

Time Calibration in the Era of Man

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SAMENVATTING

Dateringen spelen een belangrijke rol in het reconstrueren van de evolutie van de mens. De belangrijkste dateringsmethoden met hun voor- en nadelen worden besproken.

SUMMARY

Datings play an important role in reconstructing the evolution of man. The most important dating techniques are discussed. The advantages and disadvantages of the various techniques are given.

The dating of human fossils and artefacts is of universal concern to paleoanthropologists and archaeologists. Without such dates it would not be possible to reconstruct patterns of change in human anatomy and behaviour through evolutionary time. Scientists working in these fields have therefore become so hungry for - and dependent on - the magic of the various dating techniques that they, unfortunately, accept most results eagerly, sometimes taking at face value answers from the dating laboratories that fly in the face of all their instinct and deductions.

In order to date hominoid relicts and to place them in the correct chronological order, one relies in the first instance on the conventional stratigraphic and magnetostratigraphic methods. But these usually do not allow the assignment of precise absolute ages, in years, to human fossils and artefacts. For this, one needs reliable and precise chronometers with sufficient resolution. Any chronometer for measuring passed time must contain some sort of mechanism that meets three requirements:

1. it has to be based on an irreversible process,
2. it must operate at a known or predictable (but not necessarily constant) rate, and
3. it must be linked to a recording system of some kind, in which the beginning of the passed time interval is clearly marked.

Paleoanthropologists these days benefit from a range of dating techniques that more or less fulfill these requirements. The most important techniques fall into two basic categories:

1. The Physical Methods, particularly radio-isotopic methods based on the atomic disintegration of natural radioactive components in the sample material or its surrounding environment, and
2. the Organic & Inorganic Chemical Methods, based on time-dependant chemical changes in the sample material.

Of all dating methods applied in the Era of Man, the last 2.5 million years or so, it are only a number of isotopic methods that are able to provide reliable and accurate absolute ages over the whole range of human evolution.

Most other methods give at best only a rough approximation of the age, or an indication of the relative ages of a sequence of different samples, but in these cases it is sometimes possible to calibrate the relative age technique by absolute isotopic methods.

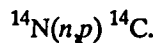
Isotopic dating techniques are base in one way or another on natural radioactivity. In general terms, these methods fall in one or another of four groups, those which measure:

1. the quantity of a radio-isotope as a fraction of a known initial level, notably Radiocarbon Dating,
2. the build-up of a stable radiogenic daughter product, notably Potassium-Argon Dating,
3. the measurement of radiation damage due to natural irradiation, notably Thermoluminescence Dating, Electron Spin Resonance Dating and Fission Track Dating, and
4. the degree to which members of a chain of radioactive decay are restored to radioactive equilibrium following some initial external perturbation, notably Uranium-Series Disequilibrium Dating.

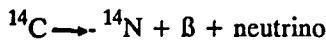
We have two options for seeking the absolute age of fossils or artifacts - direct and indirect dating. Direct methods produce an age for the objects themselves, using a build-in chronometer. This is, of course, the preferred procedure. But, unfortunately, for most materials of interest - ancient fossils and most stone tools - there are no methods as yet available for reliable direct dating. In practice, therefore, the typical approach is mostly that of indirect dating. With this approach the age of the human fossil or artifact is inferred by correlation of the specimen with objects associated with them or with strata elsewhere whose chronometric age have been determined. But, of course, such correlations inevitably introduce some degree of uncertainty and subjective interpretation.

The Radiocarbon Dating Method is a technique that allows the direct dating of the fossil material. Over the last 40 years it has become a highly successful and indispensable tool in Late Quaternary research. This technique makes use of the radioactive carbon isotope car-

bon-14 that is produced in the upper atmosphere by neutron bombardment of atmospheric nitrogen atoms:



The neutrons are produced by cosmic radiation emerging into the upper atmosphere. The carbon-14 atoms are rapidly oxidized to carbon dioxide, which diffuses downwards and mixes with the rest of the atmospheric carbon dioxide and hence enters into all living organisms through photosynthesis. The production rate of carbon-14 in the upper atmosphere is essentially constant, about 7.5 kg each year. Once produced, carbon-14 begins to decay to nitrogen, with the release of a β particle (electron):



Before the onset of the industrial revolution, which released much old carbon, there was an essentially constant steady-state concentration of radiocarbon everywhere in the environment and all living organisms in equilibrium with the environment. As soon as an organism dies, the exchange and replacement of carbon-14 from the atmosphere ceases. From that moment on the carbon-14 content of the dead organism declines as the radiocarbon decays to nitrogen, and the remaining radiocarbon content is henceforth purely a function of time - the radiocarbon clock has been activated.

Radiocarbon dating has become a standard method for the dating of all types of organic matter, such as bones, teeth, hair, horn, ivory, wood, charcoal, seeds, leaves, resin, peat and shells, but also secondary carbonate deposits in caves, as well as soil, groundwater and ice. There are, of course, various pitfalls and uncertainties in the application of radiocarbon dating, but these can mostly be overcome with prudence and expertise. The essential shortcoming for paleoanthropology is the relatively short half-life of carbon-14, only 5,570 years, which limits the use of the method to the dating of materials up to 50,000 year old when using the conventional techniques, or a maximum age of some 75,000 year with the newly developed accelerator mass spectrometer technique. Thus, in paleoanthropology, only the era of Neanderthal and Modern Man. It should also be noted that the accepted half-life of 5,570 years, which is used by agreement in all radiocarbon age calculations, is actually too low by about 3 percent - all published radiocarbon ages should thus be 3 percent higher to be rigorously correct.

This limitation does not exist with the Potassium-Argon Dating Method, so far the most important dating technique in providing a time framework for human evolution. But in paleoanthropology the potassium-argon method is exclusively a method of indirect dating. The method depends upon the slow radioactive decay of the rare isotope potassium-40 to the stable isotope argon-40, an inert gas, and calcium 40. The half-life of potassium-40 is $1.25 \cdot 10^9$ year. Minerals that contain po-

tassium thus steadily accumulate argon-40 in their lattice, provided that the quantity of potassium-40 is also known and that the mineral through its lifetime has remained a closed system. A key factor in this approach is that the clock has been set to zero at some point in the past. This occurs, for example, in potassium-bearing minerals that are ejected during volcanic eruption - the argon-40 present in the upwelling lava and originating from the decay of potassium-40 in the source rock of the magma, in the upper mantle or deep crust, is as a rule released to the atmosphere during the eruption. All radiogenic argon-40 that is present in volcanic material is therefore mostly accumulated since the eruption - but not always.

Two techniques are used in potassium-argon dating. The conventional technique is to split the sample in two portions. In one portion the potassium-content is measured by conventional chemical analysis. The other portion is used to determine the radiogenic argon-40 content by means of a mass spectrometer. The assumption made, of course, is that the two aliquots of the sample are chemically the same. In the majority of instances this assumption holds good, but sometimes separate aliquots of a seemingly homogeneous sample yield different potassium contents. Another disadvantage of the conventional potassium-argon dating technique is that rather large samples of several grammes are required.

Both shortcomings are avoided by a modern analytical variation of the potassium-argon dating method, the laser-microprobe argon-40/argon-39 technique. The sample mineral grains down to a weight of 0.2 mg can be dated with this technique. The sample is irradiated in a nuclear reactor with fast neutrons, inducing the conversion of the potassium isotope potassium-39 into argon-39. The argon-39 produced in this way is radioactive, and decays to ^{39}K with a half-life of 269 year. After cooling for a couple of weeks, the irradiated sample is placed in a vacuum chamber built into a microscope and attached to a laser and a mass spectrometer. The laser beam, which can be focused to within a few mm, is focused on the mineral grain to free the argon in it. The isotopic composition of the released argon is then measured by means of the mass spectrometer. From the argon mass spectrum, which includes both the argon-39 and the argon-40 signals, the potassium-40 and radiogenic argon-40 contents and the age of the grain are determined through a rather complicated set of calculations.

Usually, the sample is degassed by heating in steps with increasing temperature, the so-called stepwise of incremental heating. Argon is released in steps, first at the lowest temperature from the outer layers of the mineral grain, and finally at the highest step from the center of the grain. The argon released at each step is measured separately. In this way, several determinations are made on the same sample yielding a spectrum of apparent ages, whereby each age value is associated with a specific

heating temperature. If the mineral during its lifetime suffered no natural heating or other disturbances, the age spectrum will be a horizontal line, giving the age. A sample that has suffered natural heating may have lost some of the accumulated argon-40, giving a false young age for the degassed outer layer. Eventually, but not always, the true age is revealed as a plateau, produced from gas released from the center of the grain.

There is no upper limit to the age range wherein K-Ar dating can be applied but a lower limit is set by the condition that enough argon-40 must have accumulated to allow the determination of the argon-40 content. In practice this means that reliable K-Ar dating becomes possible for minerals older than some 50,000 to 100,000 year. K-Ar dating was first applied in paleoanthropology in 1960, using the conventional technique, when volcanic ash above the famous Zinjanthropus skull found at Olduvai Gorge by Mary Leakey was shown to be more than 1.75 million years old, rather than the 0.75 million years that had been inferred by other means. With this age determination a revolution in the dating of human evolution had begun.

A next major step in the setting up of a time framework in paleoanthropology was the invention of the laser-microprobe argon-40 / argon 39 technique. This is an analytically much more complicated technique than conventional K-Ar dating, but it is by far the most reliable dating method available at present for the time-span of human evolution, although unpleasant and unexpected surprises can always be encountered. But even this technique is solely a method of indirect dating, allowing a precise and accurate age determination of volcanic minerals such as micas, sanidine, hornblende, and leucite in lavas and ashes associated with the fossils, or above and below them, but it is not applicable to the fossil remains themselves. Any correlation of fossil remains with volcanic material will usually be a matter of interpretation in the field, subject to personal and maybe erroneous judgement, so the datings, however accurate they are physically, have to be looked upon critically - they do not necessarily represent the ultimate truth as far as the age of the fossils or artifacts are concerned. The objects to be dated may originate from a disturbed stratigraphy, for example because the volcanic deposits have been reworked by biological activity, streaming water or winds, or bones may have fallen into a channel that had been cut into old ash layers by streaming water. These are many natural processes that may bring fossil material in contact with significantly older or younger mineral grains.

All other dating methods are less reliable than the potassium-argon and radiocarbon techniques. Of the other isotopic methods, the most widely applied are the thermoluminescence, electron spin resonance, fission track and uranium-series methods.

Thermoluminescence Dating is based on the radiation damage in solid material due to internal and external nuclear radiation. This radiation comes from radio-isotopes that occur as impurities in the sample itself and in the surrounding matrix, particularly uranium and thorium and the radioactive isotopes of their decay chains, as well as potassium-40 and maybe sometimes from cosmic rays. This radiation detaches electrons from their parent atoms. Most detached electrons fall back immediately after it occurs, but a small proportion of the freed electrons is trapped at a metastable level for a virtually infinite time at crystal lattice defects. The number of trapped electrons increases linearly with time, provided the received radiation does remain constant, but only up to a certain level, the saturation level, which is dependent on the material involved. As long as the saturation level is not reached, the number of trapped electrons is thus a measure of the time that the mineral has been exposed to radiation.

Heating of the sample causes the trapped electrons to be kicked out from their traps and to fall back to the stable level - they recombine with positive 'holes'. This recombination is accompanied by the emission of light: one photon per electron. This phenomenon is known as thermoluminescence, TL, which can be detected by sensitive photomultipliers. The TL intensity is proportional to the number of trapped electrons that are released. Because heating releases the trapped electrons, effectively setting the clock to zero, measurement of TL emission by heating in the laboratory gives thus an indication of the time which has elapsed since the sample was last heated.

To determine the TL age of a sample one has to measure the natural thermoluminescence level that has built up in time and the intensity of emitted light as a function of the heating temperature. Particularly the part between 300° and 500°C is important, since the glow in this range is emitted by electrons which have been in traps deep enough to ensure their long-term storage. But before an age calculation is possible, it is necessary first to determine for each sample two specific parameters:

1. The equivalent dose, archaeological dose or paleodose, dED. This parameter is a function of the 'sensitivity' of the sample to acquire TL, which is a property specific to each individual sample, and the total dose of radiation that is needed to obtain a luminescence signal of the same size as the natural signal. The parameter is determined in the laboratory by exposing the sample to artificial radiation.
2. The radiation dose rate, r , in units per year. The dose rate is assessed by measuring the quantities of uranium and thorium and their descendent isotopes, as well as potassium, in the sample and the surrounding matrix, plus the cosmic radiation at the sampling site.

The time that has elapsed since the target material was set at zero during the last heating can then be derived from the equation

$$\text{age} = d_{ED}/r$$

provided that r has remained constant through time.

The most difficult problem in thermoluminescence dating is to estimate the long-term radiation dose rate for the sample. This introduces an inherent uncertainty and the accuracy of thermoluminescence dating may therefore at best approach ca. 10 %. As it is a relatively cheap method, the technique is nevertheless widely used in archaeology and paleoanthropology. The useful timescale for TL dating begins at about 100 years, but does not exceed some 1 million years or less, due to saturation of the electron traps. The method can be applied to materials that have undergone man-induced heating to such a degree that the TL clock was reset. Such man-heated materials are obsidian tools that have been heated in fireplaces, uranium-rich glass artefacts, bricks, rocks upon which fireplaces were built, campfire stones, pottery, potsherds and other ceramics. It is also increasingly used for the dating of geologically young terrestrial sediments, especially eolian sediments, as exposure to sunlight during weathering and erosion also 'empties' the original thermoluminescence and resets the 'TL clock' to zero prior to the deposition of the sediment. Unfortunately, the TL dating of human remains is complicated by the chemical changes that go on in fossil bones and teeth - for example the absorption of uranium from the surrounding matrix, which alters the internal radiation dose. This can be accounted for in calculations, but it adds an uncertainty to the calculated age. TL dating cannot at all be applied to tooth enamel, because the heating in the laboratory induces chemical changes which also release light, thus confounding the measurement.

Electron Spin Resonance Dating is a young and not fully developed technique, closely related to the thermoluminescence technique. It is likewise based upon the phenomenon that the electrons trapped at a metastable level act as paramagnetic centers and give rise to characteristic signals, known as electron spin resonance, ESR. The signals can be measured by ESR spectrometry and the strength of the ESR signal is proportional to the number of trapped electrons. But, contrary to the instrumentation needed for TL dating, an ESR spectrometer is very expensive. The great advantage over the TL method is that an electron spin resonance analysis can be repeated many times with the same sample and requires little time. Also, the amount of sample needed is very small.

At the present time, the reliability of ESR dates is often over-estimated. Nevertheless, the method is nowadays widely applied on most of the materials that are also used for TL dating. The technique can also be applied

to tooth enamel, but not to obsidian or pottery because the crystal lattices in these materials are insufficiently ordered for the clear production of an ESR signal by trapped electrons.

Another isotopic dating method based on radiation damage which is increasingly applied in Late Quaternary geology, is the Fission-Track Dating Method. In this case the radiation damage is due to the spontaneous fission of the uranium isotope uranium-238 in solid material. The half-life is so far only approximately known, but must lie somewhere between $8 \cdot 10^{15}$ and $10 \cdot 10^{15}$. This 20 % uncertainty translates, of course, in an uncertainty in the age determined on the basis of this process. The spontaneous fission of a uranium-238 nuclide produces two heavy, positively charged fission fragments of approximately the same mass and a kinetic energy of about 200 MeV. These two fragments recoil in opposite directions. Along the path of a spontaneous fission fragment, positive ions are produced, which repel each other electrostatically. In this way the charged high-energy fission fragments leave evidence of their passage through solid material in the form of tracks of lattice damage. The tracks are 10-20 micrometer (10^{-3} mm) long. After chemical etching of the sample these tracks become visible under a normal optical microscope, a value for the track-density is obtained. This density is a function of the uranium concentration and the age of the sample. When the uranium concentration is known, the fission-track age of the sample can thus be calculated. The uranium concentration is usually determined by counting the density of artificially induced tracks which are produced in the same sample surface by neutron-induced fission of uranium-235 in a nuclear reactor.

Fission tracks are stable only below a certain temperature that is specific for each material, the so-called annealing temperature. If the annealing temperature is exceeded, the tracks disappear. Common materials used for FT dating are two minerals that are common constituents of many natural rocks and man-made ceramics, apatite, with an annealing temperature of about 100° C, and zircon, with an annealing temperature of around 250° C. As it is a relatively inexpensive method, not requiring expensive equipment if one has access to an operating nuclear reactor, the fission-track clock is increasingly used to obtain ages, although only as a rough approximation of the true age because of the high uncertainty in the half-life. In paleoanthropology, the dating method is mostly applied to volcanic minerals, volcanic glass such as obsidian and pumice. In this case it is, just like the K-Ar method, an indirect dating method, although with a much higher degree of uncertainty. But fission-track dating is also used as a direct dating method on materials that have undergone man-induced heating to such a degree that the annealing temperature of one or more enclosed minerals was reached, thus setting the fission track clock to zero. Such man-heated materials are obsidian tools that have been heated in fi-

The method is based on the fact that amino acids occur in two different structural forms, each configuration being a mirror image of the other, It occurs because the molecules are asymmetric. Both forms are optically active: when the plane-polarized light passes through a solution of the compound, the one configuration rotates the light to the left and is called the L-isomer, and the other rotates it by an equal amount to the right and is called the D-isomer. Amino acids that are formed in living organisms are exclusively isomers that rotate plane polarized light to the left.

Once the organism has died, the amino acids convert reversibly into D-isomers, ultimately leading to an equilibrium of L- and D-isomers that is not anymore optically active. This process is known as racemization. The ratio of D- and L- isomers determines the optical activity of an amino acid. During the course of aging this ratio increases from 0 to 1 and the optical activity decreases to zero. This is thus a direct measure for the age of fossils of bones, teeth and ivory. But, the rate of conversion is strongly dependent on the ambient temperature, the state of preservation, and environmental factors during the time the sample was in the ground. For example, a variation of the ambient temperature from 0° to 37°C brings about a change in the half-time for racemization of some amino acids by a factor of thousand, resulting in a corresponding shift in the calculated age. This is a great disadvantage for the application of this method to paleoanthropology, because temperatures have varied widely during the Quaternary, particularly at higher latitudes.

Amino-acid dating is quick and less expensive than most of the other dating methods. For paleoanthropologists it is also attractive owing to the small amount of sample required, and the large range that can be dated, up to 1 to 2 million year, virtually covering the whole time-scale of human evolution. But, because of the strong dependence of the rate constants for racemization on

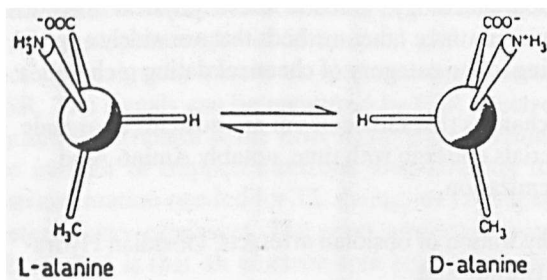


Fig. 2: Het principe van aminozuurracemisatie. Linksdraaiende aminozuren worden na de dood van een organisme omgezet in rechtsdraaiende zuren, totdat een evenwicht is bereikt.

fig. 2. Mechanism of Amino-Acid Racemization. L-isomers of amino acids convert after the death of an organism into R-isomers, until an equilibrium is reached.

environmental conditions, the constants must be determined anew for each site and material. Absolute dating of fossil bone, tooth and ivory samples by amino-acid dating is therefore only possible if properly dated samples from the same site are available for calibration - which annuls, of course, the advantage that the method can be applied directly and independently to the fossil material to be dated. At the present time, relative dating of samples coming from the same site seems therefore the only practical application of amino-acid dating in paleoanthropology.

The other chemical dating methods are based on chemical reactions that proceed with time through reactions of artifacts or fossil relicts with the environment.

Obsidian Hydration Dating makes use of the phenomenon that obsidian and other glasses, including man-made glass, absorb water on the surface, where it becomes chemically bound, forming a hydrated layer with a water content of about 3.5 %. This is about ten times that of the original silicate. The process is due to the diffusion and reaction of soil moisture on the surface of obsidian artefacts. The hydrated layer grows very slowly with time. For any obsidian artefact the thickness of the hydrated layer (d) can be measured easily under a polarizing microscope. The relationship between the measured thickness and the age of the sample (t), is derived from the law of diffusion

$$d^2 = k.t$$

where k is the hydration rate constant. This value depends on the chemical composition of the obsidian and the ambient temperature of the sample through time. As far as the dependence of the hydration rate on the chemical composition is concerned, this can be determined for each type of obsidian in the laboratory, but the temperature dependence remains a source of uncertainty in the age calculation. Nevertheless, the hydration method has proven to be a fairly reliable method to establish, in the age range up to some 100,000 year, the date at which a piece of obsidian was fractured - thus the date of the artifact fabrication.

The Fluor-Uranium-Nitrogen Adsorption Method (FUN Test) provides a rough and usually only relative dating of Quaternary bones, antler and tooth enamel. The method is based on the continuous adsorption of fluor and uranium from groundwater by irreversible ionic exchange, and the decomposition with time of proteins, especially collagen, involving the loss of nitrogen. The advantage of this method is its simplicity and the small amount of sample required, but the precision of this dating method is extremely poor. In fact, the method is only suitable to distinguish between old and young samples, such as between recent and ancient skeletal materials. For example, the FUN Test was used some 25 years ago to prove that the notorious Piltdown fossils are a hoax.

In summary, the chronometric methods that nowadays play a role in dating human fossils and artefacts are:

- Radiocarbon (Carbon-14) Dating. Up to 40,000 (75,000) years; fossil organic material, calcite deposits associated with the fossil material; reliable and accurate.
- Potassium-Argon (K-Ar) Dating, in two techniques (conventional & $^{40}\text{Ar}/^{39}\text{Ar}$). From 100,000 (50,000) years up to unlimited; K-bearing volcanic minerals associated with the fossil material; reliable & accurate.
- Thermoluminescence (TL) Dating. From 100 to (<) 1 million year; man-induced heating of rock & artefacts, exposure to sunlight of eolian sands, (fossil bones & teeth, not tooth enamel); rather high uncertainty.
- Electron Spin Resonance (ESR) Dating. Same range and material as TL dating (but including tooth enamel); rather high uncertainty.
- Fission Track (FT) Dating. From about 1,000 to hundreds of million year; man-induced heating of rocks & artefacts, U-bearing volcanic minerals associated with the fossil material; reliable, but rather inaccurate.
- Uranium-Series Disequilibrium (Th-230 & Pa-231) Dating. Thorium-230/Uranium-234 from 1,000 to 350,000 (500,000) year, Protactinium-231/Uranium-235 from 1,000 to 200,000 year; calcite deposits associated with the fossil material, peat, (fossil bones & teeth); fairly reliable & accurate.
- Amino Acid Racemization Dating. Up to 1-2 million year; fossil bones, teeth, ivory; unreliable & inaccurate.
- Obsidian Hydration Dating. Up to 100,000 year; fabrication (fracturing of obsidian tools; fairly reliable and accurate.
- FUN Test (fluor & uranium adsorption, protein decomposition). Only to establish very large age differences; fossil bones, antler & tooth enamel; highly inaccurate.

These are the tools that are applied in the setting up of a chronological framework for human evolution - but it is obvious that the chronometric results have had themselves a strong impact on the evolutionary scenarios. The datings have to be carried out in special laboratories by specialists, and they need to be performed in dialogue between the dating specialist and the consumer paleoanthropologist and archaeologist. A single dating or dating method rarely gives a unambiguous answer concerning the age of a human fossil or artifact. There can be a site-to-site variability in the reliability of the results and some sample materials are not as suitable

for dating as others. Many dates have to be inferred from correlation with materials that are suitable for proper dating. Therefore, for each dating a critical assessment of its reliability has to be made. Never should the dates produced by the dating laboratories be taken at face value.

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