PRINCIPLES BEHIND CARBON DATING AND ITS VARIOUS USES

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Introduction

Sometimes we are very curious to know the age of ancient objects whose origin and age cannot be determined exactly by normal means, for example, objects dug up by archaeologists. If the object contains radioactive element, an element capable of emitting radiations spontaneously in the form of alpha particle, beta particle or gamma ray, then it is possible to estimate its age using radiometric (also called radioactive) dating method. There are a number of radiometric dating methods such as radiocarbon dating, uranium-lead dating and potassium-argon dating, etc. Among them, carbon dating is the most well-known method used in dating of archaeological specimens. Carbon dating is applicable only to organic materials, that is, the material must once have been a part of living things such as bone, wood, etc. In this method, the age of ancient objects are estimated by measuring their content of carbon-14 (C-14), a radioactive form of carbon with a nucleus containing 6 protons and 8 neutrons, called radiocarbon. This method is known as carbon dating or radiocarbon dating. However, this method cannot be applied to date metal, stone and pottery unless there is some organic material left as a residue. For objects that were never living, other radiometric dating methods are used.

Here, we will be taking only carbon dating and first, we will discuss about different types of carbon atoms, called isotopes that is atoms whose nuclei contain same number of protons but different numbers of neutrons. The known carbon isotopes vary from C-8 to C-22. However, only three isotopes : C-12 , C-13 and C-14 occur naturally on earth. Out of these, C-14 is unstable. In unstable nuclei, the binding energy per nucleon is less than that of the stable nuclei. In order to achieve stability, the unstable nuclei emit radiation. In C-14, the ratio of neutron / proton is 1.33 which is above the band of stability. Hence, it emits beta minus particle which can be counted. Carbon dating is based on measuring the ratio of two types of carbon: (i) the rare radiocarbon C-14; and (ii) the abundant stable C-12 found in the organic material at the time of its death and also at present. Willard. F. Libby and his co-workers at the University of Chicago developed the carbon dating technique in 1949. Libby, Anderson and Arnold in 1949 were the first to measure radiocarbon's rate of decay and found that the half-life ($T_{1/2}$) for C-14 is 5,568 ± 30 years. In 1960, Libby received the Nobel Prize in Chemistry "for his method to use carbon-14 for age determination in archaeology, geology, geophysics and other branches of science" (Libby, 1955, 1960).

This article is on the physics and the principles behind carbon dating. First, we will discuss how radiocarbon is produced and how it gets into the different parts of the environment.

Formation of Radiocarbon

Cosmic radiations, from outer space, enter the earth's atmosphere in large numbers every day (Anderson et al., 1947). For example, each of us is hit by about half-a-million cosmic radiations every hour. These radiations consist of charged particles (protons 92 per cent, alpha particles 7 per cent and massive nuclei 1 per cent). When these protons strike ordinary atoms in the upper atmosphere, neutrons are produced.

Some of these thermal neutrons (E ~ 0.025 eV) collide with nitrogen gas, the major constituent of the atmosphere, and produce the radioactive isotope C-14 in the upper atmosphere, i.e., in the stratosphere and upper troposphere:

$$n + {}^{14}_{7}N \rightarrow {}^{14}_{6}C + p \qquad (1)$$

where ${}^{14}_{7}N$ represents a Nitrogen-14 atom, n represents a neutron and p represents a proton. The proton takes an electron with it and becomes an atom of hydrogen. We may mention that radiocarbon can be produced through a number of nuclear reactions; however, the most important one for radiocarbon dating is given in Eq. (1).

Basic Principles of Carbon Dating

The observed production of C-14 is usually two to three atoms per sq. cm per second. This variation is due to changes in the cosmic radiations reaching the earth's atmosphere based on the strength of the earth's magnetic field. However, the overall cosmic radiations reaching the earth's atmosphere is expected to remain constant unless there is supernovae contribution which occurs occasionally. The highest rate of C-14 production is observed at altitudes of 9 to 15 km (30,000 to 50,000 ft) and high geomagnetic latitudes. Since chemically C-14 behaves like ordinary carbons, it combines with oxygen to give carbon dioxide (${}^{14}CO_2$),

$${}^{14}_{6}C + O_2 \rightarrow {}^{14}_{6}CO_2 \qquad (2)$$

The carbon dioxide diffuses in the atmosphere and is dissolved in the oceans, in the form of carbonates, bicarbonates and carbonic acid. The CO_2, that is present in the atmosphere, consists almost entirely of stable C-12 (98.89 per cent) with a small admixture of stable C-13 (1.11 per cent) and only one out of every trillion C-12 atoms is C-14.

During photosynthesis, when a plant absorbs CO_2 from the atmosphere and reduces it to sugar and starch with the help of water and sunlight, the entire plant tissue becomes radioactive as the CO_2 in the air. The plants are eaten by animals, therefore their tissues also become radioactive. Even animals eating animals become radioactive as all animals finally depend on plants for food. That means every living organism continuously takes up C-14 along with C-12 in the same ratio that C-14 and C-12 exist in the air. The production and distribution of C-14 is shown schematically in Figure 1. So an organism, or a bone, or a piece of wood, contains

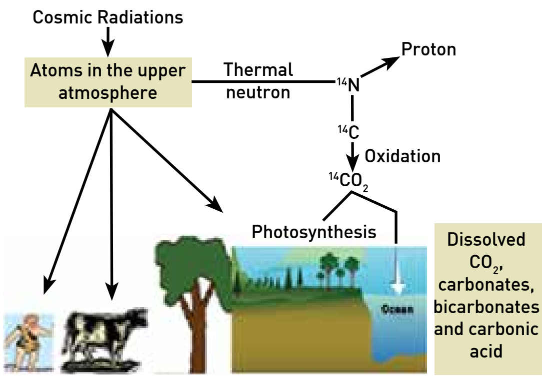

Figure 1. Production and distribution of ${}^{14}C$

radiocarbon. However, the C-14 atom within a living organism decays continually, but the organism exchanges both types of carbon with its environment keeping the ratio about the same as the atmosphere. At this moment, our body has a certain percentage of C-14 atoms in it, and all living plants and animals have the same percentage.

If we take a sample of air and count how many C-12 atoms there are for every C-14 atom, we will find that

$$\frac{C-14}{C-12} \approx 1.3\times10^{-12} \qquad (3)$$

At any given time, the above ratio will remain constant as C-14 is well mixed up with C-12. Even if we sample any part of a plant or a part of our body we will find this ratio. Once an organism dies, it ceases to acquire further C-14 atoms. As time passes, the C-14 in its tissues is converted back into nitrogen:

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + e^{-} + \overline{\nu}_e \qquad (4)$$

where e^{-} is the electron (beta minus particle) and $\overline{\nu}_e$ represents the electron antineutrino. In Eq. (4), a neutron present in the unstable C-14 nucleus is converted into a proton with the emission of an electron, to conserve charge, and an electron antineutrino, to conserve energy and angular momentum. The emitted beta minus particles carry maximum energy of 156 keV, while their average energy is 49 keV. So the amount of C-14 in that once-living thing decreases as time goes on, which gives the smaller C-14 / C-12 ratio. This behaves like a "clock" which starts ticking the moment something dies. We can estimate the amount of time that has passed since the death of the organism by comparing the C-14 / C-12 ratio in the current sample and that in the original living organism. Remember that this works only for things which were once living and cannot be used to date rocks, for example. There is a quantitative relationship between the decay of C-14 and the production of a beta minus particle. The decay is constant but spontaneous. That is, the probability of decay for an atom of C-14 in a discrete sample is constant, thereby requiring the application of statistical methods for the analysis of counting data.

Computation of Ages and Dates

When an organism dies, it stops exchanging carbon with the atmosphere and its C-14 content then starts to decrease at a rate determined by the law of radioactive decay (Krane, 1988).

If N be the number of atoms at any time t in a radioactive sample, the number of atoms dN that will decay during the time t to t + dt must be proportional to N and also proportional to dt. Then

$$dN \propto -N\,dt \qquad (5)$$

The negative sign indicates that number of atoms of the radioactive element decreases with time. The above equation can be expressed by the following differential equation,

$$dN/dt = -\lambda N, \qquad (6)$$

where the constant of proportionality λ is called the decay constant, has a different value for each radionuclide. Integrating Eq. (6) we have

$$\int_0^N \frac{dN}{N} = -\lambda \int_0^t dt$$

where N_0 is the number of atoms in the original sample at t = 0 and N be the number of atoms at any time t. This gives

$$N = N_0\, e^{-\lambda t} \qquad (7)$$

We know that in one half-life $T_{1/2}$ half the number of radiocarbon atoms in a given sample decay. Thus, putting $N = \frac{N_0}{2}$ and t = $T_{1/2}$ in Eq. (7) we have

$$T_{1/2} = \ln_2 / \lambda = 0.693/\lambda \quad (8)$$

If $T_{1/2}$ of the radioactive element is known, its decay constant can be calculated. There are two $T_{1/2}$ values for radiocarbon available in literature.

(i) Libby value. $T_{1/2}$ = 5,568 ± 30 years (Anderson and Libby, 1951).

(ii) Godwin value. $T_{1/2}$ = 5,730 ± 40 years (Godwin, 1962), which is thought to be a more accurate value.

However, researchers are still using Libby value in calculations in order to maintain consistency.

Sometimes we need the value of activity of a radioactive sample to estimate its age. The activity is defined as disintegrations per second (dps) and is denoted by R. This is obtained by differentiating Eq. (7),

$$dN/dt = -\lambda N_0 e^{-\lambda t} \quad (9)$$

When t=0, (dN/dt)_(t=0)=$-\lambda N_0$. Hence Eq. (9) gives

$$dN/dt = (dN/dt)\_(t=0)\, e^{-\lambda t}$$

$$\text{Or, } R = R_0 e^{-\lambda t} \quad (10)$$

where R= dN/dt, and $R_0 = \left(\frac{dN}{dt}\right)_{t=0}$. The activity of the sample is given by

$$R = \left|\frac{dN}{dt}\right| = \lambda N_0 e^{(-\lambda t)} = \lambda N \quad (11)$$

Thus, the activity of a sample R is proportional to the product of N, the number of atoms present and the decay constant λ.

The unit of activity is curie, named after Madam Curie, and defined to be equivalent to 3.7×10^{10}dps. Originally, one curie was defined as equal to the number of disintegrations that occur per sec in 1g of radium - 226 by α – emission. There is another unit of activity, called Rutherford, named after Ernest Rutherford, which is equal to 10^6dps. The SI unit is the becquerel, named after Henri Becquerel, which is equal to 1 dps. From Eq. (11), we obtain

$$t = \frac{1}{\lambda} \times 2.303 \times \log\left(\frac{R_0}{R}\right)$$

$$= \frac{T_{1/2}}{0.693} \times 2.303 \times \log\left(\frac{R_0}{R}\right),$$

Or,

$$t = 3.32 \times T_{1/2} \times \log\left(\frac{R_0}{R}\right) \quad (12)$$

where t is the amount of time that has passed since the death of the organism.

Measuring Age with Carbon-14

Using Eq. (12), we can estimate the age of a given sample provided we know (i) how much C-14 the object had at the beginning, and (ii) how much C-14 the object has now. However, in practice, we do not measure the total amount of C-14 in the sample, since that depends on the size of the sample. So, instead we measure the original and current C-14 / C-12 ratio. Thus in Eq. (12), R is the current C-14 / C-12 ratio in the sample and R_0 is the original C-14 / C-12 ratio of the living organism. We can then calculate the amount of time t that has passed since the death of the organism. However, this method breaks down for periods of the order of t ~ 10 $T_{1/2}$, that is, about 50,000 years, because so little C-14 remains after almost 9 half-lives that it may be hard to detect and obtain an accurate reading, regardless of the size of the sample.

Taking Libby half-life it has been found that 1g of carbon from a living plant decays at a rate of 14 decays per minute (dpm). This means that if the plant dies after 5,568 years, its activity will be dropped to 7 dpm. By measuring the count rate produced by the carbon in archaeological specimens of wood or charcoal, the time which has elapsed since the original plant died can be estimated.

Reliability of Carbon Dating

The carbon dating method has been checked by comparison with wood samples of known age. For example, Libby and Arnold took two wood samples from the tombs of two Egyptian kings and found that the radiocarbon dating gives a fairly reliable result, which launched the "radiocarbon revolution" in archaeology.

The ancient trees can be dated by dendrochronology, a scientific method of dating based on the growth rings of trees. Using this method one can date the time at which tree rings were formed, in many types of wood, to the exact calendar year. Radiocarbon dating may be compared with dendrochronology. From the dating of ancient bristlecone pine trees from the western U.S., a correction curve for the carbon dating over the range back to 5000 BC has been developed. Trees dated at 4000 BC show the maximum deviation of between 600 and 700 years, too young by carbon dating. A tree-ring calibration now allows for correction of radiocarbon dates; however, older radiocarbon dates cannot be corrected. For this reason, older radiocarbon dates are not regarded as true year dates; such dates are reported as radiocarbon years.

Techniques Used to Measure Radiocarbon

Libby measured the C-14 fraction of a sample by using the radioactivity of these unstable nuclei. By rubbing carbon sample on the inner wall of a Geiger counter, he was able to count each emitted beta particle from C-14 decays and hence he estimated the current C-14 content in the sample. This is known as solid counting system. However, this method is very slow because in one year only 0.01 per cent of the C-14 atoms in a sample decays. Again, it is found that most Geiger counter are not able to detect the presence of C-14 in amounts less than 10^5 dpm. Hence, this method is not efficient. Nowadays there are three principal techniques used to measure C-14 content of any given sample. They are gas proportional counting (GPC), liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS).

(i) Gas Proportional Counting

In this method, the sample is converted to carbon dioxide gas. Then this gas is filled in a proportional counter. The radioactive C-14 content of the gas emits beta particles within the counter and this electrical discharge is counted electronically. Sometimes, the sample is also converted to methane gas which is used in place of carbon dioxide in carbon dating counters.

(ii) Liquid Scintillation Counting

In this case the sample is in liquid form, i.e., it is converted to a carbon-rich aromatic liquid (benzene). A scintillator is added to it and placed in a clear container. Whenever a beta particle, emitted by a given sample, strikes the scintillator it produces a flash of light. Sensitive photo multiplier tubes are placed near the container and count the flash of light. The performance of such system is superior to GPC because if the age of a sample is greater than 35,000 yr BP, the uncertainty of ages determined by the GPC method increases as net count rate declines towards the limit of detection. This technique was popular in the 1960s.

Both GPC and LSC methods count beta particle emitted from the sample. But the decay of a radioactive atom is a random event. So, the measurement needs to be performed over a period of 2–7 days depending on the age of sample. Moreover, a large amount of sample is required in both the techniques. A modern radiocarbon dating method, known as AMS, was developed in 1970.

(iii) Accelerator Mass Spectrometry

In AMS, the radiocarbon concentration in a sample is determined by counting the C-14 atoms in an ion-beam produced from the sample, using an accelerator mass spectrometer (Tuniz et al., 1998). We shall discuss the principle of this method in detail.

We can extract carbon from the material to be dated using a variety of chemical techniques. But, the chemical properties of any element are governed by the number of protons present in the element. Hence, C-14 has the same chemical property as the other carbon isotopes. So, it cannot be easily isolated by chemical means. Further, the number of neutrons does affect the physical properties of an element. Therefore, we have to rely on the physical properties of this isotope, i.e., its larger mass and its radioactivity.

We can sort relatively heavy carbon ions from a small sample of material using mass spectrometry, which uses electric and magnetic fields. In this method, the individual atoms are first released from the sample and then ionised by adding or removing electrons from each atom. As these atoms have a net charge, they are attracted towards metal plates with an opposite charge and move faster and faster as they approach the metal plates. These atoms are allowed to pass through a hole of the plates and then enter an electromagnet. Atoms with different masses follow different path through the magnetic fields. The C-14 atoms can then be isolated and counted separately.

For extremely small sample, we can use an accelerator mass spectrometry (AMS). In this case, multiple stages of acceleration and ionisation are used. The ionised atoms pass through several electromagnets. Consequently, the C-14 atoms are clearly separated. The main advantage of AMS is that it does not count beta particle but rather all C-14 atoms in a sample. AMS analysis of samples takes only a few hours whereas conventional methods take one to two days. Further, this method needs only a sample size as small as one milligram whereas conventional methods need at least 10 grams.

Factors which Affect the C-14 / C-12 Ratio

For steady cosmic radiations reaching the earth's atmosphere the C-14 / C-12 ratio in living organisms remains constant, and is the same as that in air. But, there are factors such as astronomical and human activities which affect the amount of C-14 produced in the atmosphere.

(a) Astronomical Effect

The strength of the earth's magnetic field affects the amount of cosmic radiations entering earth's atmosphere. These fluctuations affect the C-14 / C-12 ratio and hence the dating system. However, one can correct these errors using other techniques for calibration such as tree-ring data and foraminifera, a phylum or class of amoeboid protests and corals.

(b) Human Effects

Burning of fossil fuels like coal and oil adds a large amount of C-12 to the atmosphere which makes the C-14 / C-12 ratio smaller, whereas nuclear bomb testing (since 1940) makes its value large. However, these errors do not affect anything on dating over 150 years old because of the formation of fossil fuels from the remains of organisms that died millions of years ago. By this time, all the original C-14 organisms must have already been absorbed from the atmosphere.

Further, all organisms do not absorb C-14 directly from atmospheric reservoir, so in those cases we cannot use the same C-14 / C-12 ratio. This is known as reservoir effects. For example, (i) Trees absorb carbon dioxide directly from the atmosphere (one reservoir), so this does not require reservoir corrections, (ii) Seals breathe air from the atmosphere, whereas their main food supply is sea food that draws its carbon from underwater sources (a second reservoir) which is not in direct contact with the atmosphere. It takes some time for atmospheric carbon to mix deeper into the ocean, furthering the C-14 decay. This leads to a smaller C-14 / C-12 ratio than in land animals, consequently gives older radiocarbon dates unless corrected. (iii) Shell-fish living in a lake surrounded by limestone show a different (third) reservoir effect. Limestone forms from the remains of long-dead organisms that are severely depleted of C-14. Weathering of the limestone into the lake (where shell-fish will incorporate the carbon into shells) changes the C-14 / C-12 ratio. This gives older radiocarbon dates unless corrected.

Thus, researchers must carefully study each sample to know its general history and environment before measuring its age with carbon dating.

Limitations of C-14 Dating

There are a number of limitations of C-14 dating which are discussed next:

(i) The archaeological sample should be collected and packed air tight very carefully in chemically neutral materials in order to avoid contamination by new C-14. The contaminated carbons from the sample are usually removed by using purification and distillation methods. For this reason, the size of the sample should be larger. But, accelerator dating helps in working with very small samples. However, this is expensive.

(ii) In Eq. (12), the decay rate is logarithmic. This gives significant upper and lower limits. So, it is not very accurate for fairly recent deposits, where the error factor (the standard deviation) may be larger than the date obtained. The practical upper limit is about 50,000 years, because so little C-14 remains after almost 9 half-lives that it may be hard to detect and obtain an accurate reading, regardless of the size of the sample.

(iii) The C-14 / C-12 ratio is not constant in the atmosphere. It was found that this ratio has varied significantly during the history of the earth. In order to compensate this variation, the dates obtained from radiocarbon should be corrected by using standard calibration tables developed by scientists.

(v) Finally, the dates obtained from radiocarbon dating are not infallible, that is, in general, single dates should not be trusted. Thus, if possible, multiple samples should be collected and dated.

Uses of Carbon Dating

1. Radiocarbon dating method is used for estimating the age of old organic matters which were once living. For example, ancient manuscripts, historical artifacts made from wood or leather, bones, etc., can be dated. Traditional radiocarbon dating can be applied to organic remains between 500 and 50,000 years old. However, using accelerator techniques the upper limit can be extended to one million years.
2. This is used for dating the culture history or estimating the age of geological formation.
3. Using carbon dating, forensic scientists determine age and year of death in cases involving unidentified human remains.
4. Archaeology and other human sciences use radiocarbon dating to prove or disprove theories. C-14 provides a radioactive clock for anthropologists just as uranium provides a radioactive clock for geologists. The C-14 half-life is suitable for the dating of cultural history, just as the half-life of uranium is suitable for the dating of history of the earth. Using radiocarbon dating, archaeologists have been able to obtain a much needed global perspective on the timing of major prehistoric events such as the development of agriculture in various parts of the world.
5. Over the years, Carbon-14 dating has found applications in archaeology, anthropology, geology, hydrology, geophysics, atmospheric science, oceanography, paleoclimatology and even biomedicine.
6. Carbon dating has received the most publicity after it is used in dating popular artifacts, such as the Shroud of Turin.

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