Radiocarbon Dating

by

K. C. HODGE and G. W. A. NEWTON

Summary

Radiocarbon dating is discussed with particular reference to Egyptian Chronology. Details of the technique are given as used to measure the age of bone and bandages from Manchester Mummy 1770. The results obtained were

Bone: 1000 B.C.   Bandages: A.D. 380

This implies the mummy was wrapped or re-wrapped sometime after death.

Introduction

The unravelling of ancient history is an exciting occupation and in recent years historians have captured the interest and help of scientists in this rewarding task. One important aspect of this work is age determination and the establishment of sequences and chronologies. 'Dating would be a nonsense without radiocarbon dating, and this technique has made a major contribution to archaeology'.[1]

Radiocarbon dating involves many disciplines such as history, physics, chemistry, biology and others. The technique began in 1948 in the University of Chicago under the leadership of Professor W. F. Libby,[2] and in 1960 his excellent research was recognized with the award of the Nobel Prize in Chemistry. From the beginning Egyptian chronology played an important part in the establishment of the technique because, among others, Egyptian samples (usually wood or charcoal from tombs) were used as standards of known 'historical' dates. The comparison of the radiocarbon date with the 'historical' date is important to the scientist and historian. Clearly, the validity of both methods is very significant; Radiocarbon dating is less than thirty years old and is continually being developed and improved. 'Historical' dating has centuries of tradition, but chronologies are still being modified on the basis of new ideas and discoveries. The two approaches will be considered separately. The radiocarbon dating will be considered in general terms first and then with reference to Egyptian chronology, and the 'historical' dating will be discussed in the Egyptian context only.

Radiocarbon Dating

Radiocarbon dating can be carried out mainly on living material that once formed part of the biosphere, and obviously only that part of it which contains carbon. Detailed investigation of this carbon shows that it is present as three isotopes, namely carbon 12, carbon 13 and carbon 14. The ratio of these isotopes in living matter on earth is $100:1:10^{-10}$ respectively. Isotopes contain the same number of protons in their atomic nuclei but can have different masses because they contain different numbers of neutrons in the nucleus. Protons have unit mass and unit positive charge, and in a neutral atom the positive charge is balanced by an equal number of negatively charged electrons outside the nucleus. Neutrons have unit mass and no charge. Carbon atoms always contain six protons in the nucleus, but the three isotopes carbon 12, carbon 13 and carbon 14 also contain 6, 7 and 8 neutrons respectively (12, 13 and 14 refer to the total nuclear mass of each isotope). The isotopes carbon 12 and carbon 13, that is, the bulk of the carbon on earth, are stable and are produced in stars and distributed in space at the end of the stars life, for example when it blows up as a supernova. All the carbon 12 and 13 in our bodies has its origin in some long-dead star.

Carbon 14, the isotope used for dating, is radioactive and has a different source; it is being produced continually in our atmosphere by cosmic radiation. The effects of cosmic rays were noted as early as 1900, but it required daring balloon ascents to heights of 5,000 m by V. F. Hess in 1911 to indicate that this penetrating radiation was of cosmic origin.

Although much is now known about cosmic rays, where they come from in the universe is still in doubt. A detailed understanding of cosmic rays is important to the historian because, as will become apparent, it is imperative to radiocarbon dating that the cosmic ray intensity has remained constant over the past 10,000 years, or that any variations should be known accurately. The present intensity of cosmic radiation is roughly equivalent to that of starlight and 100,000,000 times less intense than sunlight. The maximum energies of cosmic rays are enormous and cannot be produced by man even in the most powerful accelerators; in starlight the average energy is about 2 ev, whereas in cosmic rays energies as high as 1,000,000,000 ev have been observed. The primary particles which have these energies are mainly protons; these protons collide with atoms of the earth's atmosphere, mainly nitrogen, and produce secondary particles. A wide range of secondary particles are produced, and a study of these has been a very rewarding area of research in physics. Of significance to radiocarbon dating are the neutron secondary particles which are knocked out of nuclei in the earth's atmosphere. These secondary neutrons can interact with nitrogen nuclei in the earth's upper atmosphere to produce carbon 14:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \rightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{p}$$

nitrogen + neutron → carbon 14 + proton

The superscript refers to the mass of the atom, that is, the total number of neutrons plus protons; the subscript refers to the number of protons which determines the element (carbon has six protons and nitrogen has seven protons). In the nuclear reaction depicted above, nitrogen is converted to carbon 14 by the secondary neutrons in the earth's atmosphere.

If the cosmic ray intensity was constant with time, then the secondary neutron concentration would be constant also, and if carbon 14 was stable then its concentration would increase with time. However, carbon 14 is not stable, it is radioactive and decays back to nitrogen:

$$^{14}_{6}C \rightarrow\ ^{14}_{7}N +\ ^{0}_{-1}\beta + \nu$$
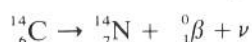
carbon 14 → nitrogen 14 + beta particle + neutrino

The notation is the same as before, the –1 on the beta particle (electron) implying a negative charge. This beta particle is emitted from the atom and can be detected by suitable equipment; it is this beta particle which is measured in radiocarbon dating.

Radioactive isotopes decay by first order kinetics and are characterized by a constant time period called the half-life; this is the time in which any radioactivity decays to half its initial value. The measurement of these half-lives requires careful control of instrumentation and errors are involved. In the past twenty years there has been a change in the measured half-life of carbon 14; Libby[2] used a value of 5568 ± 30 years, whereas the current[3] value is 5730 ± 40 years. There is a vast quantity of radiocarbon dates based on the Libby half-life, therefore this value is still used in calculations. It is easy to convert from one to the other; if a radiocarbon age based on the Libby half-life (5568 years) is multiplied by 1.029 this will give a radiocarbon age based on the 5730 year half-life.
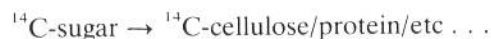
Carbon 14 is being continually produced by cosmic radiation and it is continually decaying by beta particle emission, therefore there is the possibility that it will reach some equilibrium in living matter and its concentration will remain constant with time. Let us consider how carbon 14 gets in to living matter.

The bulk of carbon in the atmosphere is present as carbon dioxide and the carbon 14 produced by cosmic rays would be rapidly oxidized to carbon (14) dioxide, and this would mix rapidly with the carbon (12, 13) dioxide in the atmosphere. Carbon is distributed in various compartments in the earth, the whole being in equilibrium; this relationship is known as the carbon cycle and is shown in Figure 1. The four major compartments, the atmosphere, biosphere, oceans and sedimentary rocks are shown in the square boxes. The figure in each box shows the total carbon content of the compartment in grammes. The compartments are linked by arrows which show the direction and mechanism of carbon exchange; the figure on each line shows the rate of exchange in grammes per year. From the diagram it can be seen that it takes about 100 years for the carbon content of the biosphere to be completely replaced once by photosynthesis of atmospheric carbon dioxide. This means that carbon 14 becomes uniformly distributed throughout the biosphere after about 100 years.
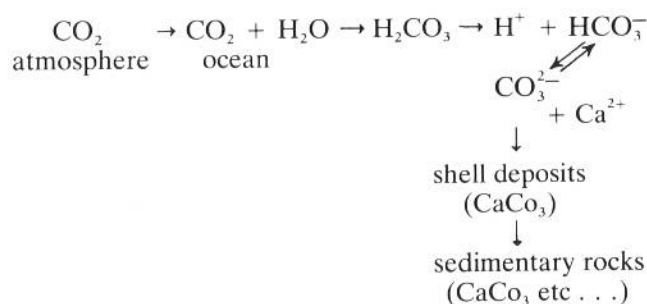
The overall mechanism of photosynthesis is:

$$6\ ^{14}CO_2 + 12H_2O \rightarrow\ ^{14}C_6H_{12}O_6 + 6O_2 + 6H_2O$$
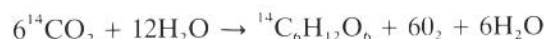
^{14}carbon dioxide + water → ^{14}C-sugar + oxygen + water

$$^{14}\text{C-sugar} \rightarrow\ ^{14}\text{C-cellulose/protein/etc} \dots$$

In the grazing food chain (there are other food chains in the biosphere) the plants are eaten by herbivores, herbivores by carnivores, and so ^{14}C-proteins become distributed in the biosphere. A similar argument can be applied to the oceans where after about 500 years the carbon 14 from atmospheric carbon dioxide would be uniformly distributed throughout the bicarbonate ions in the oceans. These bicarbonate ions are in equilibrium with carbonate ions which form the shells of marine animals and ultimately become limestone deposits.

$$CO_2 \rightarrow CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$
atmosphere   ocean

$$CO_3^{2-}$$
$$+ Ca^{2+}$$

shell deposits
(CaCo$_3$)
↓
sedimentary rocks
(CaCo$_3$ etc . . .)

On death the ^{14}C cellulose/protein/etc. is returned to the atmosphere as $^{14}CO_2$ by the process known as respiration:

$$^{14}C_6H_{12}O_6 + 6O_2 + 6H_2O \rightarrow 6\ ^{14}CO_2 + 12H_2O.$$
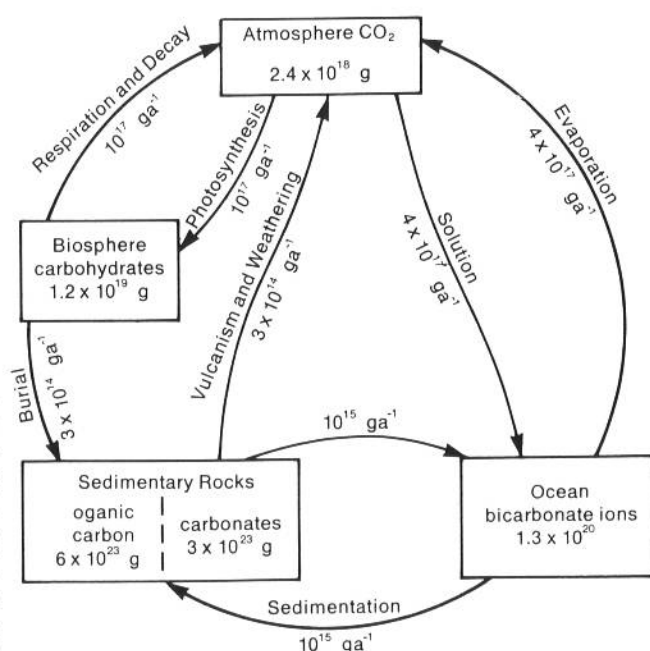

FIG. 1.   Carbon Cycle

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In some cases, example a tree, the process of respiration or decay is long compared with the half-life of ^{14}C. On death the tree no longer takes in $^{14}CO_2$ by photosynthesis, and since decay is slow the ^{14}C content of the tree will decrease by the known half-life of ^{14}C. If the radioactivity of the tree was known at death, and the radioactivity measured sometime later, then the time elapsed since death can be calculated. This is the principle of ^{14}C dating.

Several assumptions are involved in the application of this technique:

1. The ^{14}C content of living matter in antiquity was the same as at present.
2. This implies that cosmic rays had the same intensity in antiquity as now.
3. There is a constant rate of mixing and exchange between ^{14}C in the atmosphere, the biosphere and the oceans.

These concepts, originally proposed by Libby, have been found wanting in view of subsequent research, and it is now clear that there have been fluctuations in the cosmic ray intensity over the past 10,000 years.[4-8] Various reasons have been put forward for these variations, including variations in the geomagnetic dipole,[8] sunspot activity and variations in the mixing of atmosphere and marine reservoirs of ^{14}C. In an attempt to overcome these deficiencies calibration procedures were introduced.

Calibration of Radiocarbon Dates

To overcome the difficulties outlined above, various calibration procedures have been developed, most involving dendro chronology[9-17] and some involving Egyptian 'historical' dates.[18-22] The most popular method is to use tree-rings to establish the age of a piece of wood, and then to measure the ^{14}C content of that same piece of wood.[23] In this way a calibration curve is established as shown in Figs 2–5. Several such curves have been established and they all agree in principle, but differ in detail. It is this detail that disturbs the historian. These differences are discussed in more detail below with reference to Egyptian Dates. However, from the

FIG. 2.   Tree Ring Corrective Curve

beginning the results obtained for Egypt in the dynastic period from the radiocarbon method were not of much value in the reconstruction of Egyptian history.[24]

The reverse, that is the use of Egyptian chronology in calibrating radiocarbon dates should be possible and relies on the fact that the sequence should be correct at least. There is an interesting discussion of bristlecone pine corrections and Ancient Egypt by Clark.[25]

Historical Dates

Egyptian chronology has been established by the writings of classical authors, regnal years, astronomical data, and detailed archaeological studies. Psammetichus I was the founder of the 26th Dynasty and his dates were 664–610 B.C. on astronomical, Babylonian and Greek evidence. Since then the facts are taken to be those recorded by classical historians. In the second millenium B.C. astronomical records were used. The Egyptians used three calendars, one the original lunar calendar, one an official 365 day civil calendar, and a modified lunar calendar. The Egyptian contribution to measuring time was the 'Egyptian Year' of a fixed length of 365 days.[26] All other calendaric systems involved religious and political considerations or situations of complex astronomical reckoning. The year was divided into three seasons, akhet, peret and shemu each of agricultural origin (associated with the state of water in the Nile) and nothing to do with astronomy. Each season was divided into 4 months of 30 days, that is, 360 days in all plus five epagomenal days to complete the year.

For fixing time in the Egyptian Middle Kingdom a record of the heliacal rising of the star Sothis (Sirius) was valuable.[18,26,27] The heliacal rising of the star fell one day earlier in the Egyptian civil year every four years, after $4 \times 365 = 1460$ years it would have regained its original position in the civil calendar; this is known as the 'Sothic Cycle'. The Egyptians ignored leap year. According to Neugebauer[26] 'The "Sothic Cycle" of 1460 years can be explained as the result of connecting the agricultural year with a yearly recurring astronomical phenomenon, the heliacal rising of Sirius (Sothis), which roughly coincides with the beginning of the inundation (of the Nile), whereas the beginning of the schematic Egyptian year of 365 days was "wandering" through the course of time through all seasons'.

Censorinus, the Roman author, reports the heliacal rising of Sirius took place on the first day of the first month (1 Thoth) of the Egyptian civil year in A.D. 139, equivalent to 20 July in the Julian calendar.[28] The most ancient Egyptian record was for a heliacal rising of Sirius on the sixteenth day of the eighth month of the seventh year of a King. This King must have been Sesostris III of the XII Dynasty from documents in the same Archive. Thanks to the regular displacement of the civil calendar to the true astronomical year it is possible to count back from A.D. 139 and place the year in question at 1870 ± 6 B.C., with 1872 B.C. being most favoured.[27] Further details of these calculations are described elsewhere.[18] This puts the start of the reign of Sesostris III at 1878 B.C. as quoted.[24]

The Old Kingdom poses different problems. There are no recorded dates of heliacal risings of Sirius, and
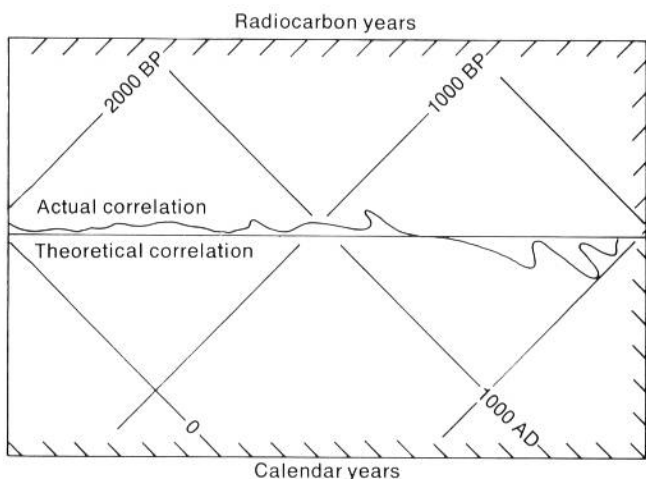
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dates are based on archaeological evidence and information gleaned from the Turin papyrus and the Palermo stone. The Turin document gives 143 years as the duration of the XI Dynasty and Sesostris III's predecessors (from 1870 B.C.) amount to 120 years in the XII Dynasty; the start of the XI Dynasty is about 2133 B.C. A large part of the X Dynasty was contemporaneous with the XI Dynasty and the IX Dynasty was very brief (a few decades), then the end of the Old Kingdom was about 2160 B.C.[24] Further, the Turin Canon of Kings gives the length of the Old Kingdom as 955 regnal years, which places the beginning of the Old Kingdom at about 3114 B.C.

Radiocarbon Dating and Egyptian Chronology

As outlined above the Egyptian chronology has been established with its own uncertainties. Even more difficult is to relate the artefact submitted for radiocarbon dating to that chronology. This in part can account for the disarray in the relationship between Egyptian chronology and C-14 dates. However, the technique is not blameless as inter-laboratory comparisons on the same sample have shown. This is not the place to present detailed arguments about the comparisons of C-14 and historical dates of Egyptian samples, this has been done by others. A very detailed list of Nubian and Egyptian samples has been presented,[22] and the general thesis is that the radiocarbon dates are useless to the historian. One must agree, although the reason is perhaps not as clear-cut as the author would suggest. It is the general view[22] that tree correction curves based on Californian redwoods and New Zealand kauri trees are different and that neither are relevant to Egypt for geographical reasons. This may well be true but the sequence should be valid. That some dates are too old and some too young is a cause for worry. Other authors[20,21] have questioned the provenience of some of the artefacts. In some cases,[24] particularly when wood and reed samples are chosen, the agreement between 'historical' Egyptian dates and 'corrected' radiocarbon dates is quite good. It is clear that there is still scope for a systematic study of artefacts with sound provenience from Egyptian collections. Perhaps this can be achieved with the new techniques which are being developed using a Tandem van de Graaff or a mass spectrometer.[30]

In conclusion, it is a personal view that absolute radiocarbon dates are of little value, but that establishing sequences and contemporaneity should be possible with some precision and both are of considerable value to the historian.

Experimental

The method described below is the one applied to the bones and bandages of Mummy 1770, but it is a general procedure for carbonaceous material. At each stage a discussion will be included giving reasons for the step and the possible sources of error.

Ideally about 5–10 g of carbon are required for each sample, the older the sample the lower the count rate and therefore the larger amounts of carbon are desirable. Clearly, the amount of sample required depends on its carbon content and for charcoal, wood and cloth weights of about 10 g are adequate. Bone is very different because the organic content can decrease with time, and this will depend very much on how the bone was stored either by the curator or in the archaeological site. It is advisable to determine the carbon content on a small sample before dating, and then the appropriate weight of sample can be taken. As a general rule this can require anything from 200–500 g of bone. In some cases it will be impossible to date bone samples by the radiocarbon method because although the bone has its original skeletal structure there will be no carbon left, the bone will be entirely inorganic, that is apatite (calcium phosphate).

The selection of the appropriate sample for dating is extremely important and requires close co-operation between the historian or archaeologist and the group who are making the measurement. It is essential that the sample be well documented, that is geographical co-ordinates, site of origin, layer (depth below the surface), and other appropriate information be recorded.

The sample is then pretreated, and this is a very critical stage. Ideally, the only carbonaceous material required is the ^{14}C organic material that was present in the sample at death, for example, collagen in bone or cellulose in wood. In Mummy material there is the real possibility that the bones and bandages have been impregnated with carbonaceous material of fossil origin, for example bitumen from the Dead Sea area (possibly used in embalming). Any of this present in the sample would reduce its specific activity and make the sample appear older than it really is. If samples of different origin are to be compared, as in the case of bones and bandages of Mummy 1770 (animal and plant origin), then purification is extremely important. Pretreatment can cause confusion if the sample is very heterogeneous, for example a sample of peat which contains wood, leaves and humic acids each of different origin and age; different pretreatments in different laboratories could select different components and hence give apparently different ages for the peat sample.

The widely used technique and the one adopted here was to soak the samples in dilute hydrochloric acid and sodium hydroxide alternately for several weeks each until no colour was extracted. In the case of the bone specimens the inorganic material was disintegrated by
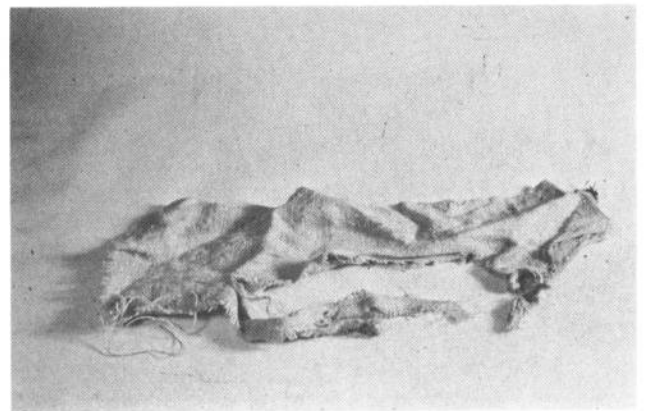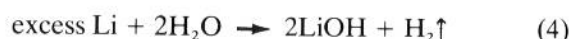

PLATE 1

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this procedure and the fibrous collagen remained — this was pale brown in colour. With the cloth and bandages, these retained their original form, but they were treated until white in colour. Plate 1. For wood samples cellulose was extracted by a procedure described by Rebello and Wagener.[31] All materials were air dried, and up to this stage required two to three months preparation.

The next stage of the procedure is to convert all the carbon in the air dried sample to benzene. The reaction scheme used by Barker[32] and also by Noakes[33] is the one employed in this project:

$$C + O_2 \rightarrow CO_2\uparrow \qquad (1)$$

$$2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O \qquad (2)$$

$$Li_2C_2 \rightarrow 2LiOH + C_2H_2\uparrow \qquad (3)$$

$$\text{excess } Li + 2H_2O \rightarrow 2LiOH + H_2\uparrow \qquad (4)$$

$$\text{and } Li_2O + H_2O \rightarrow 2LiOH \qquad (5)$$

$$3C_2H_2 \rightarrow C_6H_6 \qquad (6)$$

Apparatus A schematic diagram is shown in Figure 6. It consists of four parts:

1. The carbon dioxide inlet and trapping system,
2. the lithium furnace,
3. the acetylene trapping system, and
4. the benzene synthesis system.

The system is evacuated by a two stage rotary oil pump down to pressures of 10^{-2} mm Hg.

1. *The Carbon Dioxide System* The carbon is converted to CO_2, either by oxidation (with $KMnO_4$ in the case of oxalic acid) or by combustion in a tube furnace. The CO_2 is dried with Analar conc. sulphuric acid and trapped at liquid nitrogen temperature for the oxidation route and in $Ba(OH)_2$ for the combustion route. The $BaCO_3$ product is acidified and the CO_2 trapped at 77°K as above.

2. *The Lithium Furnace* This is shown in Plate 2. The reaction chamber is 2 litres capacity made from 5 mm thick stainless steel. The top one-third is provided with a cooling coil of soft ¼" copper tubing soldered on. The lower part is shielded with asbestos and heated with a bunsen burner.

3. *The Acetylene Trapping System* This consists of four cold traps, 2 conventional and 2 convoluted (Fig. 6) to prevent loss of solid C_2H_2.

4. *The Benzene Synthesis System* This is shown in Plate 3 and Figure 6. The acetylene is dried by passing through a large U tube containing phosphoric acid on glass beads. The apparatus also comprises a catalysis vessel and a small flask for the collection of the benzene product. Two requirements for the metal catalyst for benzene synthesis emerge from these studies:

1. It must contain cations of charge +5 or greater, and
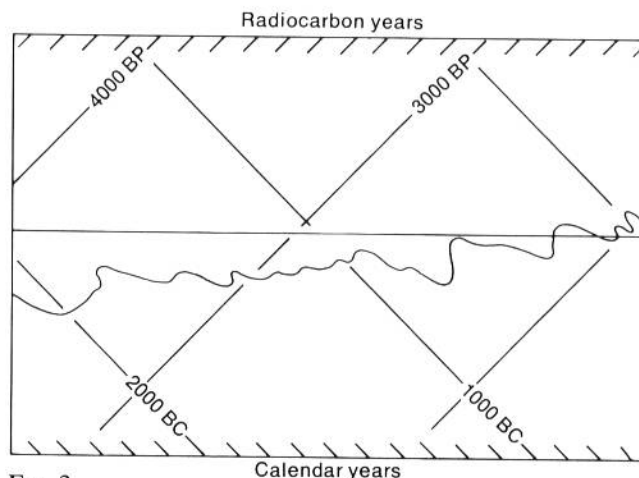2. the cations must be combined with a matrix of large surface area, greater than 200 m^2g^{-1}.
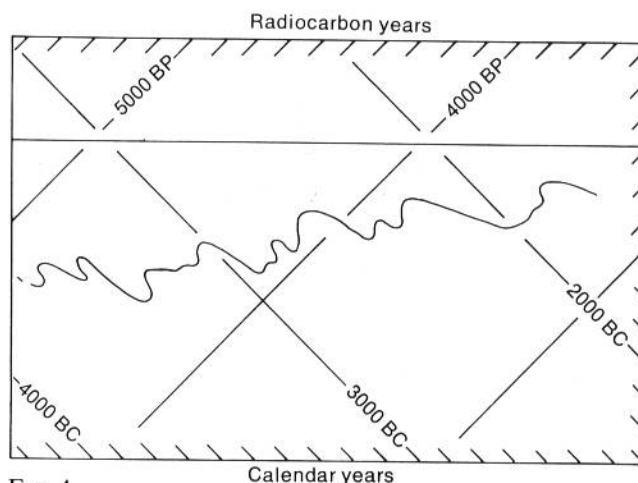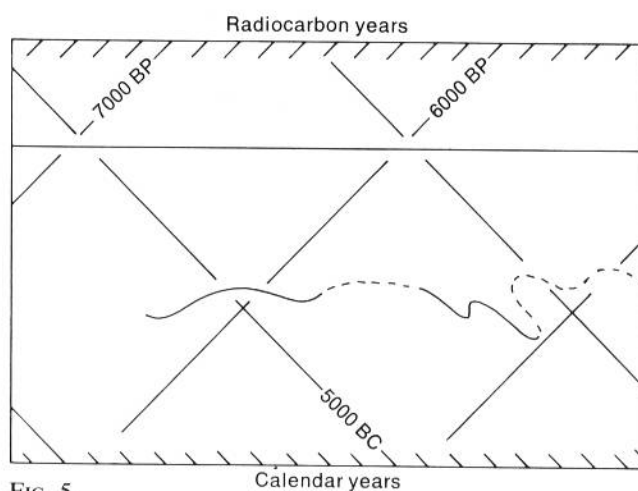
FIG. 3.

FIG. 4.

FIG. 5.

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The postulated mechanism of the reaction is a polarization of acetylene by the cation, and subsequent induced polarization of two other acetylene molecules. Angular rotation then makes the formation of a benzene ring possible.

The catalyst used in this project is based on vanadium in a silica-alumina support. The catalyst base consists of beads of $c.4$ mm diameter, and has the formula $Al_2O_3.Si_{16}O_{32}$. The activation procedure was as follows. The reagents used are: X g catalyst base, X/10 g V_2O_5 (G.P.R.), 2X ml H_2O_2 (100 vol.), and 4X ml distilled water. The vanadium pentoxide was weighed out and mixed with the water in a large beaker which was cooled in ice-water. Hydrogen peroxide was then added in small quantities (10–15 ml) at fifteen minute intervals. An unstable peroxy complex of vanadium (V) was formed and the solution gradually assumed a very intense yellow/red colour. After standing overnight, the solution was decanted into a large crystallising dish

PLATE 2

cooled in ice-water. The catalyst beads were poured in slowly to form a monolayer, and left for several hours. The solution was then poured off, and the beads washed several times with distilled water, and left to dry in air at room temperature for several days. They were then transferred to a screw-top bottle and stored ready for use.

Experimental Procedure

1. Preparation of the apparatus.
2. Combustion of the sample.
3. Formation of lithium carbide.
4. Dehydration of the catalyst.
5. Hydrolysis of lithium carbide.
6. Conversion of acetylene to benzene.
7. Distillation of benzene.
8. Counting procedure.

The whole process takes approximately twelve hours, and is conveniently done by carrying out steps 1–3 on one day, leaving the system overnight, and performing steps 4–7 the following morning.

1. *Preparation of the apparatus* The lithium needed for carbide formation was loaded into the furnace. The lithium used was supplied by BDH Chemicals Ltd. This was packed under liquid paraffin, and was washed five times with sodium-dried diethyl ether. A 50% excess of metal above the stoichiometric amount was used. The metal was spread evenly over the floor of the furnace chamber, and the system mounted and sealed. The entire vacuum system was evacuated and left overnight to check for leaks.

2. *Combustion of the sample* The preweighed sample (about 5 g C) was placed in the furnace and heated in air (purified from CO_2) to 1000°C, the air flow was then changed to oxygen and heating continued for about 80
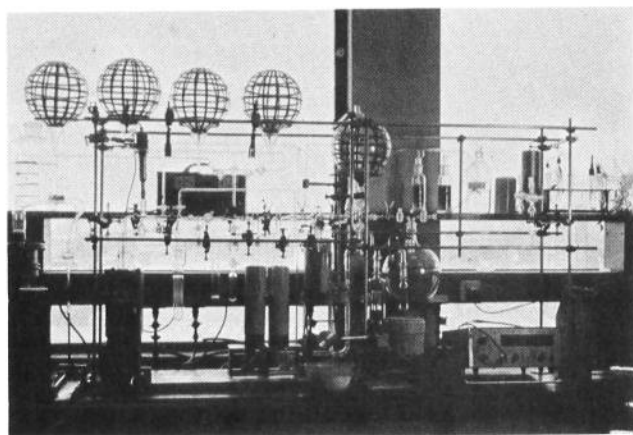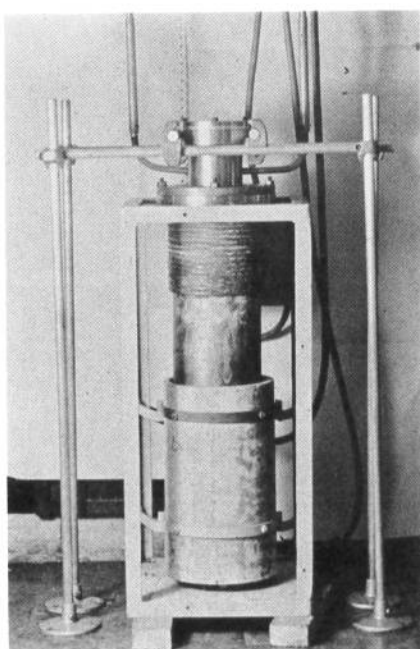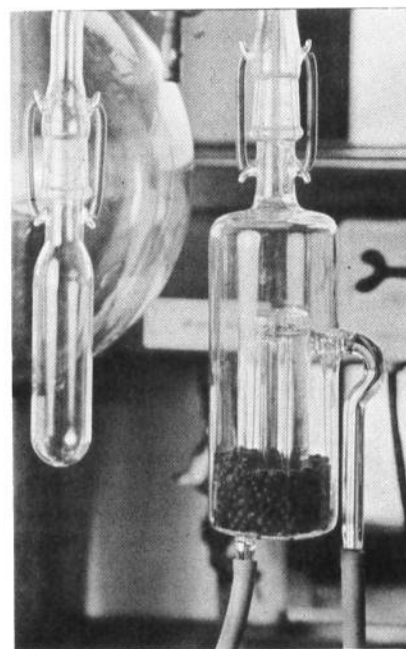

PLATE 3

PLATE 4

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minutes. The CO_2 was collected in initially CO_2 free $Ba(OH)_2$. The $Ba(OH)_2$ was acidified with 50% Analar HCl and the resulting CO_2 dried with sulphuric acid and collected in traps at 77°K. The whole process was carried out with a continuous flow of purified white spot N_2.

Carbon dioxide was evolved vigorously, carried into the vacuum system with nitrogen, and trapped out. Reaction was complete in approximately thirty minutes and the acid flow stopped. The reaction mixture was stirred briskly for a few minutes to ensure complete mixing of the sediment and acid, and to purge the mixture of dissolved carbon dioxide, and the cold-traps were then isolated. Nitrogen gas left in the system was slowly pumped off, and the traps isolated from the pump. The Dewar flasks on the second and third traps were removed and the traces of carbon dioxide that had accumulated in them allowed to evaporate into the first, main trap.

3. *Formation of lithium carbide* The lithium furnace was opened to the pump, and a swift flow of water through the cooling coil begun. Heating was commenced with a small flame, which was gradually increased. A considerable amount of gas was given off by the warm lithium. After approximately fifteen minutes the lithium could be seen glowing a very dull red and the pressure in the furnace was $3-4 \times 10^{-2}$ mm of mercury. Continuing the heating, the furnace was isolated from the pump, and opened, via the 3-way tap, to the carbon dioxide traps. The Dewar flask was removed, and carbon dioxide allowed to evaporate and diffuse over to the hot lithium. After about five minutes, the reaction began and the lithium glowed a bright red

colour. All the carbon dioxide evaporated after about forty-five minutes, and the pressure over the whole system, as monitored by the mercury manometer, had reached 2–3 mm.

After one hour, the furnace was opened to the pump; a brief increase in pressure registered on the Pirani gauge. Pumping was continued for ninety minutes, keeping the furnace at reaction temperature. This was done to remove any radon present which might otherwise contaminate the sample. The furnace was then isolated, heating stopped, and the reaction chamber allowed to cool overnight while still maintaining a flow of water through the cooling coil.

4. *Dehydration of the catalyst* Prior to hydrolysis, the catalyst must be dehydrated and left in vacuo ready for reaction. The quantity used was 5 g activated catalyst per litre of acetylene; this was roughly weighed out and loaded into the catalysis vessel. A vacuum was pulled, and the vessel heated to 350°C with a small tube furnace which can be raised round the lower half of the vessel, controlled by a 2 amp. Variac. Water vapour was pulled off and the Pirani gauge showed a slow decrease in pressure. At $c.10^{-2}$ mm of mercury (usually after one hour), heating was stopped and the catalysis vessel isolated and allowed to cool.

5. *Hydrolysis of lithium carbide* The furnace was opened to the pump via the acetylene traps, and Dewar flasks placed round the second, third and fourth traps. The aspirator was filled with $c.4$ l. of distilled water, and hydrolysis begun by allowing a very slow trickle of water into the furnace. A very violent reaction proceeded, and
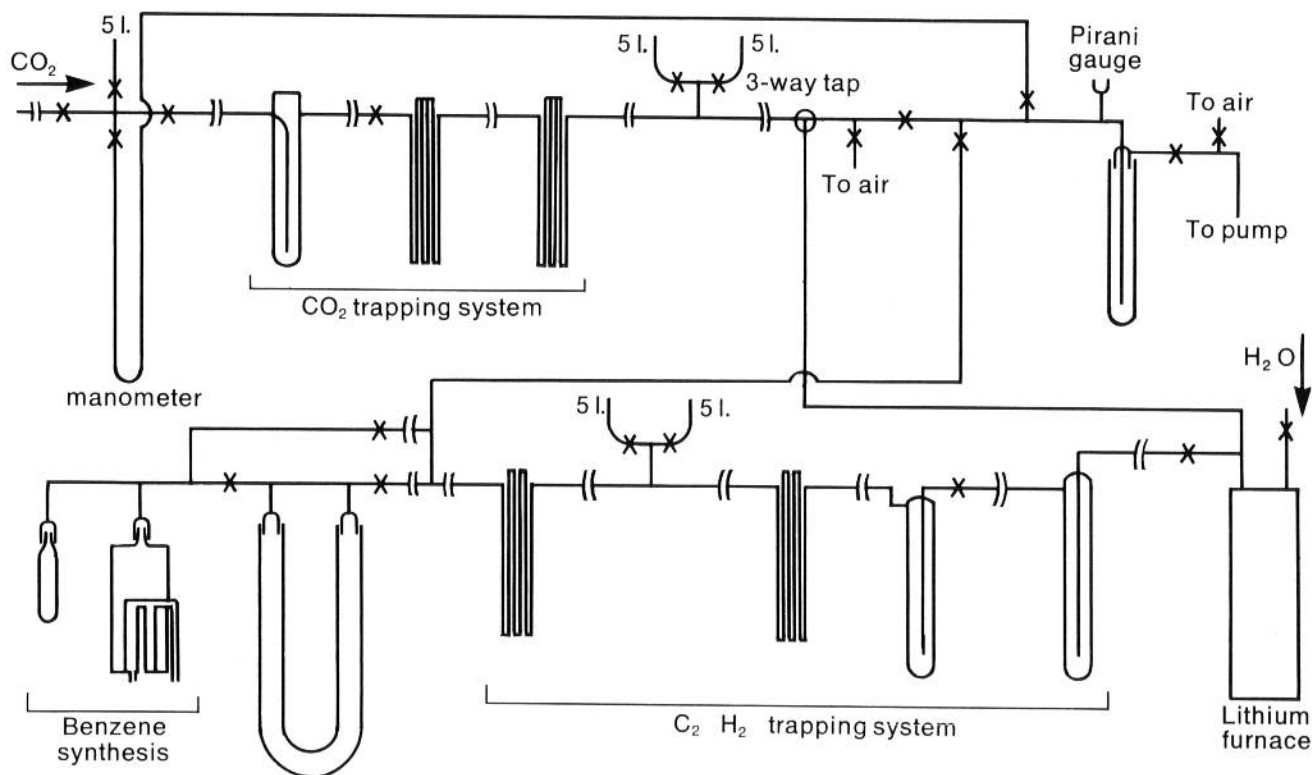

FIG. 6. ^{14}C Vacuum Apparatus

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excessive frothing could be seen through the viewport. The reaction took about thirty minutes to complete, using c.1.5 l. of water. As the reaction proceeded, the flow of water was gradually increased so as to provide an adequate volume; if a high yield is to be obtained from the reaction, it is necessary to have the solution after hydrolysis as dilute as possible. Throughout the reaction, water was circulated through the cooling coil and the base of the furnace was also cooled with a bath of ice-water.

When gas was either not being evolved, or evolved very slowly, as indicated by the Pirani gauge, the acetylene traps were isolated from the furnace and hydrogen left in the system pumped away. The traps were then isolated from the pump, and all the acetylene distilled into the second trap.

6. *Conversion of acetylene to benzene* The polymerization reaction goes at room temperature but evolves considerable heat; consequently the catalysis vessel was cooled with a swift flow of water through the inner jacket, and also on the outside with a 1.5 l. beaker containing an ice/water mixture.

The catalysis vessel was opened to the acetylene traps via the U-tube containing phosphoric acid by opening the relevant taps on either side of the tube, and the Dewar flask was removed from the second trap. Acetylene evaporated and diffused on to the catalyst through the phosphoric acid column. The phosphoric acid removes water, some of which was always carried over into the acetylene traps during hydrolysis, and ammonia which originated from traces of nitrogen left in the carbon dioxide traps before carbide formation, presumably forming ammonium phosphate.

The reaction was allowed to proceed for one hour, and the catalysis vessel was then isolated.

7. *Distillation of benzene* Benzene produced in the last reaction remains adsorbed on the catalyst. It was distilled off in a similar manner to the catalyst dehydration process, but at a temperature of 150°C, and collected in the small trap adjacent to the catalysis vessel under liquid nitrogen. After one hour, heating was stopped and the system opened up to air. The benzene trap was quickly removed, and any silicone grease round the cone joint taken off with a Kleenex medical wipe.

Difficulties of development of the process Considerable difficulty was encountered during construction of the apparatus and development of the process; most of this was due to the fact that the apparatus was built on a very small scale, and that the chemical reactions involved are extremely vigorous (e.g. the hydrolysis of lithium carbide). This means that the reactions have to be carried out at a carefully controlled rate to avoid problems of excessive pressure. The oxidation ahd hydrolysis stages are examples of this; unless done at the correct rate, there is a danger of carbon dioxide and carrier nitrogen venting through the separating funnel in the former, and similar venting of acetylene and hydrogen through the aspirator in the latter case. If hydrolysis is carried out too quickly, there is also the problem of excessive frothing causing a lithium carbide/water/gas mixture to enter the acetylene trapping system; for this reason the first trap after the furnace was not provided with a Dewar flask, but left clear to act as an emergency reservoir.

The second major problem was that of a low yield in the reaction

$$3C_2H_2 \rightarrow C_6H_6$$
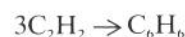
Vanadium catalysts similar to the one used are known to be highly efficient but yields of only 50% or less were initially realised. This was found to be due to the two 5 litre reservoirs which were originally included in the acetylene system during catalysis; later these were isolated, so that the only residual volume was that formed by the cold-traps and the part of the benzene synthesis system not occupied by the catalyst. Acetylene then evaporates and diffuses on to the catalyst at a much higher pressure. Yields of over 80% were realised once this technique was adopted.

The lifetime of the catalyst was not specifically studied. No deterioration in efficiency was noted when performing subsequent runs with the same batch however, in fact if anything there was a slight increase in efficiency.

8. *Counting Procedure* Immediately the frozen benzene had liquefied it was transferred to a 20 ml polythene low background scintillation vial containing 10 ml scintillator solution ready for counting. The benzene yield was obtained by weight. The scintillator was the commercial preparation 'Lipoluma', manufactured by Lumac Systems A.G., Aeschengraben, 6 CH-4051, Basel.

The samples were counted in a Searle Model 6880 Mark III liquid scintillator counter in the following sequence, Background, NBS oxalic acid, in-house ^{14}C benzene standard, sample 1 . . . sample 6, in-house ^{14}C benzene standard, Background. The samples were counted for 10 min. each and cycled until the appropriate statistics were obtained.

Results and Discussion

The count rates of the various samples and controls are shown in Table 1.

TABLE 1

Count Rates of Samples and Controls

Sample	Count rate (cpm)
NBS oxalic acid 1	13.44 ± 0.16
1770/469 R. Scapula	9.14 ± 0.20
1770 L. Scapula	9.09 ± 0.19
1770 Outer bandage	10.55 ± 0.16
1770 Part 4 bandage	10.40 ± 0.17
NBS oxalic acid 2	13.43 ± 0.16
In-house oxalic acid	13.50 ± 0.16
In-house benzene	13.60 ± 0.16

$^{12}C/^{13}C$ ratios were done on some of the samples, these are given in Table 2.

TABLE 2

$^{13}C/^{12}C$ Ratios of Samples and Controls

Sample	$^{13}C/^{12}C$ Ratio	$\delta^{13}C^{\circ}/oo$
NBS oxalic acid	1.107×10^{-8}	-15.1
In-house standard oxalic acid	1.106×10^{-8}	-16.2
1770/469 R. Scapula	1.095×10^{-8}	-26.0
1770 Part 4 bandage	1.096×10^{-8}	-24.3
Belemnite standard (PDB)	1.12372×10^{-8}	—

The results were calculated as follows:

The radioactive law of decay gives

$$\frac{dN}{dt} = -\lambda N \qquad \ldots (1)$$

where N is the no. of radioactive atoms remaining at time t and d is the decay constant for the particular isotope.

$$\lambda = \frac{.693}{t_{1/2}}, \text{ and } \tau = \frac{t_{1/2}}{.693}$$

$$\therefore \frac{1}{\lambda} = \tau$$

In the case of ^{14}C:

$t_{1/2}$	λ yrs.	τ yrs.	
5568 ± 30	1.245×10^{-4}	8035	(Libby)
5730 ± 40	1.210×10^{4}	8267	

On integration of equation 1 and substituting

A (activity) $= \frac{dN}{dt}$, then

$$A = A_o e^{-\lambda t}$$

A = activity at time t,

A_o = activity at some original time,

$$\therefore \log_e \frac{A_o}{A} = \lambda t.$$

$$\text{and } t = \tau \log_e (A_o/A) \qquad \ldots (2)$$

This enables the age of a sample (t yrs) to be determined from the carbon 14 count rate at death A_o and the carbon 14 count rate at present A.

Initially it is assumed that the radioactivity of the sample at death was the same as modern ^{14}C radioactivity. The widely used reference is NBS oxalic acid, although because it is a recent preparation it contains some activity from weapons testing. The generally accepted[30] ^{14}C radioactivity standard is $0.95 A_{ox}$ ($A_{ox} = ^{14}C$ radioactivity of NBS oxalic acid).

Therefore $A_o = 0.950 A_{ox}$.

(The factor 0.950 arises because 1890 oak wood — occurring early in the industrial revolution and before weapons testing — has 95% ^{14}C radioactivity of NBS oxalic acid.)

A small correction is applied for the decay of ^{14}C in NBS oxalic acid between the time of preparation

(1 January 1958) and the time of use. In this case this was twenty years and the correction factor is:

$$A_o = 0.950 A_{ox} e^{\lambda t}$$

$$= 0.950 A_{ox} e^{1.210 \times 10^{-4} \times 20}$$

$$= 0.950 A_{ox} 1.00242$$

$$\underline{A_o = 0.9523 A_{ox}} \qquad \ldots (3)$$

Results are often quoted as the difference between the sample activity and the modern reference activity.

$$\delta^{14}C \text{ is defined as } \left\{ \frac{A_{sample}}{A_o} - 1 \, 1000 \right\} \qquad \ldots (4)$$

$$\therefore A_o/A_{sample} = \frac{1000}{\delta^{14}C + 1000}$$

$$\text{and } t = \tau \log_e \frac{1000}{\delta^{14}C + 1000} \qquad \ldots (5)$$

From equations 2, 3 and 5 the ages and ^{14}C values were calculated for the samples using the count rates given in Table 1:

TABLE 3

Ages of 1770 samples

Sample	$\delta^{14}C$	Age (yrs BP)	Age
1770/469 R. Scapula	-285.6	2780 ± 180	822 BC
1770 L. Scapula	-289.5	2826 ± 173	868 BC
1770 Outer bandage	-175.4	1594 ± 126	364 AD
1770 Part 4 bandage	-187.1	1713 ± 135	245 AD

$(A_o = 0.9523 A_{ox} = 12.794 \text{ cpm})$

These dates quoted earlier[31] ignore isotope fractionation in the preparation of CO_2 from the sample and oxalic acid. This can be mentioned by using the more abundant ^{13}C isotope measured mass spectrometrically on a sample of the CO_2.

By definition:

$$\delta^{13}C = \left\{ \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{std}}{(^{13}C/^{12}C)_{std}} \right\} 1000$$

The enrichment of ^{13}C due to isotope fractionation is only half that of ^{14}C.

$$\left\{ \frac{A_{ox(N)} - A_o}{A_o} \right\} 1000 = -2\delta^{13}C \qquad \ldots (6)$$

Ox(N) $= A_o$ (meaning as before) corrected for isotope fractionation. Factor of 2 for reason above, — sign because ^{14}C activity must be increased due to loss of ^{13}C by fractionation.

The reference standard used is usually PDB calcium carbonate. This is a Cretaceous belemnite (Belemnitella

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americana) from the Peedee formation of South Carolina. As seen from Table 2 PDB has a $^{13}C/^{12}C$ ratio of 1.12372×10^{-8}. Several measurements of NBS oxalic acid have shown that it has a $^{13}C/^{12}C$ ratio of 1.1015×10^{-8} giving a $\delta^{13}C$ value of $-19.77°/oo$. From equation (6)

$$A_{ox(N)} = A_o \left\{ 1 - \frac{2(19.77 + \delta^{13}C_{ox})}{1000} \right\}$$

In the present work $\delta^{13}C_{ox} = -15.1°/oo$

$$\underline{A_{ox(N)} = 12.675 \text{ cpm.}} \quad (A_o = 12.794 \text{ cpm})$$

A new set of ages of 1770 samples are given in Table 4 based on isotope fractionation in oxalic acid alone.

TABLE 4

1770 ages allowing for fractionation in NBS oxalic acid

Sample	Age (BP yrs)	Age
1770/469 R. Scapula	2702	744 BC
1770 L. Scapula	2748	790 BC
1770 outer bandage	1517	441 AD
1770 Part 4 bandage	1635	323 AD

In addition to fractionation in the oxalic acid there is also the possibility of fractionation in the sample.

By definition:

$$\delta_s{}^{13}C°/oo = \left\{ \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)PDB} - 1 \right\} 1000$$

$$\Delta^{14}C°/oo = \delta^{14}C - (2\delta^{13}C + 50)\left(1 + \frac{\delta^{14}C}{1000}\right)$$

(The value of 50 appears because it has been shown that nineteenth-century woods have a $\delta^{13}C$ value around $-25°/oo$. Therefore the $\Delta^{14}C$ will fall close to zero if this constant is included.)

$$\Delta^{14}C = \delta^{14}C \text{ if there is no isotope fractionation.}$$

The age can be calculated from equation (5) if $\Delta^{14}C$ is substituted for $\delta^{14}C$. This has been done in Table 5 where a new set of dates have been calculated allowing for fractionation in both the sample and the oxalic acid.

TABLE 5

1770 Ages allowing for isotope fractionation

Sample	$\delta^{14}C$	$\Delta^{14}C$	Age BP	Age
1770/469 R. Scapula	−278.9	−277.5	2687	729 BC
1770 Part 4 bandage	—179.5	−180.6	1647	311 AD

The radiocarbon ages are shown in Table 6.

TABLE 6

1770 Radiocarbon ages

Sample	No fractiona-tion	Oxalic fractiona-tion	All fractiona-tion
1770/469 R. Scapula	822 BC	744 BC	729 BC
1770 L. Scapula	868 BC	790 BC	—
1770 outer bandage	364 AD	441 AD	—
1770 Part 4 bandage	245 AD	323 AD	311 AD

Finally, it is necessary to consider the variation in ^{14}C activity in the last 2000–3000 years. This can be done with reference to the tree ring correction curve of MASCA[16] shown in Figs 2–5.

The corrected values are shown in Table 7.

TABLE 7

1770 Dates with tree ring corrections[16]

Sample	Corrected for fractionation	Tree-ring Correction
1770/469 R. Scapula	744 BC	900 BC
1770 L. Scapula	790 BC	1100 BC
1770 outer bandage	441 AD	441 AD
1770 Part 4 bandage	323 AD	323 AD
On average bones	~ 770 BC	1000 BC
bandage	~ 380 AD	380 AD

The conclusion is clear that the bones appear older than the bandages, and this conclusion is independent of any corrections. It is possible that the bones contain more organic carbon of fossil origin, example bitumen from the Dead Sea area which could have been used in the mummification process. However, because of the careful pretreatment of the samples we consider this unlikely. The remaining conclusion is that the body was wrapped or rewrapped in bandages some considerable time after death.

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