

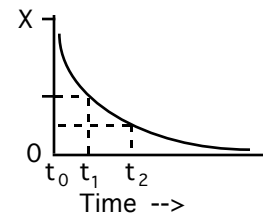


There are several chemical methods for relative dating: **fluorine** dating measures the amount of fluorine absorbed from groundwater since burial, and **nitrogen** dating looks at how much  $N_2$  has been lost through the decay of amino acids in collagen. The rates of both processes depend on local conditions (they are diagenetically sensitive), so they are used mainly for dating different fossils within a site: e.g., fluorine dating showed that Piltdown's mandible and calvarium were very different ages, helping to expose the hoax.

**Paleomagnetism:** For reasons I certainly don't understand (and I think are not known) the magnetic polarity of the Earth periodically flips. Today we are in a period of "normal polarity" in which a magnetic needle points north; during a period of "reversed polarity" it would point south. Iron-bearing rock (volcanic or some sedimentary rocks) will record the polarity in the orientation of magnetic crystals; by measuring the orientation one can tell if the specimen was deposited during a normal or reversed period. This only helps if you have an independent idea of *which* normal (or reversed) period it comes from (e.g., by some absolute method). There have been 12 major periods of reversed polarity in the last 4.5my, ranging in length from about 100ky to 600ky. The most recent reversal, between 200 and 300kya, is useful as a check on the "muddle in the middle" between K/Ar and  $^{14}C$  (see below).

### III. Absolute Dating

There are a variety of methods that yield actual calendrical dates for fossils. Most actually date the strata the bones are in, or associated materials, and not the fossils of interest. A number of them are radiometric methods, that make use of the decay of radioactive isotopes (atoms with the same number of protons but different numbers of neutrons are isotopes of the same element; e.g., uranium  $^{235}U$  and  $^{238}U$ ). There are several sorts of decay (alpha decay: lose 2 protons & 2 neutrons [ $^{238}U \rightarrow ^{234}Th$ ]; beta decay: neutron turns into proton [ $^{87}Rb \rightarrow ^{87}Sr$ ]; electron capture: proton turns into a neutron [ $^{40}K \rightarrow ^{40}Ar$ ]). Each element has a characteristic decay behavior and rate that can be measured in the laboratory. The decay constant of an element (K) is the probability of an atom decaying in any one year (and hence the proportion of atoms that decay in a year). Starting with X atoms of the parent isotope, at the end of a year there will be  $X - (X \cdot K)$  parent and  $(X \cdot K)$  daughter atoms. With a constant rate of decay, there will be a characteristic time at which half the atoms of the original isotope have decayed ( $t_1$ , here); this is the *half-life* of the element. Another half-life later, half of that first half has decayed ( $t_2$ ), etc. Because a constant *percent* is decaying per year, the amount of change is greater early on (50% of 1,000 = 500, vs 50% of 4 = 2). If you are trying to count atoms, practically speaking it is easier to measure the differences earlier -- the difference between 1,000 and 500 is much easier to measure than between 4 and 2.



SO: if one knows the ratios of isotopes present at  $t_0$ , comparing the ratios at some later time permits calculating how long the decay has been going on--that is, how long the item has been there. How one knows the starting ratios depends on the technique.

**Carbon-14 ( $^{14}C$ ):** This is one of two methods that can date fossil bone directly.  $^{14}C$ , an unstable isotope, is formed when cosmic rays hit  $^{14}N$  in the atmosphere; organisms take it up (along with the common  $^{12}C$ ) during life. Once an animal or plant dies, the  $^{14}C$  is not replenished and the ratio of  $^{14}C/^{12}C$  drops as the  $^{14}C$  decays with a half-life of  $5,730 \pm 40$  years. Knowing the half-life, by comparing the atmospheric ratio to the specimen ratio permits one to calculate the age of the specimen when it died (over the last ca. 40ky [improving measurement methods can boost this to close to 70ky but accuracy falls off]. There are some wrinkles (the amount of radiocarbon in the atmosphere appears to vary slightly with both latitude and time). Back to about 9kya, these can be directly calibrated using wood samples dated by dendrochronology (below).

**Potassium-Argon (K-Ar) and Argon-Argon ( $^{40}Ar/^{39}Ar$ ):**  $^{40}K$  decays to  $^{40}Ar$  with a half-life of nearly 1.3 billion years; under about 100-500kya there isn't enough  $^{40}Ar$  to measure (depends who you ask), but the method works from there to the age of the Earth. Since Ar is a gas, the technique is ideal for volcanic materials: all gasses are boiled off during the lava stage, and Ar begins to accumulate only after cooling. Provided the Ar cannot diffuse out of the mineral (e.g., a crystal found in

consolidated ash, or *tuff*), the K/Ar ratio thus measures the length of time since the rock was molten. Two samples must be measured, one for the amount of K and one for the Ar, and this amplifies experimental error;  $^{40}\text{Ar}/^{39}\text{Ar}$  is a recent modification of the method that works on single crystals. **Single-crystal fusion** takes advantage of this, using a laser to melt a very small bit of specimen (thus reducing contamination, and the amount of specimen needed for dating).

**Uranium Series (U-S):** Uranium is a common trace element, and various isotopes decay in various patterns. The best for dating is thorium-uranium ( $^{230}\text{Th}$ - $^{234}\text{U}$ ). The method relies on the fact that daughter isotopes continue decay into other isotopes; at equilibrium, then, the first daughter is decaying as fast as it is being formed, so the ratio to the parent isotope is a constant (takes a bit of thinking, at least for me...). To illustrate: travertine is a form of calcium carbonate that forms in wet caves (dripstone). Because daughter  $^{230}\text{Th}$  is not soluble in water (but U is), when the rock is formed the  $^{230}\text{Th}/^{234}\text{U}$  ratio is zero. It will increase as  $^{234}\text{U}$  decays into  $^{230}\text{Th}$ , but the ratio will reach a maximum of 1.0 when equilibrium is reached and  $^{230}\text{Th}$  is decaying as fast as it is formed; this takes about 350ky (so this is an upper limit for the dating method). There are various other isotopes and materials (including stalagmites etc) that can be used in a similar fashion.

**Fission Track:**  $^{238}\text{U}$  will spontaneously fission (nucleus splits into two or more particles which explode apart); if it is located in a crystal (e.g., zircon), these explosions leave visible damage. By counting the number of scars per unit area, the age of the crystal can be estimated from the known rate of fission. In principle it can date rocks ranging in age from decades to billions of years. Because intense heating of zircon will melt the tracks (zeroing the "clock"), F-T can be used to date fired pottery.

**Thermoluminescence (TL) and Electron Spin Resonance (ESR):** Radioactivity from traces of radioactive elements or from ionizing radiation (cosmic rays, even sunlight) can sometimes interact with atoms in the soil to drive electrons to a higher energy state. In TL, heating the material above about 450°C can free the electrons, which return to their stable energy states and release the "excess" stored energy in the form of light (thermoluminescence). The amount of light given off is thus a measure of how long the material has been accumulating excess energy since being "zeroed" by heat, crystal formation, burial, etc. First, one heats the specimen and measures the light given off; then one gives it a known dose of radiation and measures it a second time (to calibrate the sample's sensitivity). This tells you how much radiation it had absorbed in total; one then calculates the amount of radiation it would have been exposed to per year by measuring the concentrations of radioactive trace elements in the parent rock, and use the two figures to calculate the time it's been accumulating radioactivity (age = total dose/annual dose). Clearly one needs to be careful about the sedimentary history, since exposure to sunlight/cosmic rays can have an effect. TL has been used especially on materials heated by fires--pottery, flint from a hearth, glass, etc.

ESR is based on the same principle, but gets at the number of trapped electrons by measuring their absorption of microwave radiation. The advantage of this is that one can re-date the same specimen (unlike TL, in which the electrons are zeroed out by the testing process). The method works on tooth enamel, and because it is non-destructive it can be used on precious fossils; it also works on shell, corals, and cavestones. It theoretically works for the period between a few thousand and about 1mya, but estimates over 300kya are uncertain.

**Dendrochronology:** Counting growth rings in trees. Because these annual rings vary in width according to climate, particularly good (or bad) years leave a "signature" in a particular trunk. One can (with a great deal of work!) start with modern trees at a site, identify some signature years from when the tree was young, and match these to the outer rings of a dead log; by looking for signatures from *this* log's sapling days and matching them to those of the outer rings of a yet *older* log, one can extend the count back in time much farther than the lifespan of any one tree. This has been done to about 9kya; I don't know if the limit is theoretical or the patience of the researchers.  $^{14}\text{C}$  dating of the known-age wood permits calibration of  $^{14}\text{C}$  (see above).

**Finally**, two methods that are "absolute" but so sensitive to local conditions that they are really more relative/corroborative:

**Amino acid racemization:** Amino acids ( $\alpha\alpha$ ) exist in two forms (optical isomers--same chemical elements, but different structures), known as L- $\alpha\alpha$  and D- $\alpha\alpha$ . On Earth, living organisms use only the L form, but after death they begin converting to the D form until they reach equilibrium at a 1:1 ratio; the process is *racemization*. This is a chemical process and so depends on a variety of factors including temperature (the half-life can vary between days at 100°C to thousands of years at 20°C), and the rate is different for each  $\alpha\alpha$ . Because of the sensitivity to chemistry and temperature, it is best applied to stable environments--deep sea cores or deep cave deposits--but because it can directly date bone (and eggshells, mollusk shells) it is used, carefully, elsewhere for materials between a few hundred to several hundred thousand years old.

**Obsidian hydration:** When obsidian (volcanic glass) is fractured (as in flaking to make a tool), the glass begins to absorb water from the surroundings and this forms a microscopically observable hydration layer. Given the rate of growth of the layer and its thickness, one can calculate time since fracturing. The problem is that rate of hydration depends on temperature and on the exact chemical composition of the obsidian (which varies from volcano to volcano), and so it has to be calibrated for each locality, and multiple specimens examined and averaged, to have anything like a reliable date. In principle, it works back to about 120kya but most use is within the last 10ky, in conjunction with other methods. *Within* a site, it can be used for relative dating without so much concern over diagenesis.

#### SUMMARY:

**Carbon-14** ( $^{14}\text{C}$ ): Any organic material (charcoal best); few hundred to about 60kya

**Potassium-Argon (K-Ar) and Argon-Argon ( $^{40}\text{Ar}/^{39}\text{Ar}$ ):** Volcanics;  $\approx$ 250kya -- 4 billion+

Note the gap between 60kya (old end for  $^{14}\text{C}$ ) and 250kya (young for K/Ar). This is right about when modern *H. sapiens* was evolving... Sometimes referred to as "the muddle in the middle" because of difficulty dating many sites.

**Uranium Series (U-S):** Cavestones & others; up to nearly 1my, depends on the particular isotopes

**Fission Track:** Natural [volcanic] glass or crystal; few ky and up (more reliable as it gets older)

**Thermoluminescence (TL) and Electron Spin Resonance (ESR):** Pottery, burned flint, tooth enamel; few ky to about 1my

**Dendrochronology:** Wood; today to about 9kya at some localities

**Amino acid racemization:** Bone, shell; few hundred to few hundred ky (and very sensitive to diagenetic processes)

**Obsidian hydration:** Obsidian; few hundred to about 120kya (and very sensitive to composition of the obsidian and diagenetic processes).