CARBON·14

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Introduction

"The discovery of cosmic-ray carbon has a number of interesting implications . . . particularly the determination of ages of various carbonaceous materials in the range of 1,000-30,000 years." These are the words with which Willard F. Libby and his coworkers concluded their report on the first successful detection of ^{14}C in biogenic material (Anderson et al., 1947). It was quite an understatement. Libby's pioneering work on the development of the radiocarbon dating method won him the Nobel Prize in Chemistry in 1960, and as one of his nominees aptly observed: "Seldom has a single discovery in chemistry had such an impact on the thinking of so many fields of human endeavor. Seldom has a single discovery generated such wide public interest." (Taylor, 1985).
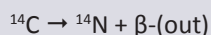
Radiocarbon dating has come a long way since then. Its physical and chemical principles are better understood, high-tech instrumentation has improved its range and sensitivity, and there are currently more than 130 active radiocarbon laboratories around the world. The amount of literature on the subject is vast and what follows is just an overview of the essentials. The details may be found in any of the books listed among the references at the end of this article. And so . . .

Basic Principles

Carbon-14 (^{14}C) is a cosmogenic* radioactive isotope of carbon that is produced at a more-or-less constant rate in Earth's upper atmosphere by the reaction of neutrons generated by high-energy cosmic rays with nitrogen-14 (^{14}N):[†]

$$^{14}N + n(in) \rightarrow {}^{14}C + p(out)$$

where n is a neutron and p is a proton. Carbon-14 decays back to ^{14}N by emission of a β- particle (electron) with a half-life (T½) of 5,730 ± 40 years:

$$^{14}C \rightarrow {}^{14}N + \beta\text{-(out)}$$

* Produced by cosmic rays.
[†] Minor amounts are also derived from ^{15}N, ^{16}O, and ^{17}O.

About 1 part per trillion (10^{12}) of Earth's natural carbon is ^{14}C. The rest, effectively 100%, is made up of an approximately 99:1 mixture of the stable isotopes carbon-12 (^{12}C) and carbon-13 (^{13}C) (fig. 1).
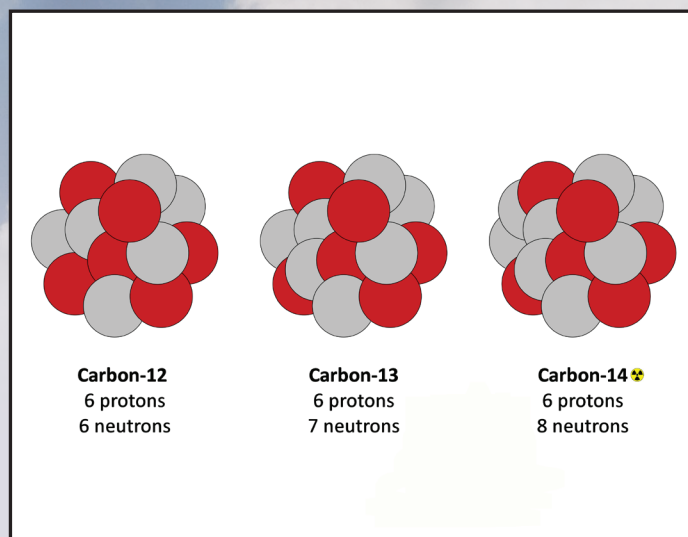

Figure 1. Carbon nuclides. A nuclide is an atomic species characterized by the number of protons (red spheres) and neutrons (gray spheres) in its nucleus. Nuclides that have the same number of protons (i.e. the same atomic number, Z) but different numbers of neutrons are called isotopes. Carbon (Z = 6) has three naturally occurring isotopes. Although the terms nuclide and isotope are commonly used interchangeably, they are not synonymous.

Once formed, ^{14}C is rapidly oxidized to carbon dioxide ($^{14}CO_2$), which diffuses throughout Earth's atmosphere, dissolves in the oceans, and is taken up by green plants during photosynthesis and by animals via the food chain (fig. 2). Throughout their lives plants and animals exchange carbon with their surroundings

and thereby maintain a constant concentration of ^{14}C. Provided its production rate doesn't change, this will be equal to the ^{14}C concentration in atmospheric CO_2. When living things die carbon exchange, and thus ^{14}C replacement, ceases. Death has no effect on radionuclides, however, so the ^{14}C in the organisms' remains continues to decay and steadily depletes with time.
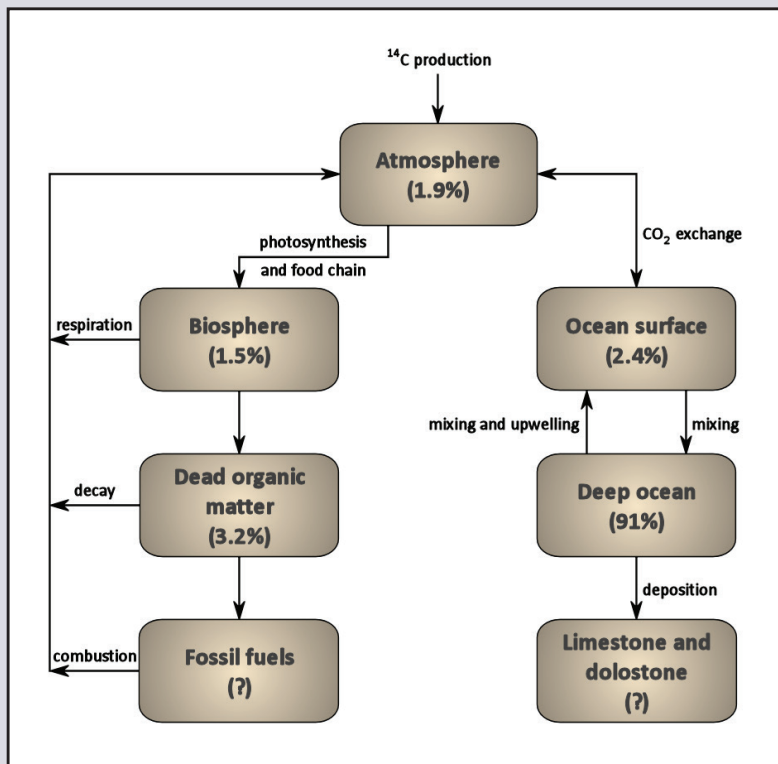

Figure 2. This simplified illustration of the global carbon cycle shows the principal carbon reservoirs with their relative sizes expressed as percentages. The amount of carbon stored in fossil fuels and carbonate rocks (geologic carbon) is unknown. Because it is so old, most geologic carbon is devoid of ^{14}C and is referred to as "dead".

Like all radioisotopes, ^{14}C decays exponentially at a rate that is proportional to the number of radiocarbon atoms in the sample (fig. 3). If N_0 is the number of ^{14}C atoms at time t = 0 (time of death) and N is the number remaining after time t, this process can be defined by the equation

$$\ln(N_0/N) = \lambda t$$

in which λ is a constant equal to $0.693/T_{1/2}$ and ln denotes a natural logarithm. Rearranging this equation and substituting for λ gives

$$t = (T_{1/2}/0.693) \ln(N_0/N) \qquad (1)$$

So in principal, assuming that the level of atmospheric $^{14}CO_2$ remains constant over time, and all living things contain the same relative proportions of carbon isotopes as atmospheric CO_2, N_0 and N are both measurable quantities. Since the half-life of ^{14}C is also known, the age (time elapsed since death) of a sample of once-living matter can be determined by solving equation (1) for t.
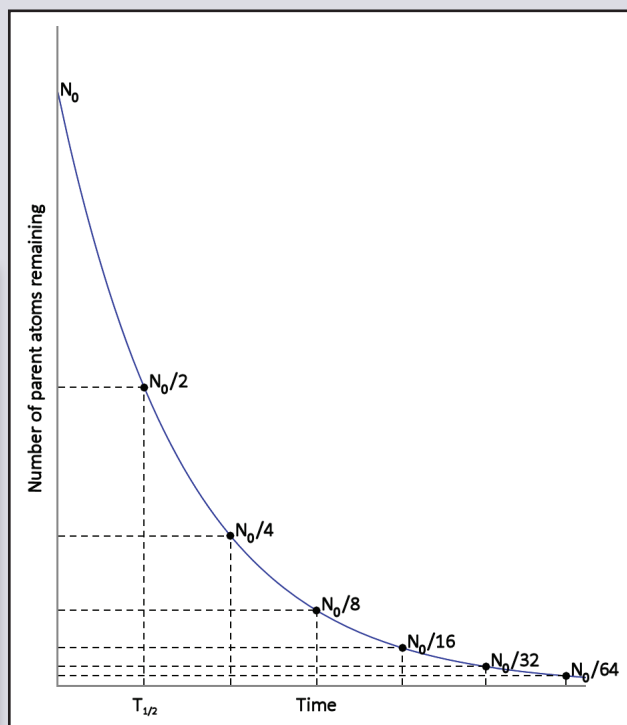

Figure 3. Radioisotopes decay exponentially, which means that the percentage of parent atoms decaying per unit of time is constant. The half-life ($T_{1/2}$) of a radioisotope is the time it takes for 50% of the atoms to decay; so if there are N_0 atoms at time t = 0, there will be $N_0/2$ remaining after the first half-life, $N_0/4$ after the second, $N_0/8$ after the third, and so on. By the time eight half-lives have passed, 99.6% of the radioisotope has decayed. Carbon-14 reaches its detectable limit at this point, when t ≈ 40,000 years.

Measuring Radiocarbon

There are two ways of measuring ^{14}C (Aitken, 2014). The conventional method, also known as "beta-counting," measures ^{14}C indirectly from its rate of decay by detecting the number of ^{14}C decay events (β particle emissions) per unit time per unit mass of sample. Conventional radiocarbon dating techniques include gas proportional counting and liquid scintillation counting (LSC).

Accelerator mass spectrometry (AMS) counts actual carbon atoms and measures the relative proportions of each of its isotopes. It is a much more efficient (and expensive) method of detecting ^{14}C than counting decay rates, but AMS's greatest advantage over conventional dating methods is that its sample size requirements are about 1,000 times smaller (milligrams vs grams). On the other hand, conventional beta-counting is able to achieve higher levels of precision and lower background interference than AMS provided the sample is uncontaminated and sufficiently large. Because of this, beta-counting tends to be the method of choice for measuring radiocarbon calibration curves.

Radioisotopes are customarily measured against an internal standard, typically a stable isotope of the same element. Carbon-14 is standardized to ^{12}C and expressed as the ratio $^{14}C/^{12}C$

so that N_0 and N become $(^{14}C/^{12}C)_0$ and $(^{14}C/^{12}C)$ respectively and equation (1) can be rewritten as

$$t = (T_{1/2}/0.693)\ \ln\frac{(^{14}C/^{12}C)_0}{(^{14}C/^{12}C)} \qquad (2)$$

In order to compare dates from other laboratories, radiocarbon ages are calculated by comparing a sample's measured $^{14}C/^{12}C$ ratio with that of a universally recognized standard. A number of these exist but the principal radiocarbon standard is the National Institute of Standards and Technology's (N.I.S.T.) Oxalic Acid 1 (fig. 4). Background radiation is measured using blank samples – typically coal, limestone or some other geologic material that contains only "dead" carbon i.e., no ^{14}C – and the value obtained subtracted from the sample's radiocarbon measurement.
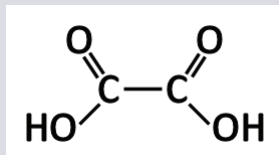

Figure 4. Oxalic acid

Dateable Materials

The relatively short half-life of ^{14}C means that radiocarbon dating cannot be applied to materials more than about 40,000 years old[‡] (fig. 3). However, provided it meets this requirement, almost any organic material can be dated, which is why the method has revolutionized archaeology more than any other science. Radiocarbon dating has also proven to be immensely useful to Quaternary geologists. Besides man-made products like paper and fabric, many natural carbonaceous materials are capable of providing meaningful radiocarbon ages. These include wood, charcoal, peat and other organic-rich sediments, twigs, seeds, pollen, pine cones and needles, animal bones, shells, and even water (fig. 5).
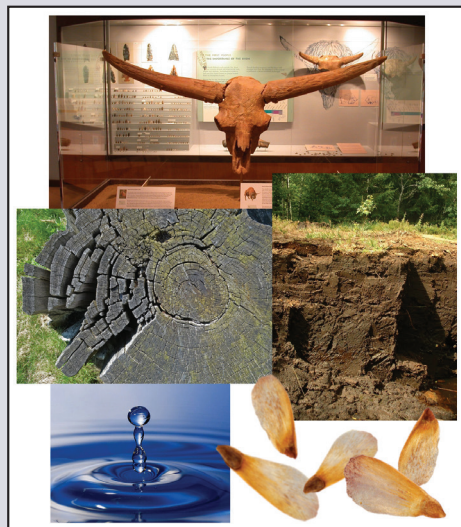

Figure 5. Materials that can be radiocarbon dated include (clockwise from top) bone, peat and other organic-rich sediments, plant material such as seeds or pollen, groundwater, and wood or charcoal.

Calibrating and Correcting ^{14}C Ages

There is more to calculating radiocarbon ages than simply plugging numbers into equation (2). Although early radiocarbon dates appeared to support the assumption that the level of atmospheric $^{14}CO_2$ remains constant over time (Libby et al., 1949), as the technique evolved it soon became clear that this was not so. Radiocarbon ages are affected by variations in the strength of Earth's magnetic field and solar activity – both of which affect the cosmic ray flux and hence the rate of ^{14}C production. Moreover, the large-scale burning of fossil fuels, which began during the industrial revolution; and mid-twentieth century above-ground nuclear tests have contaminated the atmosphere with significant

DENDROCHRONOLOGY AND ^{14}C DATING

Dendrochronology is a technique for dating events in the historical and recent geologic past based on the study of growth rings in trees.

Trees grow by adding rings, usually one a year. Growth takes place in the cambium, a layer of cells located between the bark and sapwood, which means that in a living tree, the outermost (zero-age) ring corresponds to the current year's growth. In timber and other cut wood, it marks the year the tree was felled. The width of each growth ring is a function of local climate and environmental conditions: rings formed in "good" years tend to be wider than those formed in years when conditions during the growing season were less favorable. Trees growing in the same geographic area tend to develop the same growth patterns over a given time interval. Common growth patterns can be matched from tree to tree. By comparing the patterns in live and old wood it is possible to construct timescales extending thousands of years back in time that are accurate to within one year.

Once made, a tree ring stops exchanging carbon with the biosphere and its ^{14}C content starts to decline. As a result, there is a direct correlation between the radiocarbon and calendar ages of growth rings in a single tree or dendrochronological timescale. In other words, radiocarbon ages of tree ring sequences that have been dated dendrochronologically are true calendar ages.

Peat: photo by Jeff Delonge used under Wikimedia Commons license CC BY-SA 3.0. Tree stump: photo by Selby May used under Wikimedia Commons license CC BY 3.0. Water droplet: photo by Michael Melgar used under Wikimedia Commons license CC BY-SA 3.0. Picea seeds: Steve Hurst@USDA-NRCS PLANT

[‡] Opinions on the maximum detection limit of radiocarbon dating vary from about 40,000 to 75,000 years. It all boils down to the nature of the sample, methodology, and instrument sensitivity. In conventional radiocarbon dating the main limiting factor is background, which sets the maximum age at about 40,000 years. AMS measurements are limited by factors associated with the instrument itself and an increase in the significance of possible sample contamination due to smaller sample sizes. Isotopic enrichment of samples can also extend age measurements. Dating limits vary from one laboratory to another and are usually specified on reports.

amounts of dead carbon and synthetic ^{14}C ("bomb carbon"). Fortunately, it is possible to correct for these effects because they are recorded in the growth rings of trees and can therefore be dated dendrochronologically (see box). Radiocarbon calibration curves based on the dendrochronology of long-lived trees such as the bristlecone pine and oak extend to about 11,000 BP (before present) (Friedrich et al., 2004). Other calibration methods have reliably pushed this limit to 26,000 years BP and beyond (Reimer et al., 2004, 2009, 2013).

The complications do not end there. Corrections must also be made for natural variations in carbon isotope ratios caused by fractionation and in the distribution of ^{14}C between and within carbon reservoirs.

In radiocarbon dating, isotopic fractionation refers mainly to the preferential uptake of lighter carbon by natural biochemical processes such as photosynthesis and bone growth, which can lead to significant depletions of both ^{13}C and ^{14}C relative to ^{12}C in plants and animals. Comparison of a sample's $^{13}C/^{12}C$ ratio (known as δ^{13}) with an isotopic standard such as the international Pee Dee Belemnite (PDB) standard carbonate§ or the equivalent Vienna-PDB standard (Coplen, 1994) quantifies the amount of fractionation that has occurred with respect to ^{13}C. The necessary correction is then applied by assuming that the effect of fractionation on ^{14}C is double that on ^{13}C.

Plants and animals that obtain carbon from sources other than the atmospheric reservoir often yield anomalously high radiocarbon ages. The radiocarbon ages of fish bones and charcoal known to be the same age, for example, might differ by as much as several hundred years. In the marine environment this offset is the result of the sheer vastness of the ocean and the extreme slowness and complexity of the processes that drive the circulation of its waters. The distribution of dissolved ^{14}C (as $^{14}CO_2$) throughout the world's oceans is consequently uneven both vertically and laterally. The net effect is a reduction in the ^{14}C content of the surface water, which gives it an apparent radiocarbon age of about 400 years. Known as the marine reservoir effect, this is not a problem likely to concern geologists in North Dakota, but its freshwater counterpart is.

Lake and river waters are generally more homogeneous than ocean waters, so except in very rare cases the marine reservoir effect is absent. High apparent radiocarbon ages in freshwater systems are caused primarily by the hard water effect – the presence of dead carbon in the form of dissolved carbonates derived from calcite-rich rocks and sediments like limestone or marl. Old or dead carbon may also be introduced as CO_2 released from sources that include humus, glacial meltwater, and volcanism. Or the water may become ^{14}C-depleted owing to a reduction in the rate of CO_2 exchange with the atmosphere caused by prolonged ice cover or unusually slow mixing of deep

and shallow lake water (Philippsen, 2013). Although the hard water effect is largely a freshwater phenomenon, it can also affect the marine environment in estuaries and other places where there is a large influx of carbonate-rich fresh water.

Unlike fractionation, reservoir effects are difficult to quantify because they are influenced by so many variables. For marine samples a global marine reservoir correction is automatically applied to radiocarbon ages (Reimer et al., 2009, 2013), which may be further modified with an additional correction to account for regional variations in the marine reservoir effect. Correction factors for different oceanographic regions around the globe are stored on the Marine Reservoir Correction Database at Queen's University in Belfast, Northern Ireland (Reimer and Reimer, 2001). These data are based on radiocarbon dates obtained from live specimens of known age collected before nuclear testing began in the 1950s, and the assumption that the calculated values are constant for a given region. Age discrepancies due to the hard water effect range from a few decades to several centuries and are often unknown. Where possible, the magnitude of the effect is determined by following the marine protocols i.e., by comparison with modern analogues from the same species and locality under assumed stable conditions (Bowman, 1990).

It is generally assumed that materials considered suitable for radiocarbon dating are closed systems in the sense that all carbon exchange with the biosphere has ceased. However this is rarely true because direct exposure to other sources of carbon, which may affect their ^{14}C content, is unavoidable. This is especially so in the natural environment where dissolved inorganic carbonates, humic acids or modern plant fragments in soil, for example are common contaminants. Contamination can also happen if a sample is improperly handled after it has been collected. Contact with modern carbon-containing products like paper, cloth, certain plastics and even the collector's bare hands can all lead to inaccurate radiocarbon dates (table 1). Various physical and chemical pretreatment methods are used to decontaminate samples prior to ^{14}C analysis but they are not always successful (Bowman, 1990). The best option, especially where modern contaminants are concerned, is to minimize or avoid them altogether by adopting careful sampling and handling procedures.

Sample age	Contamination					
	0.1%		1%		10%	
	modern	old	modern	old	modern	old
2,500	-3	+8	-30	+80	-290	+850
5,000	-7	+8	-70	+80	-670	+850
10,000	-20	+8	-200	+80	-1,770	+850
15,000	-45	+8	-430	+80	-3,510	+850
20,000	-90	+8	-840	+80	-5,980	+850
30,000	-320	+8	-2,750	+80	-13,070	+850
40,000	-1,080	+8	-7,180	+80	-21,990	+850

Table 1. The effect (in years) of modern and old (dead) radiocarbon on actual ^{14}C age (Bowman, 1990).

§ The PDB Marine Carbonate Standard was obtained from a Cretaceous-age marine fossil, *Belemnitella americana*, from the PeeDee Formation in South Carolina. The PDB has a higher $^{13}C/^{12}C$ ratio than almost all other forms of naturally occurring carbon. For convenience, its δ^{13} value is defined as zero, which means that the δ^{13} values of most carbonaceous materials are negative.

Calculating and Reporting ^{14}C Ages

Radiocarbon ages are calculated using equation 2 according to a recommended convention that includes the following:

- Use of the Libby half-life of 5,568 years (Libby, 1955), which is about 3% too low, rather than the more accurate (Cambridge) half-life of 5,730 years. Equation 2 then becomes

$$t = 8033 \ln \frac{(^{14}C/^{12}C)_0}{(^{14}C/^{12}C)}$$

  The reason for using a half-life that is known to be incorrect is a historical one. The Cambridge half-life was officially recognized in 1962 (Godwin, 1962). Prior to that, radiocarbon dates were calculated using Willard Libby's estimate of 5,568 years. For the sake of consistency and to avoid errors when comparing pre- and post-Cambridge half-life radiocarbon ages, it was agreed that the Libby half-life should be retained. Radiocarbon calibration curves automatically correct for the 3% error in the calculated age this practice incurs.
- The assumption that the atmospheric ^{14}C level is constant.
- Use of Oxalic Acid 1 or a related secondary standard as the modern radiocarbon standard.
- Correction for sample isotopic fractionation by comparison with the PDB standard.
- Ages are expressed in years BP (before present) where 0 BP is defined as AD 1950. Radiocarbon ages calculated relative to a fixed point in time are easy to compare because they are independent of the year they were measured. The choice of AD 1950 was made for no other reason than to honor the publication of the first radiocarbon dates in December 1949 (Libby et al., 1949).

Ages calculated in this way are called conventional radiocarbon ages (CRA) (Stuiver and Polach, 1977; Stuiver, 1980). A CRA is the age (in years BP) a sample would be had the early assumption about the constancy of atmospheric ^{14}C levels been correct. It is usually reported in a format that looks something like this:

Beta-104380: 8740 ± 60 BP

Where Beta-104380 is the sample reference number, consisting of the dating laboratory's identifier, which in this example is BETA (= Beta Analytic, Inc.) followed by a numeric code, 8740 is the radiocarbon age in years BP and 60 is the estimated standard error (expressed as ± 1σ). Radiocarbon ages may be rounded up according to convention (Stuiver and Polach, 1977) but not all laboratories do this. (Note: In radiocarbon dating, BP always means "years before 1950" but other dating methods that use the BP notation may define it differently. Thermoluminescence dating, for example, defines BP as before AD 1980. On occasions when a distinction has to be made, radiocarbon dates may be reported in ^{14}C yr BP i.e., carbon-14 or radiocarbon years BP.) CRAs are uncalibrated and only correct for isotopic fractionation. Reservoir corrections, where necessary, are calculated and reported separately.

Materials whose measured radiocarbon is indistinguishable from background i.e., whose age exceeds the maximum detection limit of the instrumentation cannot be assigned a finite radiocarbon age. In such cases ages are usually reported as "greater than the measurable upper age limit," a value that is dependent not only on the counting method used (beta- or AMS) but also the laboratory doing the work. An age reported as >40,000 yr., for example, means that the sample being dated is at least 40,000 years old and an alternative dating method must be considered. At the other end of the time scale, a radiocarbon age of less than 200 years is reported as "modern" or, if it falls after 1950, "greater than modern."

Calibration of a CRA translates the radiocarbon age into calendar years and corrects for the Libby half-life. Calibrated ages are always expressed as a range in terms of cal AD, cal BC, or cal BP along with the appropriate confidence level – typically one sigma (σ) statistics (68% probability) and/or two sigma statistics (95% probability). ("Cal" in this context means calibrated, not calendar.) The calibrated age at the one sigma confidence level of the CRA described above could therefore be written as:

cal BC 7950-7575 (1σ) or
cal BP 9899–9524 (1σ)

where cal BP = 1949 + cal BC (Stuiver and Pearson, 1993). (Similarly, cal BP = 1950 - cal AD, the reason for the switch from 1949 to 1950 when converting ages being that there is no year 0 in AD/BC chronology.) Because cal BC and cal AD are equal to calendar years BC and AD, calibrated radiocarbon dates are usually reported using one or other of these notations rather than cal BP. Most CRAs are calibrated dendrochronologically using programs such as OxCal (Bronk, 2009), CALIB (Stuiver and Reimer, 1993; Stuiver et al., 2013), or WinCal25 (van der Plicht, 1993).

Radiocarbon Dating in North Dakota

The Catalog of North Dakota Radiocarbon Dates (Moran et al., 1973) is a compilation of archaeological and geologic radiocarbon dates from more than three dozen sites scattered across the state. Its approximately 90 entries represent all that were known to the authors at the time, of which just over half are geologically significant (fig. 6). Apart from a handful associated with buried glacial tills that are close to or beyond the upper age limit, the majority of these dates record the timing, beginning about 13,000 years ago, of the final retreat of the Laurentide ice sheet from North Dakota during the Late Wisconsinan and the region's postglacial history.

In the forty-odd years since the catalog's publication, the number of North Dakota radiocarbon dates has almost tripled. In keeping with its authors' primary intent, which was to "spare those working on the Quaternary of this area the necessity of compiling individual lists, with attendant duplication of effort" this mainly post-1973 data has been published in a revised and updated version of the catalog (see p. 27).
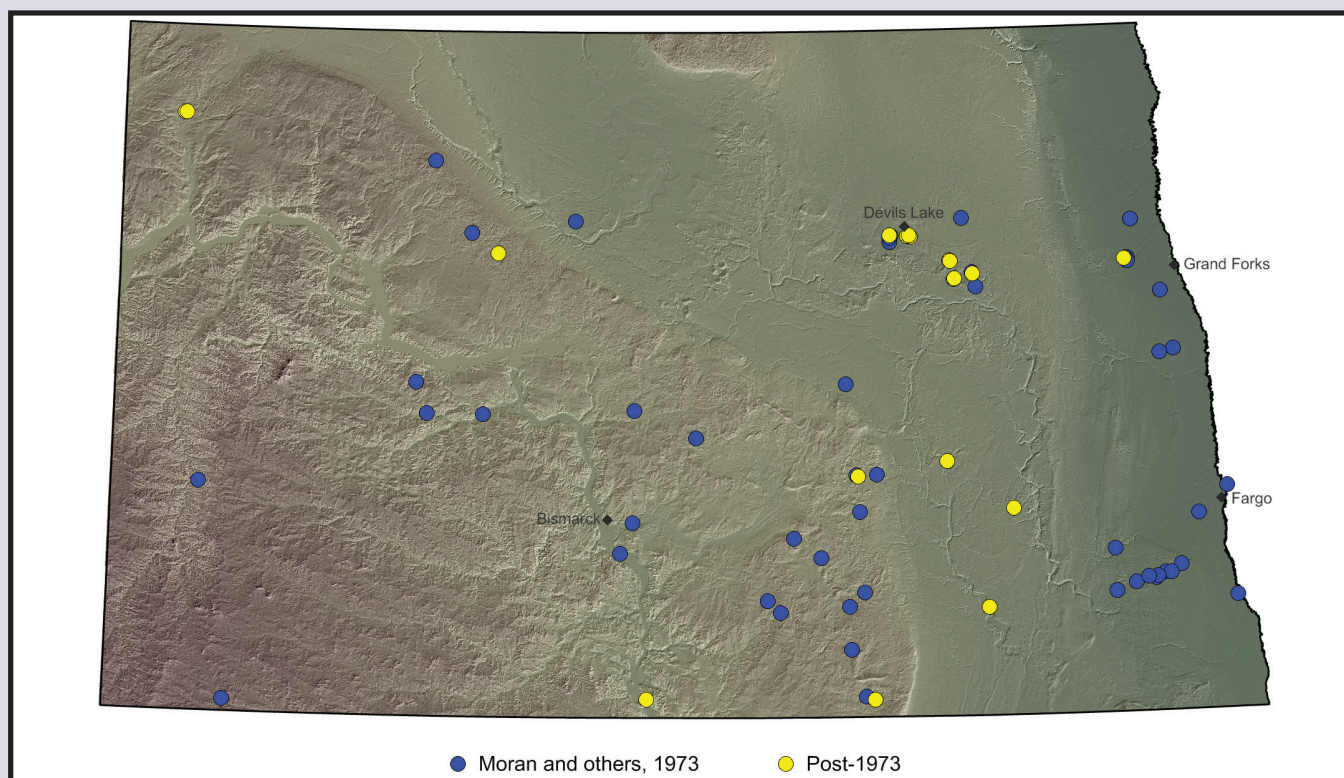
Figure 6. Distribution of geologically significant radiocarbon dates from North Dakota. Blue dots represent sample collection sites reported in the Catalog of North Dakota Radiocarbon Dates (Moran et al., 1973). Collection sites associated with dates not included in the catalog (published after 1973) are shown as yellow dots.

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