PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

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Phil. Trans. R. Soc. Lond. B 1992 **337**, 145-148
doi: 10.1098/rstb.1992.0091

Electron spin resonance (ESR) dating of the origin of modern man

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SUMMARY

Many materials found in archaeological sites are able to trap electronic charges as a result of bombardment by radioactive radiation from the surrounding sediment. The presence of these trapped charges can be detected by electron spin resonance (ESR) spectroscopy: the intensity of the ESR signal is a measure of the accumulated dose and thus of the age. Tooth enamel is ubiquitous at archaeological sites and is well suited for ESR dating, with a precision of about 10–20%. This method has now been used to date many sites critical to the biological and cultural evolution of modern man. Dates for sites in Israel and Africa have demonstrated the existence of anatomically modern humans more than 100 ka ago.

1. INTRODUCTION

Over the past few years attention of archaeologists and anthropologists has focused on the stages leading to the appearance of modern man, *Homo sapiens sapiens*, and the disappearance of archaic modern hominids including Neanderthal man. The timescale of this transition lies beyond he dating range of ^{14}C and therefore has necessitated the employment of a battery of new dating techniques. One such method which has been developed over the last decade is electron spin resonance (ESR) dating; this method is also sometimes referred to as electron paramagnetic resonance (EPR) dating. The method was invented by Zeller (1968) who did not, however, further develop it. This was left to M. Ikeya who, in a series of papers beginning in 1978, showed the utility of the technique in dating stalagmitic calcite, shells, animal bones, and teeth, all of which are found in archaeological sites. Reports on ESR dating of tooth enamel from archaeological sites began to appear in the 1980s. Grün (1989) has recently summarized the theory and applications of the ESR techniques.

2. THEORY OF ESR DATING

The principles of ESR dating are in part the same as those of luminescence dating as discussed elsewhere in this symposium by Aitken & Valladas; the main difference is in regard to the dating signal. In brief, electronic charges are trapped at defects in crystalline materials as a result of radioactive bombardment of the crystal. The age of the material can be obtained from the ratio of the amount of trapped energy to the rate of trapping. The number of trapped charges is determined from the intensity of a characteristic signal in an ESR spectrum; in luminescence dating, on the other hand, trapped charges are measured by the intensity of light emitted from the sample. The number of trapped charges is converted to a palaeodose, P, and the age, t, is then obtained from the relation

$$t = P/D, \qquad (1)$$

where D = the average dose rate (in grays per year) and P is given in grays (Gy).

In principle, any crystalline, non-conducting material could be dated, but in practice we require that: (i) the material be free of all but traces of iron or manganese whose ESR signals interfere with those produced by radiation; (ii) that the lifetime of trapped electrons be much greater than the age to be determined, say greater than 10^8 years; (iii) that the material be widely encountered at archaeological sites; and (iv) that, at the time of occupation of the site, the material should either be formed *de novo* or that the pre-existing trapped charges have been zeroed by some process, such as heating in a fire. Thus the signal is assumed to start at zero at the time of burial of the sample, and to grow steadily thereafter as a result of natural irradiation. The radiation occurs in two forms: internal, which is due to traces of the radioactive elements uranium (U), thorium (Th) and potassium (K) which are present in the material; and exernal, from U, Th, and K in the surrounding sediment, plus cosmic rays.

The material which has proven to be most useful for ESR dating at archaeological sites is tooth enamel (Grün *et al.* 1987); currently burnt flint is being investigated (Porat & Schwarcz 1991). Stalagmitic calcite and molluscan aragonite show some promise but have not been widely applied (Grün 1989). Enamel displays a single, well-defined ESR signal with

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Phil. Trans. R. Soc. Lond. B (1992) **337,** 145–148
Printed in Great Britain

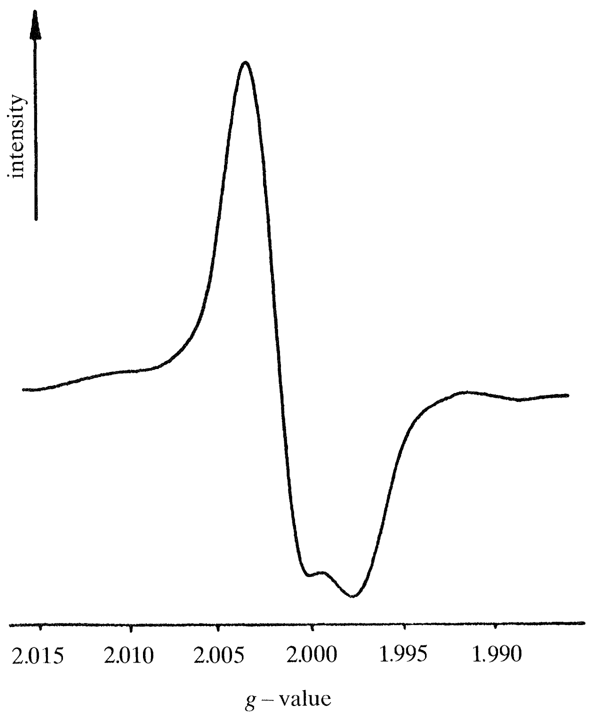

Figure 1. Typical ESR signal from tooth enamel. The signal is obtained by subjecting the sample to a beam of microwaves while it sits in a strong, varying magnetic field. The peak shown is characterized by a dimensionless parameter, g, which determines the value of the magnetic field at which the signal crosses the base line; for tooth enamel and bone, $g=2.0018$.

a g-value of 2.0018 (figure 1), whose intensity can be easily measured at room temperature. Bone, which displays the same ESR signal as enamel, is however not useful for dating (Grün & Schwarcz 1987). The applications of ESR to the evolution of modern hominids have all involved dating of tooth enamel, so we shall limit the discussion to this material.

3. ESR DATING OF TOOTH ENAMEL

Teeth of large mammals are commonly found at most archaeological sites, and provide an excellent material for ESR dating. Teeth are composed of two anatomical components: enamel which consists of relatively well-crystallized hydroxyapatite mineral, and less than 1% organic matter; and dentine + cementum, which contain much smaller apatite crystals and a much larger proportion of organic matter (more than 20% by weight). Like bone, dentine and cementum are not suitable for ESR dating. At the time of death of the animal, none of these materials contain any U, Th or K. Shortly after burial U alone begins to be absorbed by both materials, and old teeth are found to contain more than 100 p.p.m. (parts per million) of uranium in the dentine, and a few p.p.m. in the enamel.

The palaeodose of a sample of tooth enamel is obtained by measuring the intensity (I) of the $g=2.0018$ signal in unirradiated powdered enamel, as well as in eight or more portions of enamel that have been given successively larger doses of gamma radiation from a ^{60}Co source. A plot of I versus added dose

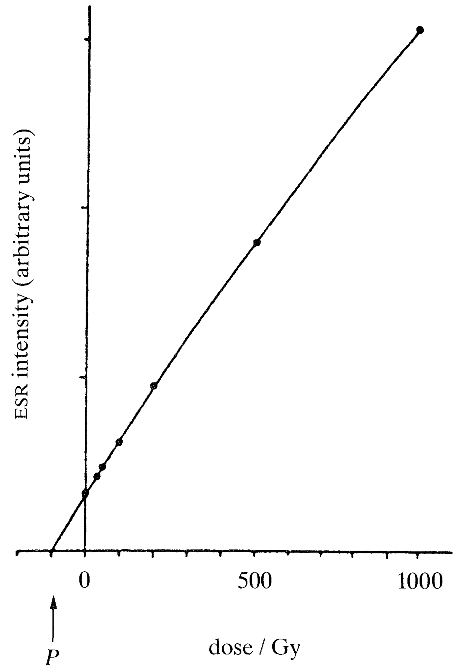

Figure 2. Growth curve for artifical irradiation of an archaeological sample of tooth enamel. P = palaeodose, obtained by logarithmic extrapolation of data (modified from Grün & Stringer (1991)).

yields a curve which can be extrapolated back to $I=0$ in order to obtain P (figure 2). The external dose rate at the burial site can be measured directly using gamma dosimeters; the internal dose rate is determined from the U content of the enamel and dentine. The age cannot be obtained simply from equation (1), however, because the dose rate D has changed (increased) through time for two reasons. First, because U has been taken up by the tooth since it was buried; and second, because U in the tooth has been increasing in effective radioactivity through time due to the growth of U-series daughter isotopes (as discussed by Schwarcz, this symposium). The latter process can be modelled exactly from physical principles, as long as the process of U uptake is known as a function of time. We generally consider two specific models of U uptake: early uptake (EU), in which U is taken up very soon after burial and then remains at the concentration observed today; and linear uptake (LU), in which U is taken up at a constant rate, culminating in the present-day concentration. Then the age can be calculated from the value of P and from the calculated temporal history of D, based on the selected model.

In general the EU age gives the lowest possible age that can be computed from a given set of data. Where independent estimates of the age are available (e.g. from luminescence or U-series dating) we find that these generally agree most closely with LU ages, and we conclude that this model most closely describes the U uptake process in most cases (Schwarcz *et al.* 1988). However, at some sites, we find better agreement with the EU model (e.g. at Le Moustier (Mellars & Grün 1991) and Pech de l'Azé (Grün *et al.* 1991)). It is possible to use simultaneous U-series and ESR measurements of tooth enamel to define the uptake process more closely (Grün *et al.* 1988). When applied to the site of Hoxne, U.K., for example, we found that U uptake must have occurred late in the burial history of the sample. The use of thermal ionization mass spectrometry (TIMS) methods will make it easier to use U-series dating to define the U uptake model for enamel and dentine samples.

Typically, we do complete ESR age determinations on several portions of enamel from a single tooth, where the size of the tooth permits. Concordance between ages obtained on these subsamples contributes to our confidence in the result. Lately Blackwell & Schwarcz (1992) have also shown that subsamples can be used collectively to define an isochron whose slope gives the age of the tooth as a whole. When using this method, however, it is still necessary to make some assumption about the U uptake model.

4. APPLICATION OF ESR DATING TO THE ORIGIN OF MODERN HOMINIDS

ESR dating has been applied to a number of sites in Israel and Africa at which anatomically modern hominids had been discovered. The first such site was the cave of Qafzeh, Israel, at which the remains of at least 20 modern ('Cro Magnon') hominids had been found buried (Vandermeersch 1981). In 1988, Valladas *et al.* (1988) reported a date of 92 ± 5 ka for this site, based on thermoluminescence (TL) measurements of heated flint. Shortly afterwards, Schwarcz *et al.* (1988) reported ESR dates for this site; Grün & Stringer (1991) have slightly revised this result, obtaining ages of 100 ± 10 ka (EU) and 120 ± 8 ka (LU). The dose rates for flint (on which TL dates were based) were dominated by the internal dose rate, whereas the dose rate to the tooth enamel at this site was dominated by the external component. Therefore these two dates are effectively independent estimates of the age. Aitken & Valladas (this symposium) have suggested that the external dose rate at Qafzeh may have been underestimated, which would cause the ESR ages to be shifted slightly towards better agreement with the TL ages.

The site of Skhul in Mt Carmel also contained a number of burials of anatomically modern hominids. Stringer *et al.* (1989) obtained an ESR date on subsamples from two teeth taken from the collection in the Museum of Natural History, London. The external dose rates were estimated from chemical analyses of associated sediments. These samples gave ages of 81 ± 15 ka (EU) and 101 ± 12 ka (LU), consistent with the dates obtained at Qafzeh.

It is interesting to compare these dates with ESR ages obtained on Neanderthal hominids from the same region. At the nearby site of Tabun, a Neanderthal skeleton had been recovered by Garrod from her excavations in the 1930s. This hominid was believed to come either from layer C or the base of layer B in the stratigraphic sequence of the site. Linear uptake ESR dates on teeth from layer B average around 100 ka whereas those in layer C average around 120 ka. These dates are comparable to the age obtained at Skhul and Qafzeh and show that both Neanderthals and fully modern hominids may have been present in the same time interval (though they need not have coexisted, given the uncertainties in dating). At the nearby cave of Kebara, a Neanderthal skeleton was found, apparently a burial into layer XII of this site. ESR dates on teeth from the immediately overlying layer X gave ages of 60 ± 6 ka (EU) and 64 ± 6 ka (LU) (Schwarcz *et al.* 1989). Valladas *et al.* (1987) had obtained a TL date of 60 ± 4 ka on burnt flint from layers XI and XII. Note that there is no significant difference between the LU and EU ages of the teeth from this site because of the low U content of the enamel from the site.

The dates obtained so far at sites from Israel have demonstrated the presence of modern hominids in western Asia long before they appeared in Europe. These results set the stage for a revolution in the chronology of the evolution of modern hominids, as discussed by Grün & Stringer (1991). These authors also noted preliminary estimates for the age of the Neanderthal from Wadi Amud, of around 50 ka.

Three important sites in Africa have also been dated. At Jebel Irhoud, mammal teeth associated with a modern hominid have yielded preliminary LU–ESR dates between 105 and 190 ka (Grün & Stringer 1991). In South Africa, two sites, Border Cave and Klasies River Mouth have been studied. At Border Cave, a long sequence of sediments contains teeth whose LU–ESR ages range from 31 ka (top) to 128 ka (bottom). The critical Howiesons Poort layer mid-way in the sequence gives ESR ages ranging from 45 ± 5 to 75 ± 5 ka (average = 62 ka) while amino-acid dates on this layer suggest an age of about 80 ka (Miller & Beaumont, this symposium). Skeletal remains of modern hominids were recovered from this site but most were found out of stratigraphic context. Specimen BC3, the buried partial skeleton of an infant, was apparently recovered from unit 4BS and would therefore have an age of about 70–80 ka (Grün *et al.* 1990*a*). Other specimens appear to correspond to younger layers.

At Klasies River Mouth, ESR ages were obtained on teeth from various strata. A modern hominid mandible had been recovered from the basal SAS layer. Subsamples of a mammalian tooth from this layer gave LU ages of 94 ± 10 and 88 ± 8 ka, consistent with U-series dates on a stalagmite that give an upper limit of 110 ka for the layer (Grün *et al.* 1990*b*). Younger ESR dates are found for the overlying layers at the site, ranging to about 40 ka.

In summary, these dates on modern hominids in African sites suggest that *Homo sapiens sapiens* was present on this continent early in the last glacial stage, and possibly during the last interglacial (stage 5). This is consistent with the dates obtained at sites in Israel and have contributed to a model of an African origin for this taxon.

5. CONCLUSIONS

The ESR method of dating as applied to tooth enamel has provided useful estimates for the ages of many of the critical anatomically modern hominid fossils in the time range from 50 to 150 ka. Thse dates have contributed to a new and longer chronology for the history of this taxon, and have helped to define the possible region of origin of our species. At the same time, ESR dates have confirmed the late Pleistocene chronology of Neanderthal hominids in western Europe (Grün & Stringer 1991; Schwarcz *et al.* 1991).

At present, the precision of the ESR ages ranges from 10 to 20% of the age, and is largely limited by uncertainties in the estimates of internal and external dose rates. Both of these are amenable of refinement, the former through U-series analyses, and the latter through the use of the isochron method.

Although all dates reported for hominid sites so far have been obtained on tooth enamel, we are now also able to obtain ESR dates on heated flint (Porat & Schwarcz 1991). Dates obtained from burned flints from the site of Kebara agrees well with that obtained by TL on the same material at this site (Porat *et al.* 1992).

This research was partly funded by grants from the National Science Foundation, U.S.A. to the University of California (BNS 8801699, to F. C. Howell), and the Social Sciences and Humanities Research Council, Canada. We appreciate the encouragement of M. J. Aitken in the preparation of this manuscript, and his critical comments as well as those of C. B. Stringer.

REFERENCES

Blackwell, B. & Schwarcz, H.P. 1992 Electron spin resonance (ESR) isochron dating: solving the external gamma problem. *Appl. Rad. Isotopes* (In the press.)

Grün, R. 1989*a* Electron spin resonance (ESR) dating. Quat. Int. **1**, 65–109.

Grün, R., Beaumont, P. & Stringer, C.B. 1990*a* ESR dating evidence for early modern humans at Border Cave in South Africa. *Nature, Lond.* **344**, 537–539.

Grün, R., Shackleton, N.J. & Deacon, H. 1990*b* Electron spin resonance dating of tooth enamel from Klasies River Mouth Cave. *Curr. Anthropol.* **31**, 427–432.

Grün, R., Mellars, P. & Laville, H. 1991 ESR chronology of a 100,000 year archaeological sequence at Pech de l'Azé II, France. *Antiquity* **65**, 544–551.

Grün, R., Schwarcz, H.P. & Chadam, J. 1988 ESR dating of tooth enamel: Coupled correction for U-uptake and U-series disequilibrium. Nucl. Tracks Rad. Meas. **14**, 237–241.

Grün, R. & Schwarcz, H.P. 1987 some remarks on 'ESR dating of bones'. *Ancient TL* **5**, 1–9.

Grün, R., Schwarcz, H.P. & Zymela, S. 1987 ESR dating of tooth enamel. *Can. J. Earth Sci.* **24**, 1022–1037.

Grün, R. & Stringer, C.B. 1991 Electron spin resonance dating and the evolution of modern humans. *Archaeometry* **33**, 153–199.

Ikeya, M. 1978 Electron spin resonance as a method of dating. *Archaeometry* **20**, 147–158.

Mellars, P. & Grün, R. 1991 A comparison of the electron spin resonance and thermoluminescence dating methods: the results of ESR dating at Le Moustier (France). *Cambr. Archaeol. J.* **1**, 269–276.

Porat, N., Schwarcz, H.P. & Bar-Yosef, O. 1992 ESR dating of burned flint from Kebara cave in the Carmel. *Ann. Mtg. Geol. Soc. Israel* (Abstract), pp. 114–115.

Porat, N. & Schwarz, H.P. 1991 ESR dating of chert. *Nucl. Tracks* **18**, 203–212.

Schwarcz, H.P., Bietti, A., Buhay, W.M., Stiner, M., Grün, R. & Segre, E. 1991 U-series and ESR age data for the Neanderthal site of Monte Circeo, Italy. *Curr. Anthropol.* **32**, 313–316.

Schwarcz, H.P., Buhay, W.M., Grün, R., Valladas, H., Tchernov, E., Bar-Yosef, O. & Vandermeersch, B. 1989 ESR dates for the Neanderthal site of Kebara, Israel. *J. archaeol. Sci.* **16**, 653–661.

Schwarcz, H.P., Grün, R., Vandermeersch, B., Bar-Yosef, O., Valladas, H. & Tchernov, E. 1988 ESR dates for the hominid burial site of Qafzeh in Israel. *J. hum. Evol.* **17**, 733–737.

Stringer, C.B., Grün, R., Schwarcz, H.P. & Goldberg, P. 1989 ESR dates for the hominid burial site of Es Skhul in Israel. *Nature, Lond.* **338**, 756–758.

Valladas, H., Joron, J.L., Valladas, G., Arensburg, B., Bar-Yosef, O., Belfer-Cohen, A., Goldberg, P., Laville, H., Meignen, L., Rak, Y., Tchernov, E., Tillier, A.M. & Vandermeersch, B. 1987 Thermoluminescence dates for the Neanderthal burial site at Kebara cave in Israel. *Nature, Lond.* **330**, 159–160.

Valladas, H., Reyss, J.L., Valladas, G., Bar-Yosef, O. & Vandermeersch, B. 1988 Thermoluminescence dates of Mousterian 'Proto-Cro-Magnon' remains from Israel and the origin of modern man. *Nature, Lond.* **331**, 614–616.

Vandermeersch, B. 1981 *Les hommes fossiles de Qafzeh, Israel.* Paris: CNRS.

Zeller, E.J. 1968 Use of electron spin resonance for measurement of natural radiation damage. In *Thermoluminescence of geological materials.* (ed. D. J. McDougall), pp. 271–279. London: Academic Press.