

Chapter XI

Age determinations based on radioactive phenomena

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1. INTRODUCTION

Very soon after the discovery of radioactivity it appeared that the exponential decay kinetics of a radioisotope could be considered as a clock that would allow the evaluation of the age of a particular sample. The age of rocks, of the earth itself and even of the moon may be calculated from measurements of the ratio between the amounts of parent nucleus and daughter product present. For example, the elements of the uranium series decay by emission of alpha particles ; the latter are trapped as helium atoms as soon as the material has crystallized. Argon generated by the ^{40}K radioisotope of potassium undergoes the same fate. The accumulation yield of helium and/or argon is a function of the time elapsed since the solidification process.

More radiochemical dating techniques have been discovered during the second half of this century ; they are based on the decay of carbone-14 or lead-210, or on the magnitude of the damage that has been created in a material that has been exposed to radiation.

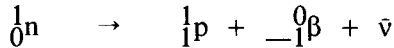
2. THE CARBONE-14 METHOD

It was while working in the frame of the Manhattan Project during World War II that W.F. Libby imagined a method of dating of samples of more archaeological and historical interest. He was able to concretize his ideas in 1949, giving birth of the now popular ^{14}C method, applicable to remains of living beings.

2.1. Principles of the ^{14}C method

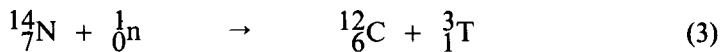
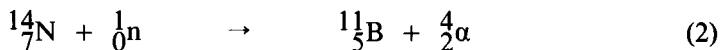
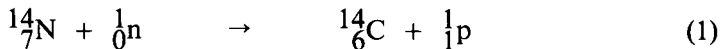
Cosmic radiation, the origin of which has remained the object of many speculations, is composed of very energetic nuclear particles, ranging from protons to iron nuclei and electromagnetic radiation. When in contact with the higher earth atmosphere this 'primary' cosmic radiation may induce several interactions and undergo numerous alterations. This 'secondary' cosmic radiation contains free neutrons. In a cone going out from its apex at the centre of the earth and having a cross section of 1 cm^2 at the earth surface, the number of neutrons present would be about 2.4. As due to magnetic effects on cosmic radiation the distribution of neutrons is not perfectly homogeneous and shows a larger concentration at a height of 15.000 m and at a latitude of 50° .

Neutrons are themselves unstable and may undergo radioactive decay, with emission of a beta particle and an anti-neutrino, being thus converted into protons :



The half-life of a neutron at rest is 10.8 minutes.

Neutrons are however also rather reactive species, since because of their absence of charge they may easily enter a nucleus and provoke nuclear reactions. When in air (80 % nitrogen, 20 % oxygen), the probability of absorption by a nucleus exceeds decay. It may therefore be concluded that a great majority of the secondary cosmic ray neutrons will be captured before the decay event occurs. The resulting nuclear reactions are the following :



Reaction (1) is the most probable to take place as its reaction cross section (measure of the probability) is 1.7 barns. Reactions (2) and (3) occur with high energy neutrons only (higher than 1 MeV and 4 MeV resp.) and have cross sections of 0.1 and 0.01 barn only. Neutron capture by oxygen is far less probable.

Most neutrons generated in the secondary cosmic radiation will thus transform nitrogen into ^{14}C , a radioactive nuclide with a half-life of 5730 years. Knowing the neutron flux (2.4 per second and per square centimeter of earth surface) and the surface of the earth ($5.1 \times 10^{18}\text{ cm}^2$), it is possible to calculate a production yield of $1.22 \cdot 10^{19}$ nuclei of ^{14}C per second. (i.e. about 9 kg per year). Production and decay have been going on for hundreds of thousands of years, so that a secular equilibrium is reached.

The total radioactivity due to ^{14}C is thus constant and amounts to

1.22×10^{19} becquerel (1 becquerel = 1 disintegration per second) ; this activity corresponds to the presence of only 74 tons of ^{14}C spread all over the earth.

The ^{14}C atoms are born, 'naked', in a chemically highly excited state and surrounded by air. They will therefore be burnt and transformed into carbon dioxide, $^{14}\text{CO}_2$. Primarily formed mainly in the higher atmosphere, this $^{14}\text{CO}_2$ will mix with regular inactive $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ to which it is chemically identical. The most severe calculations predict that a homogeneous distribution of $^{14}\text{CO}_2$ is reached after a few decades and certainly within a few centuries. All of the carbon dioxide present contains ^{14}C , up to a specific activity of 0.23 becquerel or 14 disintegrations per minute per gram of carbon.

Carbon dioxide is one of the main materials for the photosynthetic construction of the biomolecules. All living vegetal matter which is in dynamic equilibrium with the surroundings will possess a specific ^{14}C activity of 14 d/min. As the animal reign is also in equilibrium with the vegetal reign, an identical specific activity is to be ascribed to all living beings : each gram of 'living carbon' suffers 14 disintegrations per minute.

Death means rupture of the equilibrium between the organic material and its environment. The biomolecules are gradually destroyed but they are no longer replaced by new ones. No new ^{14}C is taken up by a dead body and the ^{14}C which remains present is decaying with its proper half-life of 5730 years. The specific radioactivity decreases as a function of time, as represented in Fig. 1.

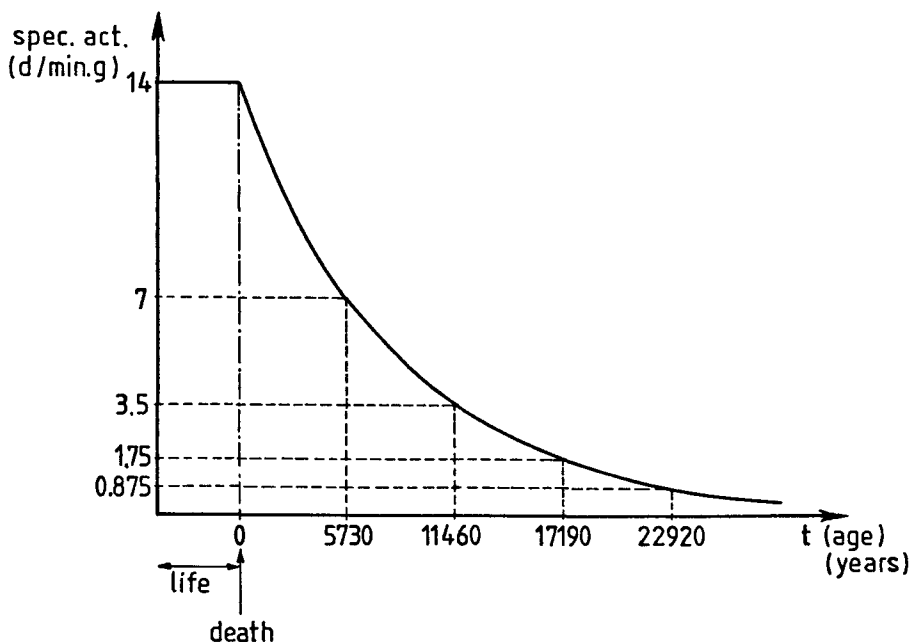


Fig. 1. Specific activity as a function of time.

The measurement of the remaining specific activity provides the age of the sample, i.e. the time which has elapsed since the death of the living organism.

In principle, the ^{14}C method is applicable to all organic remainders which may be considered as kept as a closed system from the death of the living being onwards. The condition of a closed system requires that all exchange reactions with the outside world may with certainty be excluded. Age determinations of samples of 30,000 to 35,000 years old are then quite feasible.

2.2. Experimental techniques

While the bases of ^{14}C dating seem sound and simple, the technical application of the method implies two major difficulties.

a) The energies of the β -particles emitted by ^{14}C nuclei are distributed over a broad spectrum with a maximum of 156 kiloelectronvolts (keV). This means that the most probable energy amounts to about 40 keV only ; such β -particles are very easily stopped even by very thin absorbers and only few of them are able to cross the end window of any gas filled counter. It then becomes evident that the sample has to be introduced inside the counter. It was soon proved that the use of a solid sample then leads to an unacceptable irreproducibility. The only solution is to use the sample itself as a counting gas in a proportional counter. Counters are filled with either carbon dioxide, methane, or even acetylene, which has been synthesized from the carbon contained in the sample. At atmospheric pressure and room temperature one gram of carbon produces about two liters of carbon dioxide or methane, or about one liter of acetylene.

b) As the background β -activity, due to presence of environmental traces of radioisotopes and cosmic radiation, is high, especially when large counters are used, the ^{14}C activity, ranging from a hardly detectable 0.2 to a maximum of 14 disintegrations per minute and per gram of natural carbon, becomes undistinguishable. Radioactivity is a statistical phenomenon and the error on any measurement may, according to the Poisson equation, be evaluated as the square root of the number of disintegrations recorded. A typical background radiation of 400 disintegrations per minute should in fact be understood as

$$400 \pm \sqrt{400} = 400 \pm 20$$

It is clear that the addition of a trace of ^{14}C yields a supplementary activity, which, drowned in the background, has lost any quantitative significance.

Background activities can be lowered by an appropriate shielding, made of old lead, in which all natural radioactivity has decayed, or mercury, or an

appreciable thickness of pure iron. But this shielding is not yet capable of reducing the background to a sufficiently low level.

These difficulties have been overcome by the use of a central proportional counter surrounded by a ring of an odd number of smaller counters. The set-up is connected to an electronic 'gate' system. Fig. 2 schematizes a cross section of the counter device. Any radiation from the outside necessarily crosses a ring counter before entering the main centre counter which contains the sample gas. The gate technique functions so that, whenever a peripheric counter is triggered, the central counter does not respond for some tens of microseconds and does not register the entering radiation. The background noise is lowered to only a few (1 to 4) pulses per minute and ^{14}C radiation now emerges in a satisfactory way.

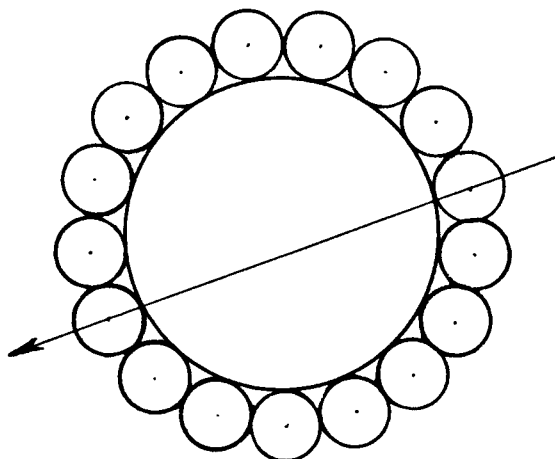


Fig. 2. Cross section of the counter assembly.

Proportional counters of one or two liters are used under a pressure of one to three atmospheres. The anodic dread is kept at a well stabilized potential of several tens of thousands of volts. The electronic device enables discrimination of pulses which might be originated by particles emitted by traces of radon.

As mentioned before, the sample is in the form of carbon dioxide (CO_2) or methane (CH_4). Acetylene (C_2H_2) is attractive, as it contains twice as much carbon for an identical volume; yet it is far less used because of explosion hazards. A counting gas must be of high purity and must be totally free of any electronegative impurities, as the latter may cause a spontaneous discharge in the counter. A satisfactory result is reached by the following treatment, which is, within slight modifications, generally applied.

Organic samples (wood, peat, charcoal) are burnt during a two-step process. The samples are placed in a double walled quartz tube which has been

previously evacuated. Under moderate heating the more volatile substances are allowed to evaporate and burn when in contact with pure oxygen which has been led between the two walls, in order to avoid explosion. When the flame is out, oxygen is carried over the sample itself for complete combustion. The gases flow through an oven, at 700° C, containing copper oxide, which transforms possibly present carbon monoxide into the desired dioxide. All carbon is thus quantitatively converted into carbon dioxide.

Inorganic samples (shells, carbonates) are treated with hydrogen chloride, and carbon dioxide is released.

CO₂-gas is purified in a series of steps :

- Halogens and their gaseous compounds are retained on silver wool at 400°.
- A trap at -80° C (solid CO₂ + acetone) eliminates water.
- Bubbling through an acid permanganate solution oxidizes sulfur dioxide into trioxide which dissolves as sulfuric acid ; also nitrogen oxides are removed.
- Two more traps at -80° C remove the last traces of water.
- At -182° C (liquid oxygen) carbon dioxide is solidified while nitrogen and oxygen are pumped off.
- Last traces of oxygen and nitrogen oxides are fixed on metallic copper at 450° C.
- Carbon dioxide is again condensed at -182° C.

Whenever methane is used, the carbon dioxide gas is mixed with an excess of hydrogen at 350° C on a nickel catalyst which is fixed on a porous substrate. Repeated recycling allows a conversion yield of better than 99 %. Purification of methane involves the following steps :

- Water, produced during the reduction reaction is trapped at -80° C.
- The excess hydrogen is oxidized by copper oxide at 300° C.
- The resulting water and the non reacted carbon dioxide are trapped at -195° C (liquid nitrogen).
- Methane is adsorbed at -195° C on silica gel, while the last traces of hydrogen are evacuated.

Methane has now the required purity and is ready to be transferred into the counter.

Some samples require a pretreatment with sodium hydroxide in order to remove all contamination by, for instance, humic acids.

The background noise has to be measured in exactly identical conditions as the sample activity, but in absolute absence of ¹⁴C atoms. This is realized by using methane synthesized from anthracite, which, with its millions of years of age, is old enough so that one is assured that originally present ¹⁴C has totally decayed.

The number of pulses recorded is not necessarily equal to the number of disintegrations that actually occur in the counter : some β -particles may vanish into the counter walls without triggering the electronic system, others may be emitted during the dead time imposed by the anticoincidence gate device and are not registered, simultaneous decays appear as one single pulse. It is therefore necessary to evaluate the counting efficiency, by measuring the number of pulses created by a sample of accurately known activity. Living wood with its constant specific activity seemed an ideal probe for this purpose.

The exponential decrease of radioactivity as a function of time is described by the classical equation :

$$A_t = A_0 e^{-\lambda t} \quad (1)$$

where A_t = present activity of the sample

A_0 = activity of living organic material

λ = decay constant = $\frac{\ln 2}{T} = \frac{0,693}{5730} \text{ year}^{-1}$

t = age = time elapsed since death.

The number of registered pulses per unit time, p , is related to the activity by a constant factor (integrating efficiency and geometry coefficients), so that equation (1) may also be written as

$$p_t = p_0 e^{-\lambda t} \quad (2)$$

It follows that the age is calculated as

$$t = \frac{5730}{0,693} \ln \frac{p_0}{p_t} \quad (3)$$

or

$$t = \frac{5730}{0,693} \ln \frac{p_L - p_A}{p_S - p_A} \quad (4)$$

where p_L = number of pulses per unit time for living wood

p_A = number of pulses per unit time for anthracite (background)

p_S = number of pulses per unit time for the sample.

In order to provide statistically meaningful results, countings should last 48 hours, and each sample measurement should be bracketed by long recordings of background noise and efficiency verification. In this way the reliability of the apparatus is constantly checked. It is also advisable that pulse rates are recorded at regular time intervals (e.g. every 30 minutes), so that abnormal fluctuations can immediately be detected. Samples are counted at least twice, at two to three weeks interval, to make sure that they have not been contaminated by any short lived activities (e.g. radon or its filiation products).

2.3. Correction of systematic errors

2.3.1. Inhomogeneity of ^{14}C distribution

Soon after the discovery of the ^{14}C method, intercomparison experiments were undertaken in a large number of laboratories spread all over the world. This led to the disturbing fact that results from identical samples showed a most peculiar scatter. When treated in a laboratory situated in large industrial cities the samples appeared younger than when they were measured in a research centre located in a more rural environment.

Hans E. Suess discovered that this discrepancy was to be attributed to the combustion of large amounts of fossile fuel in large cities and factories, thus causing localized inhomogeneities of the ^{14}C distribution in recent wood samples used for determination of the counter efficiency. In cities the photosynthesis is performed with carbon dioxide which has a lower ^{14}C content. This is verified by the ^{14}C concentration gradient which is observed in wood samples taken from trees at increasing distances from city centres or from industrial zones.

The error thus induced is easily avoided by choosing as a young standard a sample of wood of a known age of some 200 years old, i.e. dating from before the start of the industrial expansion. The same precaution also avoids present interferences of the artificial increase of ^{14}C in the atmosphere caused by the nuclear explosions of the last decennia.

2.3.2. Constancy of the cosmic ray intensity

One of the requirements for the precision of ^{14}C dating was that constancy of the cosmic ray intensity has always been assumed. Cosmologists have however proof that considerable fluctuations are provoked by changes

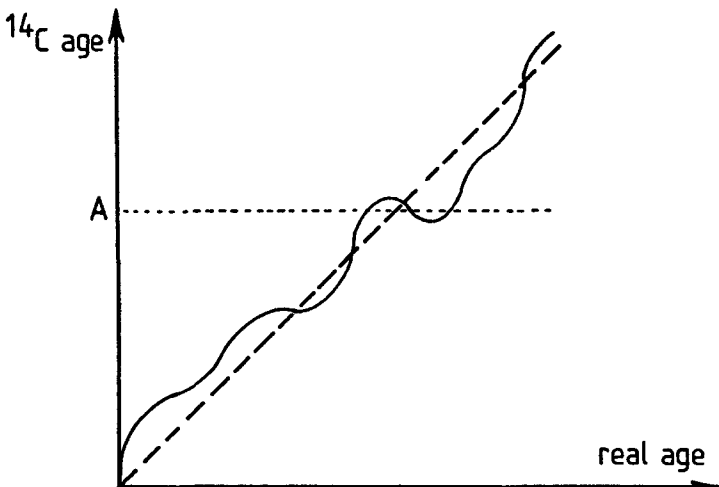


Fig. 3. Fluctuations of ^{14}C activity vs age.

of the magnetic field of the earth. Variations of the palaeomagnetism have become evident and solar cycles have also an influence. Accurate measurements of the ^{14}C content in tree rings of very old trees are available that allow corrections for the past few thousand years. Fig. 3 shows the potential deviation between an uncorrected ^{14}C age and the real age.

The precise knowledge of this kind of curve over the total interval of time for which the ^{14}C method is applicable would overcome all errors, except for a few cases as the sample noted 'A' for which three real ages may be extrapolated. At the present state it may still be affirmed that the uncertainties to which the non-constancy of cosmic radiation gave rise are still relatively small and are in most cases of the same order of magnitude as the statistical errors which are discussed further below.

2.3.3. Exchange reactions during storage time

It is evident that the ages obtained by the ^{14}C method would be totally erroneous if exchange reactions occurred during the storage time of the samples. If the original carbon has been gradually replaced by carbon present in the atmosphere, the sample will appear younger than it is in reality. While exchange probabilities are low for complex organic molecules, a definite danger threatens inorganic species such as calcium carbonate in bone and shell material.

Some reactions *in vivo* may be sensitive to isotope effects and may lead to disturbing isotope enrichments. The latter depend on the square root of the isotopic mass. An accurate determination of the $^{13}\text{C}/^{12}\text{C}$ ratio by mass spectroscopy may allow predictions of deviations in the $^{14}\text{C}/^{12}\text{C}$ ratio. Great caution is recommended when problems of this kind are dealt with.

A general agreement among most ^{14}C laboratories recommends that results should be published in the form of so-called 'Libby dates'. They are based on a half-life of 5600 years as was earlier accepted and they do not take any of the corrections of the above mentioned systematic errors into account. They yield experimental data and all corrections present or to come may now or later be applied in order to approach as close as possible the age of the sample.

2.4. Statistical errors

As has been mentioned, all radioactivity measurements imply an unavoidable statistical error, equal to the square root of the number of pulses registered. The propagation of the errors on p_L , p_A and p_S , together with the slight uncertainty on the half-life of ^{14}C , leads to an overall error on the age which is easily calculated. A superficial examination of equation (4) already shows that the error will be large when p_S lies close to either p_L or p_A , i.e. for very young and for very old samples. The error on the age is expressed as the

standard deviation, σ . It means that there exists a 67 % probability that the real age of the sample lies between $(t-\sigma)$ and $(t+\sigma)$, a 95 % probability and a 99 % probability that it lies within $(t \pm 2 \sigma)$ and $(t \pm 3 \sigma)$ respectively.

Typical examples are : 100 ± 60 years, 1000 ± 70 years, $10,000 \pm 140$ years, $20,000 \pm 380$ years. As foreseen, relative errors are larger for young and old samples. As a matter of fact, this is not too much of an inconvenience : for young samples other methods of age determination are generally available ; for old samples the stated approximation is often considered quite sufficient.

2.5. *Improvements of the ^{14}C method*

A two-fold goal is pursued by present research.

The conventional, large (1 to 2 liter) proportional counters require at least one or two grams of carbon. This often corresponds to rather large sized samples which are not always available for a destructive method of dating. Small (10 to 20 ml) counters have been developed to avoid this inconvenience. But, in order to keep the statistical errors at a reasonable level, a long procedure of counting (up to several months) with an extremely well stabilized equipment is necessitated.

The classical counting method is limited to about 30,000 years because of the steady decrease of radioactivity as a function of time. A substantial improvement would be reached if the number of ^{14}C atoms could be determined instead of their activity. Indeed, the specific activity of 14 disintegrations per minute and per gram of carbon proceeds from the presence of 6×10^{10} (sixty billion) ^{14}C atoms next to 5×10^{22} atoms of ^{12}C . A thorough physical separation and a quantitative recovery of ^{14}C should favourably further the limit of age determination. The unavoidable presence of traces of nitrogen, which has also an isotopic mass equal to 14, prevents the use of regular mass spectrographs or cyclotrons which have been adapted for mass separation purposes. The present trend is to design special tandem accelerators, one to extract nitrogen from negatively charged carbon, the second to separate the carbon isotopes. Building of this sophisticated apparatus is in progress in several research centres and preliminary results are encouraging.

3. THE LEAD - 210 METHOD

3.1. *Principles of the ^{210}Pb method*

According to their origin lead ores are to be classified in three groups :

a) Original lead was already present at the moment of the formation of the earth and consists of four stable isotopes, ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb . Wherever it is found, original lead has the same isotopic composition.

b) Radiogenic lead proceeds from the radioactive decay of ^{238}U , ^{235}U and ^{232}Th . It involves the stable isotopes, ^{206}Pb , ^{207}Pb and ^{208}Pb , and the radioactive isotopes ^{210}Pb ($T = 22$ years), ^{211}Pb ($T = 36.1$ minutes), ^{212}Pb ($T = 10.64$ hours) and ^{214}Pb ($T = 26.8$ minutes). As a secular equilibrium with their precursors has long been reached, all the radioactive lead isotopes present in an ore have identical and constant activities, until they are separated from their parent nuclides.

c) The most common lead ores are mixtures of original and radiogenic lead. The relative amount of the latter isotopes may be determined from their ratios towards ^{204}Pb which is the only isotope to be solely original. These ratios can also be used for the evaluation of geological ages up to five billion years.

Lead-210 provides a particularly attractive way for dating young lead-containing samples. This isotope is situated rather at the end of the uranium-238 family. Amongst its precursors only radon-222 is a gaseous element. Emanation of ^{222}Rn occurs at a rate of 0.7 atoms/cm².s above the continents. It has a half-life of 3.8 days and produces ^{210}Pb through a series of short-lived polonium, lead, bismuth and astatine nuclides. Created from atmospheric radon, ^{210}Pb adsorbs on aerosols and precipitates. Its concentration in glaciers allows an evaluation of their the age.

If radon cannot escape from the solid material in which it is generated, ^{210}Pb will have an activity which, because of the secular equilibrium, is equal to the radium-226 activity in the sample. When lead is extracted from an ore and purified, the equilibrium is broken and ^{210}Pb decays according to its own 22 year half-life. Any pure lead sample, which is at least partly radiogenic, will therefore show some radioactivity ; if it does not, it must be over 200 years old (ten half-lives).

These facts might be used to estimate the age of a painting, as was proposed by B. Keish. If the white lead, $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$, used by the artist was adequately pure, so that all of the radium has been eliminated, the age determination is straightforward according to the equation

$$(A_{\text{Pb}})_t = (A_{\text{Pb}})_0 e^{-\lambda t} \quad (5)$$

where $(A_{\text{Pb}})_t$ = activity of ^{210}Pb at the present time

$(A_{\text{Pb}})_0$ = activity of ^{210}Pb at the moment of the preparation of white lead

λ = decay constant of $^{210}\text{Pb} = \frac{0,693}{22}$ year⁻¹

t = age of the white lead

This condition is not readily fulfilled and, in most cases, the sample will be contaminated by traces of radium, which will continuously generate ^{210}Po and ^{210}Pb . Equation (5) is then to be rewritten as :

$$(A_{\text{Pb}})_t - A_{\text{Ra}} = [(A_{\text{Pb}})_0 - A_{\text{Ra}}] e^{-\lambda t} \quad (6)$$

where A_{Ra} = activity of radium.

The values $(A_{Pb})_t$ and A_{Ra} are easily obtained by experiment ; the term $(A_{Pb})_o$ causes a problem. It is equal to the activity of ^{238}U which was present in the mineral at the moment of the extraction of lead. Therefore one should know which ore has actually been used for producing the white lead ; this is not always the case, unless historical evidence is available. One might hope to overcome the difficulty by solving the equation

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_s = \left(\frac{^{206}Pb}{^{204}Pb}\right)_o + \left(\frac{^{238}U}{^{204}Pb}\right)(e^{\lambda_{238}\tau} - 1)$$

where $\left(\frac{^{206}Pb}{^{204}Pb}\right)_s$ = the isotopic ratio in white lead, determined by accurate mass spectroscopic measurements

$\left(\frac{^{206}Pb}{^{204}Pb}\right)_o$ = the isotopic ratio in original (= non radiogenic) lead, a constant equal to 19.0

λ_{238} = decay constant of uranium -238

τ = age of the ore

^{238}U = quantity of ^{238}U present in the ore at the time of the extraction.

^{238}U , thus also $(A_{Pb})_o$, is calculated provided one knows the age, τ , of the ore. Use of a second equation.

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_s = \left(\frac{^{207}Pb}{^{204}Pb}\right)_o + \left(\frac{^{235}U}{^{204}Pb}\right)(e^{\lambda_{235}\tau} - 1)$$

with λ_{235} = decay constant of uranium-235, does not help, as the relative abundance of ^{235}U towards ^{238}U is itself a function of time, so that one should know when the ore has been treated.

It thus becomes evident that, notwithstanding the fact of its theoretically sound grounds, the ^{210}Pb method encounters a series of experimental difficulties, unless the lead origin is historically well established. (So well established that a physico-chemical age determination becomes redundant !). Many factors interfere and their evaluation causes a propagation of errors which throw some doubt on the significance of the results.

A simplified application of the method might yet allow a statement of whether a painting, possibly attributed to an ancient artist, is original or a modern counterfeit. If ^{210}Pb is detected in excess of radium activity in the white lead, the painting is undoubtedly younger than 200 years. If no ^{210}Pb is detected, the picture is either old or the white lead has been prepared from an ore that does not contain any radiogenic lead. The relative abundance of the lead isotopes may then give indications as to the type of ore the lead was

extracted from. It then remains to verify whether that particular ore had already been discovered and exploited at the time the artist was supposed to live.

3.2. *Experimental procedure*

The white lead sample is dissolved in hot acetic acid (5 N), leaving the inorganic pigments insoluble. ^{210}Pb being more easily evaluated by means of the α -activity of its daughter product, polonium-210, the latter is quantitatively desposited on a silver plate. Lead is precipitated as lead sulfide and is quantitatively analyzed. Radium is removed by coprecipitation with baryum sulfate or on an ion exchange resin. The recovery yield of ^{210}Po and ^{226}Ra is checked by using ^{208}Po and ^{133}Ba tracers.

The α particles emitted by ^{210}Po , ^{208}Po and ^{226}Ra are counted on silicon surface barriers with very low background noise (0.04 pulses per minute). The γ rays of ^{133}Ba are counted on germanium-lithium crystals.

It is possible that an accurate determination of the lead isotopes' ratios and of some characteristic impurities might lead to a kind of 'finger print' proper to a particular artist, if it is understood that the latter always used lead from the same ore. More research in this direction seems necessary.

4. OTHER DATING METHODS

Exposure of some crystalline samples to cosmic rays and to radiation of environmental impurities (uranium, thorium and their decay products) may lead to the creation of defect centres.

Some of these have paramagnetic properties, as is the case in calcite and quartz; the nature and the number of these defects are deduced from electron spin resonance spectra. The total radiation dose to which the sample has been exposed may thus be evaluated. This 'archaeological' dose divided by the experimentally determined dose rate yields the age of the sample.

Other defects, as is the case in pottery, give rise to a typical luminescence when they are annealed by heating. The intensity of this thermoluminescence is proportional to the radiation dose that has been absorbed by the sample. This method is widely used for dating historical and geological material.

The slow racemization (conversion of the levorotatory into the dextrorotatory stereoisomer) of natural amino-acids gives information about the age of bones, teeth and shells.

At the present time these methods have had no promising applications for paintings.

5. CONCLUSION

Among the modern physico-chemical methods which are routinely used for archaeological purposes, the ^{14}C activity determination appears still most reliable, and is easily applicable to wood samples. It must, however, be emphasized that the age of a wooden substrate is not necessarily equal to the age of the painting.

As to the paint itself, the ^{210}Pb method seems promising within the mentioned restrictions.

6. BIBLIOGRAPHY

- W.F. LIBBY, *Radiocarbon dating*, University of Chicago Press, 1952.
- R. BERGER, H.E. SUSS, *Radiocarbon dating*, Proceedings of the Ninth International Conference, Los Angeles and La Jolla, 1976, University of California Press, 1979.
- W.F. LIBBY, *Radiocarbon and Tritium*, Coll. Papers, vol. 1, ed. by R. Berger and L. Marshall Libby, Geo Science analytical, Santa Monica, 1981.
- M.J. AITKEN, *Physics and Archaeology*, Oxford, 1974.
- S. FLEMING, *Thermoluminescence techniques in archaeology*, Oxford, 1979.
- Datations absolues et Analyses isotopiques en préhistoire*. Coll. intern. C.N.R.S., Tautavel, France, 1981.
- Biogeochemistry of aminoacids*, ed. by P.E. HARE, T.C. HOERING, K. KING Jr., New York, J. Wiley and sons, 1980.
- PACT 2-3, 1978-79, 6, 1982 and 9, 1983 : *Specialist Seminars on Thermoluminescence* (Oxford 1978, 1980 and Elsenøre 1982), ed. M.J. AITKEN and V. MEJDAHL.
- PACT 8, 1983, *^{14}C and Archaeology*, Symposium held at Groningen, 1981. Ed. W.G. MOOK and H.T. WATERBOLK.
- S.W.S. MCKEEVER, *Thermoluminescence of Solids*, Cambridge, Univ. Press, 1985.

7. RÉSUMÉ

Plusieurs méthodes de mesure de l'âge absolu se basent sur la décroissance d'un radionuclide ou sur les effets cumulés d'une exposition aux radiations ionisantes. Certaines sont particulièrement indiquées pour dater des échantillons d'intérêt historique ou archéologique ; ce sont principalement la mesure de la quantité de carbone-14 ou du plomb-210.

Les bases scientifiques de ces techniques et leurs domaines d'application sont passées en revue.

La création du carbone-14, la mesure de son activité et l'analyse des résultats sont successivement rappelées. Une date n'aura une réelle signification que si elle contient aussi des renseignements quant à sa fiabilité. Un traitement des erreurs statistiques permet de délimiter le degré de confiance.

De nouvelles techniques sophistiquées et prometteuses, qui permettent d'élargir l'intervalle d'âge par carbone-14, sont citées.

La méthode au plomb-210, intéressante dans le cas de peintures, est également analysée. Des difficultés inhérentes à la méthode incitent à une grande prudence, mais cette technique permet, dans certains cas, de distinguer un faux récent d'une vraie peinture ancienne.

L'impact des radiations ionisantes provenant du rayonnement cosmique ou d'impuretés radioactives peut créer des défauts ponctuels dans la matière. La guérison de ceux-ci sous traitement thermique peut s'accompagner d'une émission de lumière. Cette thermoluminescence permet de dater grand nombre d'échantillons en terre cuite.

Ces défauts présentent souvent des propriétés magnétiques. Le nombre et la nature des défauts peuvent être déterminés grâce à la résonance paramagnétique électronique. Un âge relatif peut en être déduit.

La lente racémisation des acides aminés naturellement lévogyres donne des renseignements sur l'âge des os, des dents et des coquillages.

Ces deux dernières méthodes font actuellement encore l'objet d'une recherche fondamentale et ne connaissent pas encore d'application directe pour les peintures.