give us some quantitative scale of what effects might be expected from various sources and amounts of contamination, Table 4 lists apparent ages in the range of 80,000 to 50,000 years in 10,000-year increments that would result from the addition of the indicated amounts of 2 types of environmental exogenous ^{14}C contamination.

The first column lists the apparent age effects of the addition of various amounts of “modern” carbon measured in units of parts per million (Table 4, Column [A]). “Modern” carbon is a carbon sample whose ^{14}C concentration would cause it to be assigned a “0” BP ^{14}C age. Ordinarily, we might consider “contemporary” and “modern” carbon to be synonymous in terms of exhibiting the same ^{14}C activity. However, in the measurement of ^{14}C concentrations for dating purposes, “modern” is used in a special sense.

It turns out that the ^{14}C activity of contemporary living organics obtaining their carbon directly or indirectly from *current* atmospheric or biospheric levels of ^{14}C *cannot* be used to define “0” BP on the ^{14}C time scale. This is due to the impact of the combustion of massive amounts of fossil carbon (e.g., first coal and later petroleum products) and more recently, the production of artificial or “bomb ^{14}C ” (see next paragraph). Primarily because of these two human-caused effects on contemporary ^{14}C levels, “modern” or “0” age ^{14}C content has had to be redefined as a percentage of $^{14}\text{C}/^{12}\text{C}$ ratios exhibited by specially prepared standard samples which are used by ^{14}C laboratories to define “modern,” i.e., 0 BP ^{14}C age. For additional information on the nature of “modern” standards used in ^{14}C studies, please refer to Stuiver and Polach (1977).

The second type of modern environmental ^{14}C contamination of background samples is that of “bomb ^{14}C .” The term “bomb” here refers primarily to the effects of thermonuclear weapons detonated in the atmosphere by the United States and the Soviet Union until the 1963 Partial Test Ban Treaty went into effect. One result of the detonation of these devices in the atmosphere was the production of large fluxes of neutrons which, in turn, caused the production of

Table 4 Background contamination: Effects of addition of modern and 1963 bomb ^{14}C in parts per million (ppm) amounts on apparent ages exhibited by infinite ^{14}C age carbon.

Apparent age of infinite age carbon (yr BP)	With addition of	
	[A]	[B]
	“Modern” $^{14}\text{C}^{\text{a}}$ (ppm)	1963 Bomb $^{14}\text{C}^{\text{b}}$ (ppm)
80,000	47	24
70,000	163	82
60,000	568	284
50,000	1975	988

^a“Modern” ^{14}C is defined as the $^{14}\text{C}/^{12}\text{C}$ ratio of 0.95% NBS OXI standard normalized to a $\delta^{13}\text{C}$ value of -19‰ .

^b1963 Bomb ^{14}C is defined as 200% of the $^{14}\text{C}/^{12}\text{C}$ of 0.95% NBS OXI standard normalized to a $\delta^{13}\text{C}$ value of -19‰ .

significant amounts of artificial (non-cosmogenic) “bomb” ^{14}C . The maximum amount of this artificial ^{14}C was present in the atmosphere and thus was also contained in living terrestrial organics in 1963 in amounts that resulted in almost doubling the amount of atmospheric and biospheric ^{14}C (Fairhall and Young 1970; Stuiver and Braziunas 1998). After 1963, due to the effects of the test ban treaty which prohibited continued atmospheric testing, the amounts of bomb ^{14}C in the atmosphere and biosphere have continuously declined.

By referring to Table 4, we see that the addition of about 50 parts per million (ppm) of “modern” carbon or about 25 ppm of 1963 “bomb” ^{14}C would result in having an organic sample which originally contained absolutely no ^{14}C to exhibit a measured ^{14}C age of $\sim 80,000$ BP. An age of $\sim 70,000$ BP would be measured in a background carbon sample of infinite ^{14}C age if contaminated with about 160 ppm of modern carbon or about 80 ppm of 1963 “bomb” ^{14}C . Figure 5 graphically illustrates why the addition of these trace amounts of modern or 1963 bomb ^{14}C contamination in parts per million amounts can result in major increases in measured ^{14}C concentrations in infinite age samples. Given the approximately 5700 year half-life of ^{14}C , a plot of the ^{14}C decay curve reveals that when natural ^{14}C levels are at or below that which would indicate an age 50,000 years or older only a few tenths of a percent addition of exogenous “modern” carbon will have the effect of adding from multiple thousands of years to literally several tens of thousands of years to produce pseudo-finite ^{14}C ages.

Figure 5 provides a helpful visual representation of that reality by plotting the relationship between ^{14}C concentrations in samples and their approximate inferred ^{14}C ages. We can thus easily see that when residual ^{14}C levels in samples drop below about 0.1% of modern, relatively small changes in ^{14}C concentrations in samples translate into large offsets in inferred ^{14}C ages which would be assigned to those samples. This is one of the reasons that the routine maximum finite ^{14}C ages that are cited by laboratories typically range between 50,000 and 60,000 ^{14}C years.

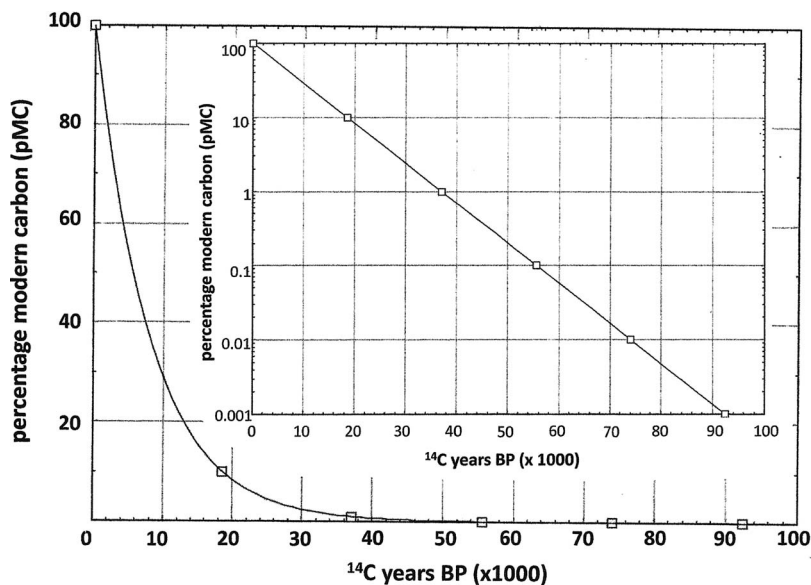


Figure 5 Relationship between ^{14}C concentrations expressed as percentage of modern carbon (pMC) measured in a sample and the conventional inferred ^{14}C age (^{14}C years BP $\times 10^3$). Inset figure plots the pMC relationship on a logarithmic scale.

Such an effect can be illustrated as the result of a phenomenon noted in routine operations of AMS-based ^{14}C measurements. We have previously noted that the majority of AMS systems convert CO_2 produced from sample combustions or acidifications into a form of synthesized graphitic carbon. Figure 6 presents the results of a series of measurements that provides direct information about the effects of a change in measured ^{14}C ages exhibited in 1140 samples of 3 types of assumed infinite ^{14}C age materials (calcite, wood, and coal) as a function of the amount of synthetic graphitic carbon produced in the graphitization process used at the UCI AMS (KCCAMS) laboratory (Santos et al. 2007, 2010). It is assumed that the calcite and coal samples derive from Mesozoic age deposits making these samples at least 60 million years old while the wood was collected from a stratigraphic context associated with oxygen isotope stage 5a or 5c indicating an age of at least 80,000 years.

We observe in Figure 6 that down to ~ 0.3 milligrams (mg) [~ 300 micrograms (μm)] of synthesized graphitic carbon from an infinite ^{14}C age sample, the measured ^{14}C concentrations held approximately constant at ~ 0.2 percent of modern carbon (pMC) which is the equivalent to an apparent “age” of $\sim 50,000$ years. However, we note that as the amount of the synthesized graphite declines below ~ 0.3 mg, there are progressive increases in the measured background levels. We see, for example, that infinite age graphite samples of ~ 0.05 mg ($= 50 \mu\text{g}$) exhibits an apparent age of $\sim 30,000$ years and at ~ 0.01 mg ($= 10 \mu\text{g}$) the apparent ages of these ^{14}C infinite age samples is $\sim 20,000$ years. What might the reason be for the consistent increasing ^{14}C background values as a function of the declining amounts of infinite age material as part of the synthesized graphite contained in sample holders?

The cause of these effects has been demonstrated to be due to the very similar amounts of micro-contamination being added to all synthesized graphite samples during the combustion/acidification and/or graphitization process that we have previously described (Vogel et al. 1987; Kirner et al. 1995; Brown and Southon 1997). The effects on the

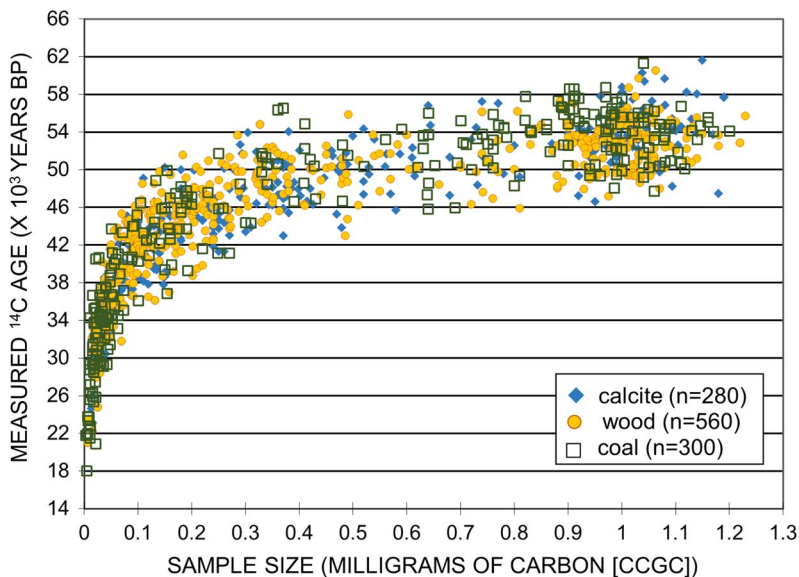


Figure 6 Relationship between sample size (in milligrams of synthesized graphite and measured ^{14}C age (in 10^3 years) of 1140 background (infinite age) samples ($>10^5$ years calcite, wood, and coal) measured on the KCCAMS instrument. *Source:* Figure 4.7 in Taylor and Bar-Yosef (2014).

net measured ^{14}C concentration in infinite age samples that contain 300 micrograms and above are not discernible at the level of precision exhibited in infinite age background measurements. However when the synthesized graphite sample weight drops below about 300 micrograms, roughly constant amounts of micro-contamination begin to be measurable as the percentage of exogenous contaminating carbon added to the graphite sample progressively increases.

One factor has been recently documented by a careful study of the effects of current levels of ^{14}C contained in atmospheric gases such as CO_2 and CH_4 (methane) on ^{14}C levels on the synthesized sample graphitic carbon. This study determined that for samples close to background levels, it was not possible to protect these samples from traces of atmospheric contamination during the periods when they are exposed to ambient conditions, even for relatively short time intervals. This contamination follows from the contrast between contemporary atmospheric ^{14}C conditions being two to three orders of magnitude higher than the ^{14}C contained in samples. Those who undertook this research concluded that “contamination on AMS sample targets by modern carbon is inevitable” (Paul et al. 2016:407).

Someone might object that even if most infinite ^{14}C age samples used for backgrounds have been graphitized, there are some infinite age samples which have not undergone a combustion/acidification and/or graphitization process and yet they exhibit finite ^{14}C ages. One example of this would be ^{14}C measurements on natural diamonds. Another would be the use of naturally formed *geological* graphite. What would reasonably explain the backgrounds measured in these samples? We now turn to instrument-based sources that are responsible for signals indicating the presence of ^{14}C ions in the detector circuitry of an AMS system when various types of samples of assumed infinite ^{14}C age which have not been subject to combustion/acidification and graphitization are being measured.

Instrument-Based Sources: The remaining four potential causes of pseudo-cosmogenic ^{14}C signals in AMS systems listed in Table 2 when measuring infinite age samples are instrument-based. The resultant backgrounds are typically collectively referred to as “machine backgrounds.” These types of backgrounds are the result of pulses recorded in the AMS system detector electronic circuitry which ordinarily indicates the presence of a ^{14}C ion which has *not* been derived from the presence of ^{14}C derived from an infinite age carbon sample converted to CO_2 , synthesized to graphitic carbon, pressed into a sample holder which is then placed the ion source of an AMS instrument. The use of natural diamonds which have been placed into a sample holder with no pretreatment applied would be an example of such a sample.

The first potential source of machine background listed in Table 2 results from an instrument anomaly in which mass 14 ions are produced at some point within the beam line itself. In our view, the manner in which ion sources operate is the most likely component that would contribute the largest percentage of machine background. We have already noted that Figures 2 and 3 illustrate the close physical proximity of different samples in the component containing the samples in one ion source. The method widely used to ionize samples involves focusing cesium atoms onto the surface of the synthesized graphitic material. The resultant production of ions from a sample is widely scattered within all parts of the small cavity where the sample ions are extracted into a focused beam that exits the ion source. Design changes and the high vacuums maintained in the ion source significantly reduces the probability that ^{14}C ions from a sample undergoing measurement will be contaminated by ^{14}C ions which had been produced by a previously ionized sample. However, *it will not totally eliminate them.*

Modifications in the design of ion sources currently used in most AMS have responded to the need to minimize these “memory effects” or “sample crosstalk.” While ^{14}C memory effects have been reduced to extremely low levels in the majority of ion sources, such sample crosstalk effects cannot be totally eliminated and a small numbers of ^{14}C ions from previous samples can contribute to the ^{14}C signal detected when subsequent samples are measured.

In the majority of finite age samples, that very low level of machine-produced contamination from memory effects is generally significantly below a level reflected in the variability introduced due to counting statistics. In any event, measured backgrounds are routinely employed to calculate net sample values. However, in a sample of infinite age which is assumed to contain no ^{14}C , ion source memory effects can be responsible for producing sufficient amounts of ^{14}C signal in the detector circuitry so that effects which cannot be distinguished from expected variations due to counting statistics for most samples become distinguishable when these background samples are measured.

EXAMPLES OF ^{14}C BACKGROUNDS IN TWO AMS SYSTEMS MEASURING ^{14}C

We have already noted that not all the potential sources of background levels of ^{14}C listed in Table 2 would necessarily contribute to the backgrounds measured in every AMS system measuring ^{14}C . The specific sources and magnitudes of ^{14}C backgrounds are unique to each AMS system and may change over time in the same instrument. To illustrate the differences and similarities in these values in different laboratories, in Table 5 we summarize the results of mostly previously published experiments undertaken to define and quantify ^{14}C background levels due to both sample-based and instrument-based sources in two laboratories. The first set of data comes from an AMS instrument was that operating in the Department of Physics at the University of Washington, Seattle, Washington, relatively early in the development of AMS-based ^{14}C studies (Schmidt et al. 1987). The second AMS system is that described in Figure 1 and Table 2, that of the instrument at the University of California, Irvine. A portion of this data has already been reported (Taylor and Southon 2007) while four measurements were obtained in conjunction with the preparation of this paper and have not been previously reported.

Data such as this particularly illustrate that, in most cases, “unprocessed” infinite age samples, where the organic itself is measured without any conversion to synthesized graphitic carbon, generally exhibit “older” ages. In the case of the University of Washington instrument, we note that a measurement undertaken using only an aluminum target sample holder defines the unique “machine” background value for this instrument at the time the experiment was undertaken. The measurement of ^{14}C signals obtained from silver packed into an aluminum target indicates for the UCI instrument a significantly different machine value obtained at the time this measurement was obtained. However, we note that diamonds used as the target material on this same instrument yielded much “older” results.

The significant variability in the inferred ^{14}C “ages” assigned to infinite age materials on the basis of their measured ^{14}C concentrations when those levels drop below about 0.1 pMC (percent modern carbon) is most reasonably interpreted as the result of the complex interactions of the many sample and instrument based contamination factors listed in Table 3. Obviously, an interpretation that these measurements indicate the presence of actual residual cosmogenic ^{14}C cannot be totally excluded. However, given the many other much more likely factors that could be responsible for the ^{14}C signals obtained on these infinite age samples, this interpretation would be, in our view, the *least likely* scientific explanation.

Table 5 AMS-based instrument and sample background measurements at two AMS laboratories measuring ^{14}C .

A. Nuclear Physics Laboratory, University of Washington, Seattle^a			
Material	Condition ^b	Inferred ^{14}C age (ka yr BP)	
None	Aluminum target	≥ 90.0	
Geologic graphite	Unprocessed (under argon)	69.03 ± 1.7	
Geologic graphite	Unprocessed (in air)	63.80 ± 1.1	
Marble	Processed	49.69 ± 0.51	
B. Keck Carbon Cycle AMS Laboratory, University of California, Irvine			
Material	Condition ^b	pMC	Inferred ^{14}C age (ka yr BP)
None	Ag in aluminum target	—	$60.9 (43)^c$
None	Ag in aluminum target	—	$59.7 (50)^c$
Geologic graphite	Unprocessed	0.032 ± 0.003	$64.6 \pm 0.07 (26)^c$
Geologic graphite	Unprocessed	0.035 ± 0.003	$64.0 \pm 0.07 (26)^c$
Diamond	Unprocessed	0.005 ± 0.01	80.0 ± 1.1^d
Diamond ^e	Unprocessed	$0.018\text{--}0.015^{d,f}$	$70.6\text{--}69.4^{d,g}$
Diamond	Unprocessed	0.02 ± 0.01	67.74 ± 0.66^d
Diamond	Unprocessed	0.03 ± 0.01	64.64 ± 0.59^d
Diamond	Unprocessed	0.05 ± 0.01	60.59 ± 0.98^d
Geologic graphite	Unprocessed	0.09 ± 0.01	56.35 ± 0.48^d
Geologic graphite	Processed	0.10 ± 0.01	55.67 ± 0.33^d
Geologic graphite	Processed	0.12 ± 0.01	54.32 ± 0.26^d
Coal	Processed	0.12 ± 0.01	54.01 ± 0.32^d
Geologic graphite	Unprocessed	0.12 ± 0.01	54.05 ± 0.90^d
Diamond	Processed	0.15 ± 0.01	52.39 ± 0.34^d
Coal	Processed	0.14 ± 0.01	52.94 ± 0.26^d

^aSchmidt et al. (1987: Table 1).

^bProcessed = sample converted to CO_2 and graphitic carbon and placed in target holder. Unprocessed = sample itself placed in target holder.

^cThis report.

^dTaylor and Southon 2007: Table 2.

^e ^{14}C measurements on six splits of the same diamond. Range in measured values reported.

^fRange in measurement precision = ± 0.01 to ± 0.02 pMC.

^gRange in measurement precision = ± 0.5 to ± 0.8 ka yr BP.

CONCLUSION

Those who dispute the validity of pre-Holocene ^{14}C age determinations have offered their opinions concerning what they view as the implications of reports of various background levels observed by AMS laboratories undertaking ^{14}C measurements. The typical ages of the organic samples used for these measurements are assumed, based on well-documented paleontological and/or geological criteria, to be greatly in excess of 100,000 years and most of these samples, such as natural diamonds, are much older than several hundred million years.

We have suggested that the cause of the confusion of these individuals is their lack of knowledge of the operating characteristics of the technology used in AMS systems as applied to the measurement of natural ^{14}C concentrations. Specifically, these individuals misunderstand the

experimental conditions and constraints that are present when AMS-based ^{14}C measurements are obtained. Because of this, in our view, there is a misapprehension and thus misrepresentation on their part of the significance of the reported “ages” of ^{14}C backgrounds reported by various AMS groups.

We have presented a list of 16 potential sources that could contribute to producing a background signal that would indicate or mimic the presence of a ^{14}C ion in the detector circuitry of an AMS system. These 16 sources have been divided into two categories: sample-based and instrument-based. We have offered evidence regarding which of these categories are most likely to produce the majority of background values observed in an AMS instrument undertaking ^{14}C measurements. Since different AMS systems make ^{14}C measurements using somewhat different sample preparation protocols and instrumental configurations, we submit that it would not be appropriate to generalize for all currently routinely operating AMS instruments. We posit that various combinations of the sources of ^{14}C detector signals indicating the presence of ^{14}C ions in infinite age organics, as listed in Table 2, are responsible for the reported background values.

We conclude that the view advanced by those who insist that these backgrounds are the result of the presence of *residual cosmogenic* ^{14}C contained in infinite ^{14}C age samples constitutes the *least probable explanation*.

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