ARTICLE

Dating fossil teeth by electron paramagnetic resonance: how is that possible?

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Introduction

Electron paramagnetic resonance (EPR) spectroscopy is a powerful and versatile technique that is frequently used for quantitative and qualitative analysis in a wide range of scientific fields such as chemistry, physics, biology, medicine, geology and archaeology. It can be especially useful for the characterisation of matter, providing information about the nature of the paramagnetic species present, as well as the structure of their local environment. Among all the existing applications of EPR,[†] its use for Quaternary[‡] geochronology is very likely one of the most original (and marginal).

Although there is quite a wide range of chronometric (≈ absolute) dating methods usually employed in Quaternary geochronology, the most widely known by the general public is undoubtedly Radiocarbon (or ^{14}C) dating. This numerical dating method is based on the study of the radioactive decay of ^{14}C in organisms after their death and may provide accurate ages for samples containing organic matter like fossil bones or charcoals. Radiocarbon is usually classified as a radiometric dating method, which corresponds to a group of techniques based on the measurement of the radioactive decay or production of specific radioelements (e.g. Argon–Argon, Uranium–Thorium, Uranium–Lead, Terrestrial Cosmogenic Nuclides). But there is also another group of dating approaches that are based instead on the evaluation of the effects of natural radioactivity on some materials over time, which are quantified in terms of the radiation dose absorbed (i.e. the energy deposited in a medium by ionising radiation per mass unit). These are usually called palaeodosimetric or trapped charge dating methods, mainly based either on the study of radiation-induced luminescence, e.g. thermoluminescence (TL), optically stimulated luminescence (OSL) or paramagnetic properties (EPR).

The first application of EPR for a dating purpose was carried out during the mid-1970s on a stalagmite from a Japanese cave,[1] about 30 years after the discovery of EPR by E. Zavoïski. Since then, numerous dating applications have been developed on many different materials such as silicates (e.g. quartz, feldspars, silex), phosphates (teeth, apatite), carbonates (speleothems, corals, foraminifera, mollusk shells) and sulfates (e.g. gypsum). A quite complete overview may be found in Reference 2. The first studies on fossil bones were published in the early 1980s, however, these were then naturally oriented towards the teeth, since enamel was rapidly found to have more suitable characteristics for dating. Since then, the method has progressively gained in accuracy over the following decades, especially via a better understanding of the EPR signal of fossil enamel and of its behaviour with the absorbed dose, as well as of the modelling of uranium uptake into dental tissues.

The objective of this article is to explain how EPR may be converted into a dating tool for fossil teeth.

Using EPR for dose reconstruction

By definition, EPR spectroscopy is a technique designed for the study of paramagnetic species, i.e. species that possess unpaired electrons. These may be either naturally present in some materials, or created by physical or chemical reactions. With regard to the latter, some materials can acquire paramagnetic properties under the effect of radioactivity. The interaction of ionising radiations with the matter may induce modifications of the electronic structure of some materials: electric charges (electrons or holes) may be trapped in the crystalline network, thereby forming radiation-nduced paramagnetic species. These species create a signal that can be detected by EPR spectroscopy, the intensity of which is directly dependent on the amount of trapped charges in the crystalline network, reflecting thus the dose absorbed by the material.

EPR spectroscopy is now widely recognised as a reference technique for routine dosimetry by many international institutions [e.g. the International Commission on Radiation Units and Measurements

[†]In Geochronology, the acronym ESR (Electron Spin Resonance) is usually preferred to EPR, but they both define the same technique.

‡The Quaternary is the most recent geological period of the geological time scale: it spans from 2.6 million years to nowadays.

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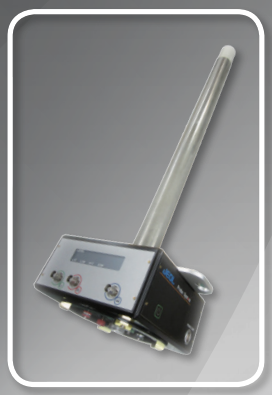

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(ICRU), the International Organisation of Standards (ISO) and the International Atomic Energy Agency (IAEA)]. Over the last decades, many applications have been developed, including those for post-accident dose reconstruction in the environment, biophysical dosimetry using human tissues, to identify irradiated foods, and some of them, such as the alanine dosimetry, have reached a high-level of standardisation.[3]

Tooth enamel: a natural EPR dosimeter

Dosimetric properties of tooth enamel have been known for more than 40 years. Hydroxyapatite, the main component of bones and teeth, is especially sensitive to ionising radiation: this material is able naturally to register doses from only a few mGy to several thousand of Gy. It is now internationally accepted as a valuable natural EPR dosimeter, and is commonly used in the field of retrospective dosimetry for persons accidentally exposed to ionising radiation. An extensive review on this aspect may be found in Reference 4.

From a mineralogical point of view, tooth enamel is mainly made of carbonated hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] like dentine or bones. Nevertheless, this is definitely the most mineralised tissue, comprising >90% of hydroxyapatite (vs ~70% for dentine), the remaining part being water and organic matter.[5] In addition, enamel is denser and more compact, with larger hydroxyapatite crystals, than either dentine or bones. These characteristics make tooth enamel especially stable over time, i.e. less sensitive to diagenetic processes than bones or other dental tissues.

The EPR signal associated with fossil hydroxyapatite is an asymmetric composite signal. The main radiation-induced signal is defined by three peaks (T1, B1 and B2, see Figure 1). Many contributions to this signal have been identified, mainly carbonate-derived radicals and some oxygen radicals,[4] but the major contribution comes from three kinds of CO_2^- radicals, whose precursors are very likely the carbonate groups CO_3^{2-} present in the hydroxyapatite. The lifetime of the main EPR signal of tooth enamel has been assessed to be ~1 Ga at 25°C, suggesting therefore the possibility to use EPR for dating over a few Ma.[6]

Basic principles of EPR dating of fossil tooth enamel

Once an animal is dead, its teeth become progressively buried by sediment during the geological periods, during which the enamel is naturally exposed to ionising radiations from cosmic rays and from the radioactivity of the sediment and the tooth itself. This natural radioactivity is due to the radioelements, mainly (^{238}U-series, ^{232}Th-series and ^{40}K elements), that are not only naturally present in the sediment, but are also progressively incorporated into the dental tissues. Ionising radiations emitted by these radioelements are alpha and beta particles as well as gamma rays (Figure 1). Together with cosmic rays, they contribute to build up a dose in the enamel over time, the magnitude of which will mainly depend on two main parameters: the duration of the exposure to radioactivity, and the strength of this radioactivity. This relationship may be converted into an EPR age equation as follows:

$$D_E = \int_0^T D(t)\,dt \qquad (1)$$

where D_E is the equivalent dose, or palaeodose (expressed in Gray—Gy), i.e. the total dose absorbed by the enamel during the time elapsed between the death of the animal ($t=0$) and the sampling ($t=T$), and $D(t)$ is the dose rate, which is the average dose absorbed by the sample in one year (usually expressed in Gy ka^{-1} or µGy a^{-1}).

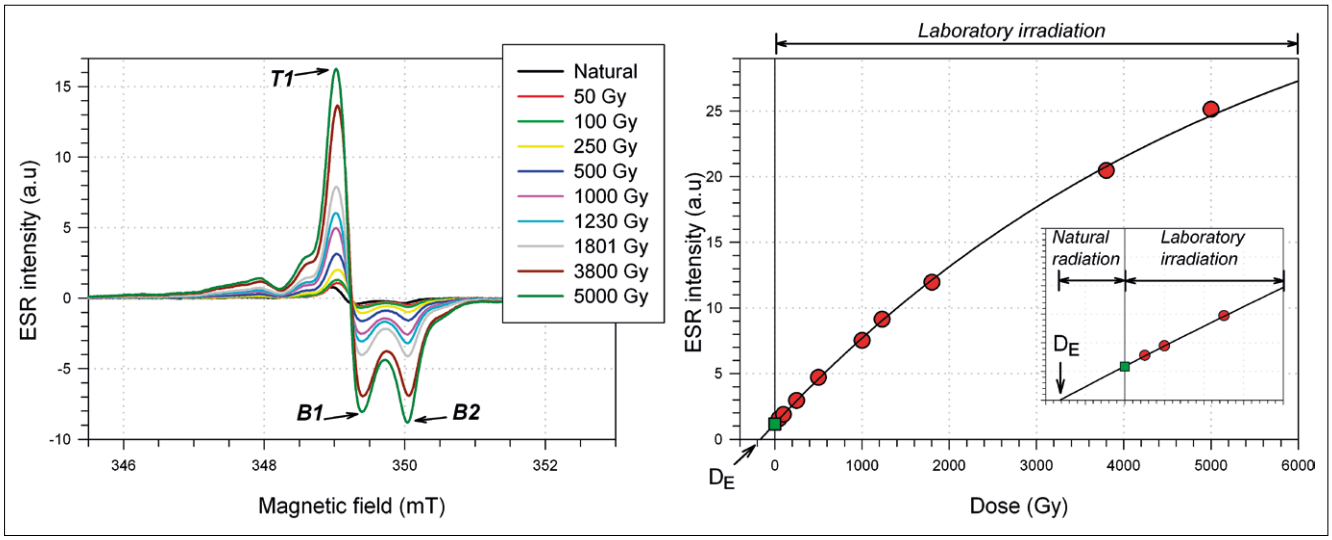

Figure 1. EPR dosimetry of tooth enamel. Left: EPR spectra of fossil tooth enamel irradiated at increasing dose steps. The intensity of the spectra clearly increases with the dose. EPR intensities are usually extracted from peak-to-peak measurements between *T1* and *B2*. Right: EPR dose response curve of fossil enamel. The EPR intensities of the natural (green square) and laboratory irradiated (red circles) aliquots are plotted versus the dose and a single saturating exponential function is fitted. The D_E value is obtained by back extrapolation to $y=0$.

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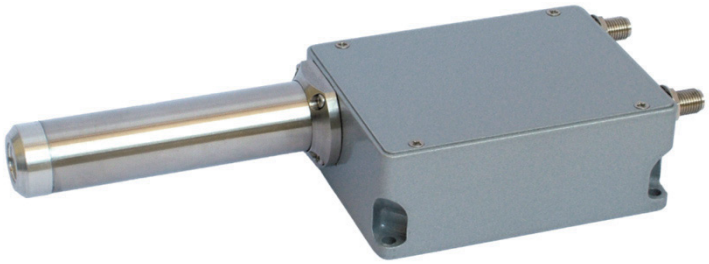

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Consequently, the challenge in EPR dating consists in determining two main parameters [$D(t)$ and D_E] in order to evaluate the duration of exposure to radioactivity (= the EPR age). This work is carried out in two different ways: the D_E is obtained by using EPR spectroscopy, while $D(t)$ is derived from the evaluation of the strength of the radioactivity present in the sample and its surrounding environment.

To obtain an accurate evaluation of the total dose rate, it is important to divide it into several components. The specificity of teeth dating relies on the complex system that has to be considered, because a tooth is usually made by several tissues (enamel, dentine and, sometimes, cement; Figure 2), having various thicknesses and composition. The geometry of the enamel and its surrounding thus has to be considered in the dose rate reconstruction. In the case of a tooth with an enamel layer surrounded by cement and dentine, the dose rate equation may be expressed as follows:

$$D[t(2)] = D_{\text{enamel}}(t) + D_{\text{dentine}}(t) + D_{\text{cement}}(t) + D_{\text{sediment}}(t) + D_{\text{cosmic}}(t) \quad (2)$$

Then, because the enamel layer is usually <1–2 mm thick, and because each kind of ionising radiation has a specific penetration range in matter (~20–40 µm for alpha particles, ~2 mm for beta particles and ~30 cm for gamma rays), some of their respective contribution may be removed (see further details in Reference 7):

$$D(t) = D_{\alpha\text{-enamel}}(t) + D_{\beta\text{-enamel}}(t) + D_{\beta\text{-dentine}}(t) + D_{\beta\text{-cement}}(t) + D_{\gamma\text{-sediment}}(t) + D_{\text{cosmic}}(t) \quad (3)$$

Consequently, with this specific configuration, the internal dose rate within the enamel comes from alpha and beta particles, while the surrounding tissues only provide an external beta contribution. The gamma rays contribution only comes from the sediment, since the absorption by the enamel of the gamma rays coming from the enamel itself and the other tissues can be neglected. In the case of a tooth with an enamel layer in direct contact with the sediment on the outer side (i.e. without cement), an external beta contribution from the sediment should be also considered.

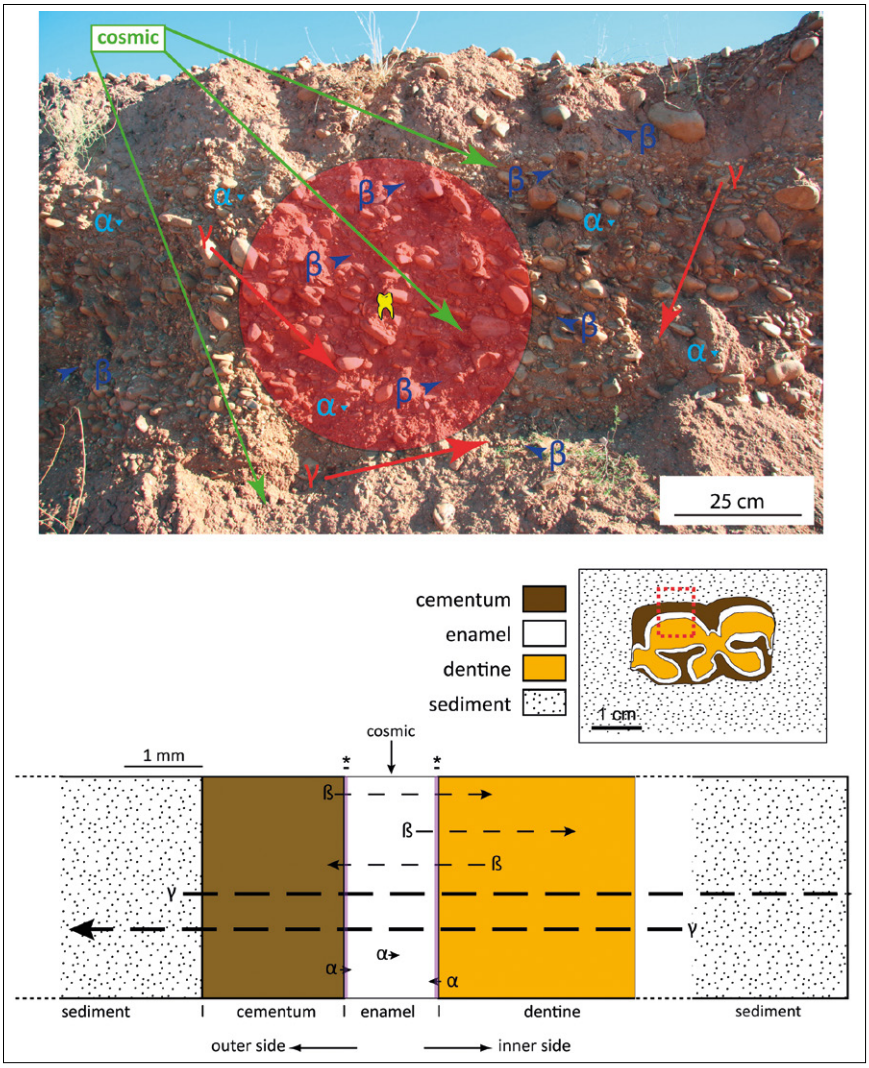

Figure 2. Schematic representation of the various components involved in the natural irradiation of tooth enamel (alpha and beta particles, gamma and cosmic rays). Top: example of a fossil tooth found in an outcrop. The reconstitution of the dose rate has to be carried out by considering all the ionising radiations within a sphere of ~30 cm-radius (= the penetration range of gamma rays in matter) around the fossil tooth (in red). Bottom: zoom at a smaller scale. Cross-section of a tooth showing all the components that are contributing to the dose accumulated in the enamel layer: alpha and beta internal components + external beta components from the surrounding tissues + gamma component from the sediment + cosmic component. The external alpha component is removed during the sample preparation by abrading both sides of the enamel layer over a few tens of µm.

Dental tissues are usually assumed to be free of ^{232}Th and ^{40}K, since their incorporation into the crystalline network is very complicated, owing to their mobility and atomic radius, respectively. Consequently, the dose rate components associated to dental tissues are directly, and only, dependent on the uranium concentration. However, dental tissues behave as open systems for U, i.e. the U concentration in a given tissue may significantly vary with time. It is therefore crucial not only to measure the actual U-content but also to know its evolution in the past. Indeed, one may intuitively understand that the total dose absorbed by the enamel will be somewhat different if the uranium was accumulated in the dental tissues shortly after the death of the animal or if it happened only

very recently. Consequently, to address the problem of the unknown U-uptake, Grün *et al.*[8] suggested to combine EPR and U-series analyses and introduced a parameter to describe the kinetics of the U-uptake. The US model defined by these authors is based on the following equation:

$$U(t) = U_m (t/T)^{p+1}$$

where $U(t)$ is the uranium concentration at the time t, U_m is the measured, present day U-concentration, T is the age of the sample and p is the uptake parameter.

With the combined US-EPR approach, U-uptake history is mathematically assessed according to the present day ^{238}U-series data and their disequilibrium measured in each tissue (U-concentration, ^{230}Th/^{234}U and ^{234}U/^{238}U). Examples of dating applications may be found in Reference 9.

Standard analytical procedure

An EPR age estimate is the result of a long analytical process, made by five main steps associating fieldwork and laboratory procedures: (i) sampling and *in situ* measurements, (ii) sample preparation, (iii) EPR dosimetry, (iv) evaluation of the natural radioactivity of the sample itself and its surrounding environment, and (v) EPR age calculation.

Fossil teeth are usually collected either on site or chosen from collections. Large mammal teeth, and especially from herbivores, are usually preferred, since they offer a thicker enamel layer. Then, *in situ* measurements of the natural radioactivity at the exact place where the sample was collected during excavations, or at least the closest possible, is carried out to evaluate the gamma dose rate. Classically, various techniques may be employed: synthetic TL dosimeters (e.g. $CaSO_4$:Dy, Al_2O_3:C) are used to register a total gamma dose-rate over several months, whereas portable gamma spectrometers with NaI or LaBr scintillation probes allow almost instantaneous measurements (<1 h).

In the laboratory, the fossil tooth is prepared by separating mechanically each dental tissue. The enamel layer is then cleaned, usually with a dentist drill, and gently powdered, in order to avoid significant angular dependence of the EPR signal within the resonator and to improve sample homogeneity. This is why EPR must be considered as a destructive dating method.

The enamel powder (usually <2 g) is divided into several sub-sample aliquots of similar weights that are artificially aged by several successive irradiations at increasing dose steps with a gamma irradiation source. Each aliquot is then measured at room temperature by EPR spectrometry in order to study the behaviour of the EPR signal with the increasing dose values (see Figure 1). Routine quantitative measurements are usually performed by X-band EPR spectrometry, since it offers a good compromise between sensitivity and measurement repeatability in comparison with higher frequency bands. The experimental setup for quantitative EPR measurements is specifically designed to ensure the stability of the system, including air conditioning and chiller to control the temperature of the water circulating in the magnet. Measurements are thus performed under controlled experimental conditions and following a standardised analytical protocol, in order to minimise any sources of uncertainty that could affect the repeatability of the measurements (see further details in Duval *et al.*[10]). EPR intensities are then extracted from each spectrum, usually by peak-to-peak measurements between *T1* and *B2* (Figure 1) and plotted vs the irradiation doses in order to obtain a growth curve (or dose response curve). A given function, usually a single saturating exponential or a double saturating exponential function, is fitted through the EPR experimental data points. By definition, this function is supposed to describe the behaviour of the radiation-induced EPR signal of tooth enamel since the death of the animal (i.e., the moment when the EPR signal = 0). Consequently, the extrapolation of the function to the abscissa axis (Y = 0) provides the D_E value (see Figure 1).

The dose rate reconstitution is carried out by considering the tooth and its environment within a sphere of ~30 cm in radius (Figure 2). If the gamma dose rate is assessed *in situ*, the beta dose rate from the sediment (if it applies) should preferably be assessed in the laboratory from the sediment sample that was collected around the tooth. Various laboratory analytical techniques may be used to calculate the radioelement contents of the sediment, e.g. high resolution gamma-ray spectrometry (HRGS), neutron activation analysis (NAA), inductively coupled plasma optical emission spectrometry (ICP-OES) or ICP-mass spectrometry (ICP-MS). Other techniques, like beta counting for example, may directly provide a total beta or gamma dose rate value. For the case of the combined US-EPR approach, U-series data from each dental tissue (U-concentration, ^{234}U/^{238}U and ^{230}Th/^{234}U) is required in order to model the Uranium uptake. To do so, mass spectrometry techniques are now usually employed [e.g., thermal ionisation-MS (TIMS), ICP-MS], replacing traditional techniques like alpha spectrometry. The radioelement concentrations are then converted into dose rate values and corrected/attenuated by several parameters such as the water content of the sample and sediment, the thickness and density of the dental tissues, or the alpha efficiency.[†] Finally, when sample depth is approximately <20 m, the cosmic dose rate contribution has to be assessed. This is done via tables, and the value depends on the depth of the sample, as well as the density of the sedimentary matrix, latitude and altitude of the site.

EPR age calculation of fossil teeth is not so straightforward since it may involve up to 25 parameters. In addition to this, the dose rate in dental tissues is not constant over time but has to be modelled from the U-series data collected. An EPR age may be obtained by iteratively solving the integral Equation (1), since there is only one solution for which the total dose rate built up over time will match the D_E value.[8] To do so,

[†]The alpha efficiency is a correction factor that takes into consideration the fact that alpha particles are not as effective as beta particle or gamma rays of creating paramagnetic centres.

non-commercial programs have been written, but the most widely used is the DATA program, which provides combined US-EPR age estimates.[11]

Why use EPR and not another method?

Not every chronometric dating method can be used on a given Prehistoric site, since by definition it depends on the presence (or absence) of suitable materials for this purpose, which is closely related to the geological context and the presumed age of the site. For example, radiocarbon dating cannot be used beyond 50–60 ka (ka = 1000 years). Figure 3 shows the time range applicability for some of the most used dating techniques in Quaternary studies. It is usually considered that the optimum time range application for EPR dating of tooth enamel lies between ~50 ka and ~800 ka. However, in some specific conditions, the real time-range limits may be potentially pushed from present-day to ~2–3 Ma.

EPR is one of the very few dating methods that may be applied to fossil remains. By definition, the dating of a tooth remains provides a direct dating of hominid or animal occupations, whereas other numerical methods can only date the sedimentary matrix that is enclosing the archaeo–palaeontological materials. Consequently, this application may be also potentially used in any sedimentary context, while other methods like Argon–Argon or cosmogenic nuclides dating can only be used on volcanic minerals and quartz grains, respectively. In addition, the EPR technique is one of the very few possibilities to date fossil remains beyond the C-14 and U-series dating time range. The precision afforded by EPR is rarely <10% at 1 sigma, while other methods have a precision lower than 1% (e.g. C-14, U–Th, Ar–Ar; an overview may be found in Reference 12), this is nevertheless one of the few methods that can be used for the Early Pleistocene period (2.6–0.8 Ma) (see Figure 3). This is a key period in European Prehistory, marked by the arrival of the first hominids in the continent and who very likely spread from Georgia, about 1.8 Ma go, to Western Europe. EPR has definitely an important role to play for the improvement of the chronological framework of the oldest hominids settlements in Europe.[13]

Conclusion

Even if the field of EPR dating is now more than 40 years old, it remains nevertheless a marginal application of EPR, with only a limited number of laboratories around the world (<10) that are able to carry out EPR dating of fossil teeth. This is very likely due to the long and complex analytical process that requires a large diversity of equipment (e.g. U-series analyses facilities, EPR spectrometer, gamma irradiation source, high resolution gamma spectrometer, portable gamma spectrometer), which make it especially complicated to setup a complete and autonomous laboratory.

However, recent developments in the field have demonstrated the potential of this method for Quaternary geochronology. Among them, the development of almost non-destructive direct dating of hominid fossil teeth is perhaps the most promising. If EPR spectroscopy is not a destructive method *per se*, the standard procedure consists in working with enamel powder, mainly for prac-

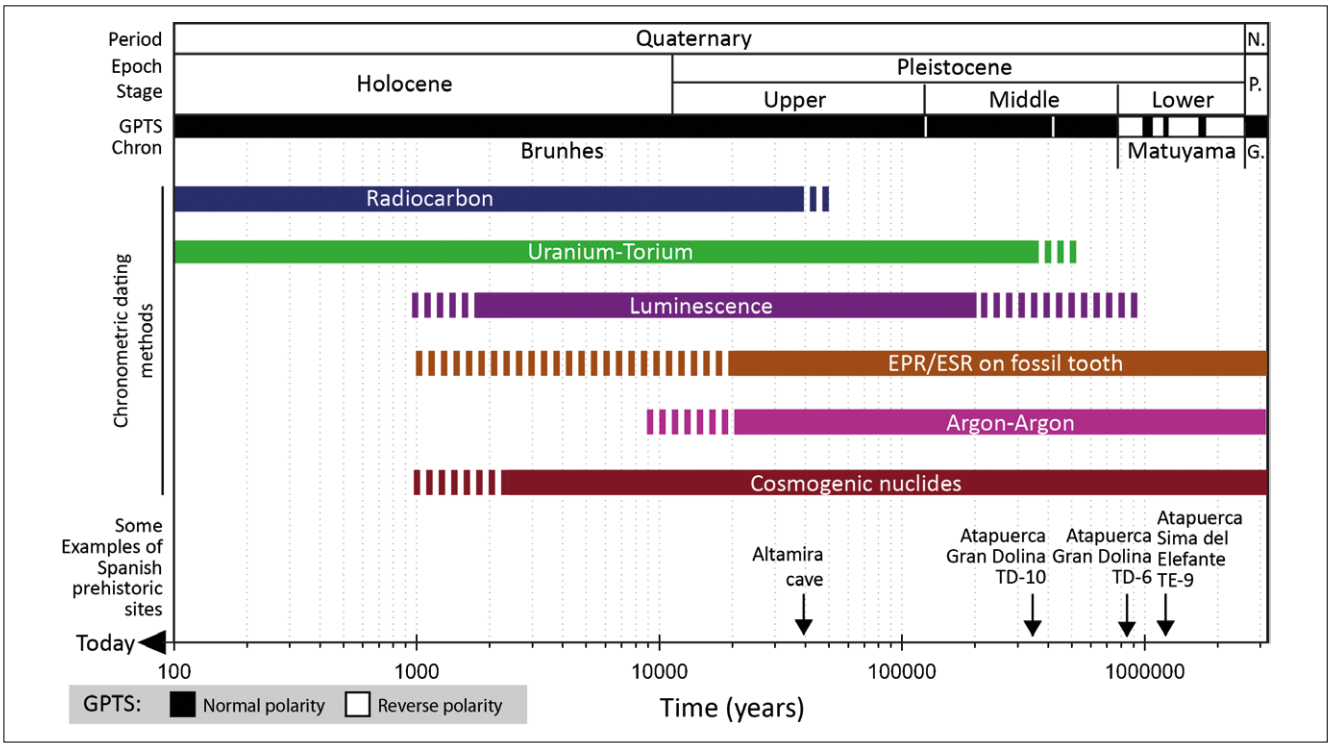

Figure 3. Examples of chronometric dating methods with approximated time range application. Time scale is logarithmic. N. = Neogene; P. = Pliocene; G. = Gauss. GPTS: geomagnetic polarity time scale.

tical reasons, to avoid the complexity induced by EPR signal anisotropy. For a long time, this aspect has significantly limited the access to rare samples, like hominid teeth. However, the recent development of EPR measurements on enamel fragments combined with Laser Ablation ICP-MS U-series analysis allows for working on human teeth without causing any visible damage.[14] Basically, the analytical procedure consists of extracting a fragment of enamel, obtain the D_E value by a single aliquot additive dose method, and finally undertaking some laser ablation analyses. Once the analyses are done, the fragment may be inserted back into the tooth in its original position. This new approach offers interesting perspectives for the EPR method by allowing direct dating of hominid remains that are beyond the ^{14}C time range.

References

1. M. Ikeya, "Dating a stalactite by electron paramagnetic resonance", *Nature* **255(5503),** 48–50 (1975). doi: http://dx.doi.org/10.1038/255048a0
2. M. Ikeya, *New Applications of Electron Spin Resonance Dating, Dosimetry and Microscopy*. World Scientific, Singapore (1993).
3. D.F. Regulla, "ESR spectrometry: a future-oriented tool for dosimetry and dating", *Appl. Radiat. Isotopes* **62,** 117–127 (2005). doi: http://dx.doi.org/10.1016/j.apradiso.2004.08.030
4. P. Fattibene and F. Callens, "EPR dosimetry with tooth enamel: A review", *Appl. Radiat. Isotopes* **68,** 2033–2116 (2010). doi: http://dx.doi.org/10.1016/j.apradiso.2010.05.016
5. J. Elliott, "Calcium phosphate biominerals", in *Phosphates—Geochemical, Geobiological and Material Importance*, Ed by M.J. Kohn, J. Rakovan and J.M. Hughes. Mineralogical Society of America, pp. 427–454 (2002).
6. H.P. Schwarcz, "ESR studies of tooth enamel", *Nucl. Tracks Rad. Meas.* **10(4–6),** 865–867 (1985). doi: http://dx.doi.org/10.1016/0735-245X(85)90101-2
7. R. Grün, "Suggestions for minimum requirements for reporting ESR age estimates", *Ancient TL* **10(3),** 37–41 (1992). http://www.aber.ac.uk/temp-ancient-tl/issue10_3/grun_atl_10(3)_37-41.pdf
8. R. Grün, H.P. Schwarcz and J. Chadam, "ESR dating of tooth enamel: Coupled correction for U-uptake and U-series disequilibrium", *Int. J. Radiat. Appl. Instrum. D* **14(1–2),** 237–241 (1988). doi: http://dx.doi.org/10.1016/1359-0189(88)90071-4
9. R. Grün, "The relevance of parametric U-uptake models in ESR age calculations", *Radiat. Meas.* **44(5–6),** 472–476 (2009). doi: http://dx.doi.org/10.1016/j.radmeas.2009.02.011
10. M. Duval, V. Guilarte Moreno and R. Grün, "ESR dosimetry of fossil enamel: some comments about measurement precision, long-term signal fading and dose–response curve fitting", *Radiat. Prot. Dosim.* **157(4),** 463–476 (2013). doi: http://dx.doi.org/10.1093/rpd/nct167
11. R. Grün, "The DATA program for the calculation of ESR age estimates on tooth enamel", *Quat. Geochronol.* **4(3),** 231–232 (2009). doi: http://dx.doi.org/10.1016/j.quageo.2008.12.005
12. K.R. Ludwig and P.R. Renne, "Geochronology on the paleoanthropological time scale", *Evol. Anthropol.* **9(2),** 101–110 (2000). doi: http://dx.doi.org/10.1002/(SICI)1520-6505(2000)9:2<101::AID-EVAN4>3.0.CO;2-W
13. M. Duval, C. Falguères and J.-J. Bahain,"Age of the oldest hominin settlements in Spain: Contribution of the combined U-series/ESR dating method applied to fossil teeth", *Quat. Geochronol.* **10,** 412–417 (2012). doi: http://dx.doi.org/10.1016/j.quageo.2012.02.025
14. R. Grün, "Direct dating of human fossils", *Amer. J. Phys. Anthropol.* **131(S43),** 2–48 (2006). doi: http://dx.doi.org/10.1002/ajpa.20516