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ARCHAEOLOGY

Quaternary dating by electron spin resonance (ESR) applied to human tooth enamel

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ABSTRACT

This paper presents the results obtained from using electron paramagnetic resonance (EPR) to analyse tooth enamel found at the Aguazuque archaeological site (Cundinamarca, Colombia), located on the savannah near Bogota at 4° 37' North and 74°17' West. It was presumed that the tooth enamel came from a collective burial consisting of 23 people, involving men, women and children. The tooth enamel was irradiated with gamma rays and the resulting free radicals were measured using an electron spin resonance (ESR) X-band spectrometer to obtain a signal intensity compared to absorbed doses curve. Fitting this curve allowed the mean archaeological dose accumulated in the enamel during the period that it was buried to be estimated, giving a 2.10 ± 0.14 Gy value. ROSY software was used for estimating age, giving a mean 3,256 ± 190y before present (BP) age. These results highlight EPR's potential when using the quaternary ancient ruins dating technique in Colombia and its use with other kinds of samples like stalagmites, calcite, mollusc shells and reefs.

Keywords: EPR/ESR, tooth enamel, Colombia, archaeological dating.

RESUMEN

En este trabajo se presentan los resultados obtenidos por datación mediante el uso de Resonancia Paramagnética Electrónica en muestras de esmalte dental provenientes del sitio arqueológico Aguazuque, ubicado en la sabana de Bogotá en coordenadas 4° 37' de latitud norte y 74°17' de longitud oeste de Greenwich. Se presume que el esmalte dental proviene de un entierro colectivo compuesto de 23 individuos entre mujeres, hombres y niños. El esmalte dental fue irradiado con rayos gamma y los radicales libres producidos fueron medidos usando un espectrómetro de resonancia del spin electrónico (ESR), banda X, con el fin de realizar una curva de intensidad de la señal versus la dosis absorbida por el esmalte. El ajuste de esta curva permitió obtener la dosis media arqueológica acumulada en el esmalte (D_A), durante el periodo de enterramiento de la muestra. El valor obtenido fue de 2.10 ± 0.14 Gy. Para estimar la edad de la muestra se usó el software ROSY, obteniendo una edad media de las muestras de esmalte de 3,256 ± 190y BP. Los resultados obtenidos muestran el potencial uso de la técnica EPR como herramienta de datación de muestras cuaternarias en Colombia y abre la posibilidad de usarla en otro tipo de muestras como estalagmitas, calcitas, conchas de moluscos y corales.

Palabras claves: EPR, esmalte dental, datación arqueológica.

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Introduction

Electron spin resonance (ESR) analysis has recently become an alternative C14 and thermo-luminescence dating method which can be applied to a variety of problems in geology, archaeology and paleoanthropology (Renfrew C *et al.*, 1992; Jonas 1997; Walker 2005; Grun 1989). ESR spectroscopy is the only method for detecting, identifying and quantifying free radicals (Halliwell & Gutteridge 2007; Punchard & Kelly 1996). For instance, this method is used for estimating the free radical level and paramagnetic centres produced in some materials by ionising radiation. The some free radicals' long mean life (above 100 MY) make it possible to reveal them in materials as old as 2 MY without the risk of overcoming the sample's saturation limits. ESR allows some materials to be dated because free radical concentration is a measurement of the total radiation dose absorbed by the sample during the time it was exposed to radiation and hence their burial time (Jonas 1977). ESR has been used for dating the formation and more recent re-crystallisation of three types of gypsum samples: massive, bedded and fracture filling gypsum; in this case, the estimated upper Miocene–Pliocene age agreed with that soil's stratigraphy (Ülkü 2004). Molodkov (2001) used ESR to date eight terrestrial shell samples from Treugolnaya (Triangular) Cave (Northern Caucasus), ages ranging from 583,000 to 393,000Y old. Shigueo *et al.*, (2003) dated a calcite formation found on a rock wall painting at Toca da Bastiana, rock shelter in Serra da Capivara National Park, Piaui, Brazil, obtaining an age of 35,000 to 43,000Y, indicating that humans lived there before 35,000 years ago (this being the date for the first humans to arrive in Brazil). Oth-

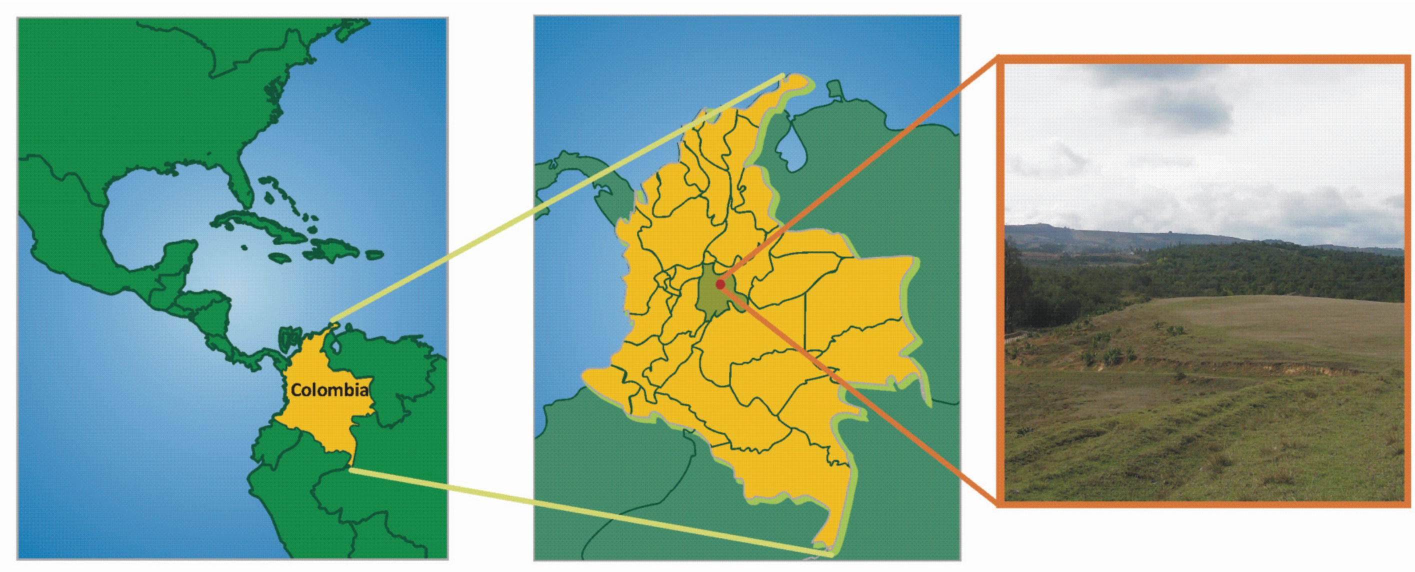

Figure 1. Location of Aguazuque archaeological site (Cundinamarca, Colombia, 40 37' North and 74°17' West). (Taken FROM Groot, A.M., 1992).

er papers dating stalagmites, calcite, mollusc shells and reefs are Renfrew *et al*., (1992), Jonas (1997), Walker (2005) and Grun (1989).

The present study was aimed at using the ESR method for dating tooth enamel from the Aguazuque archaeological site in Soacha, Colombia.

Theoretical aspect

The Aguazuque archaeological site (Cundinamarca, Colombia) is located on the savannah near Bogota at 4^0 37' North and 74°17' West (Figure 1). The human tooth used in this work was extracted from a skeleton (labelled AG-I) taken from a collective burial site where 23 people were found arranged in a foetal position; men, women and children were identified. The burial site was circular shaped (4.5 m diameter) and as burnt bones and lacerated skeletons were found outside the circle, partially painted red and black, it was deduced that cannibal practices were common by the group responsible for the burial (Correal 1990). Archaeological research concerning the early and middle Holocene period has led to reconstructing the way of life for human groups in the region, thereby showing a transition from hunters and gatherers to agricultural societies (Groot 1992). A way of life based on hunting several sized mammals has been recorded during a lapse of 11,000 to 5,000 years before today, with rock shelters providing favourites housing places, such as the archaeological sites of El Abra, Tequendama and Nemocón 4 in Cundinamarca (Correal 1979). Sites such as Chía I (Ardila 1984) and Aguazuque (Correal 1990) have been investigated and the aforementioned research has led to establishing changes in the form of settlement and adaptation mechanisms (Groot, 1992).

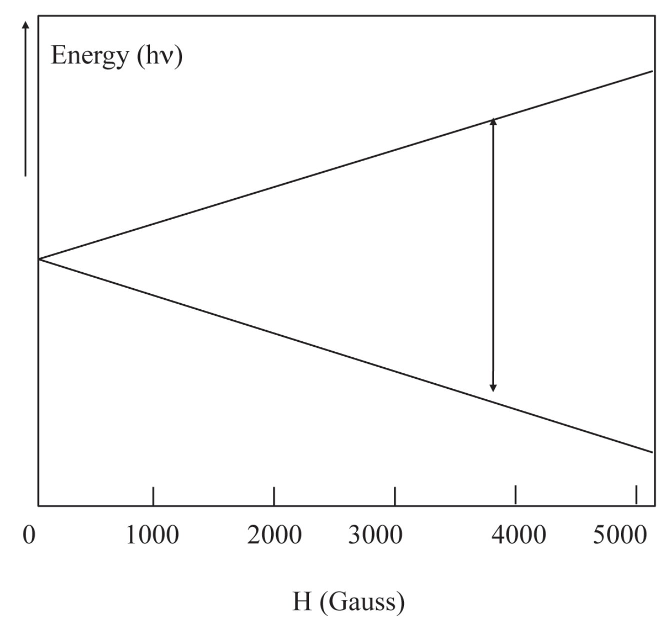

Figure 2. Energy levels of an electron placed in a magnetic field. The arrow shows the transitions induced by microwave radiation.

Electron spin resonance (ESR) consists of the resonant absorption of electromagnetic energy during electron-spin transitions. A static magnetic field should be applied to resolve different electron-spin levels. Unpaired electrons from free radicals have spin equal to ½. There are two magnetic levels (+½ and –½) in a magnetic field, both having different energy (Figure 2); the transition between these two levels is possible in the following resonance condition:

$$h\nu = g\beta H \qquad (1)$$

where ν is resonance frequency, h is Plank's constant, g is the g-factor (which is a constant = 2 for ½ spin), β is the Bohr magneton which is an electron magnetic dipole moment and H is the magnetic field. An important conclusion derived from this formula is the linear dependence between the applied magnetic field and resonance frequency. The most frequently used microwave energies drop in what is called the X band. This is because it is a good compromise between sensitivity, sample size and water content effects; $\nu \approx 9.8$ GHz and $H \approx 350$ mT for the X band.

ESR dating and dosimetry are based on the fact that ionising radiation produces paramagnetic centres having long lifetimes in a number of materials. Such centres' concentration in a given sample is a measure of the total radiation dose to which a particular sample has been exposed. This effect can be used to determine the length of time of such exposure and hence, in many cases, a sample's burial time (Jonas 1997). ESR has been used with tooth enamel for determining the age of Palaeolithic archaeological sites, mainly because tooth enamel is ubiquitous in these contexts and because it allows dating beyond the ^{14}C dating time range (40–45 Ka max.). It is thus also very useful in important sites regarding human evolution studies, sites having palaeontological interest within a quaternary time frame and because many sites lack the volcanic materials needed for K – Ar and $^{40}Ar/^{39}Ar$ dating (Rink 1997).

The aim is to determine the accumulated dose (D_A) to which a sample has been exposed whilst being buried; the exposure time is then determined by comparing D_A to the average dose rate over such period:

$$T = \frac{D_A}{(D)} \tag{2}$$

However, no significant difference in the accuracy of dose reconstruction has yet been found using different calibration methods (Wieser *et al.*, 2000). Each sample's radiation sensitivity is individually calibrated for dose assessment by the additive dose method; each sample is incrementally irradiated with at least 14 additional doses up to 100 Gy or more (avoiding the sample becoming saturated). A linear regression analysis is applied to the ESR measurements at each dose increment and the original measurement (laboratory-un-irradiated sample). The original D_A in the sample is obtained from the negative intercept of the regression line with the dose axis; is estimated as being the total radiation provided by all radioactive elements present in a sample and soil and also cosmic radiation (Ikeya 1993; Jonas 1997; Walker 2005; Grun 1989).

Materials and Methods

The dentine was initially removed from teeth using a dental drill and water cooling. The enamel was then placed in a 30% NaOH solution for one day to disinfect it and separate any remaining dentine (IAEA Report 2002); 1.4 mm mean enamel thickness was obtained for AG-I.

The sample was air-dried at room temperature for three days; a dental drill was used to strip around 50 ± 5 µm from the inside and outside of the enamel surface to ensure that alpha radiation had no effect. The molar enamel powder was divided into nine aliquots. Each aliquot was placed inside a plastic capsule for irradiation using ^{60}C standard radiation equipment at room temperature and 8Gy/min mean dose rate; the doses ranged from 0 to 740 Gy. After irradiation, the ESR signal was measured with a Bruker ESP300 X-band spectrometer. The $\boldsymbol{g}_{\perp}$ and $\boldsymbol{g}_{//}$ signals' peak to peak height was used for calculating amplitude. The spectrometer parameters used were: 336 mT central field, 0.02 T scan range, 0.1 m T amplitude modulation, 100 kHz modulation frequency, 0.328 s time constant and 20 mW microwave power. The aliquots were then irradiated with additional doses and the same process was repeated until getting 9 data points from ESR signal amplitude as a function of γ-ray dose.

Soil samples were also collected from the Aguazuque site and sent for U, Th and K content analysis by gamma spectrometry. Radiometric analysis is widely used for determining natural radioisotopes in geological samples by means of spectroscopic methods and, especially, for quantifying the uranium, thorium and potassium present in samples. These samples were analysed at INGEOMINAS' Nuclear Technology Group's Environmental Radiometrics' Laboratory which has a low-level gamma spectrometry system with 15 cm lead shielding and high-resolution GeHP hyperpure germanium detector (Canberra model GC2019), having 1.89% absolute detection efficiency for 661.6 keV.

Results and Discussion

Figure 3 shows the ESR spectra for enamel sample AG-I having an irradiation dose ranging from 54 to 324 Gy. A linear model was used for fitting ESR signal intensity to dose, as has been done by other authors (Baffa *et al.,* 2000; Hefne *et al.,* 2002; Kinoshita *et al.,* 2001a, 2008b; Mascarenhas *et al.*, 1982); very good agreement with linear fit was shown (Figure 4). The archaeological D_A obtained using this method was D_A = 2.10 ± 0.14 Gy.

ROSY software (Brennan *et al.*, 1999) was used for calculating the enamel sample's age, based on the given D_A, cosmic radiation dose rate (determined at 251 ± 15 µGy/year), U, Th and K content obtained from

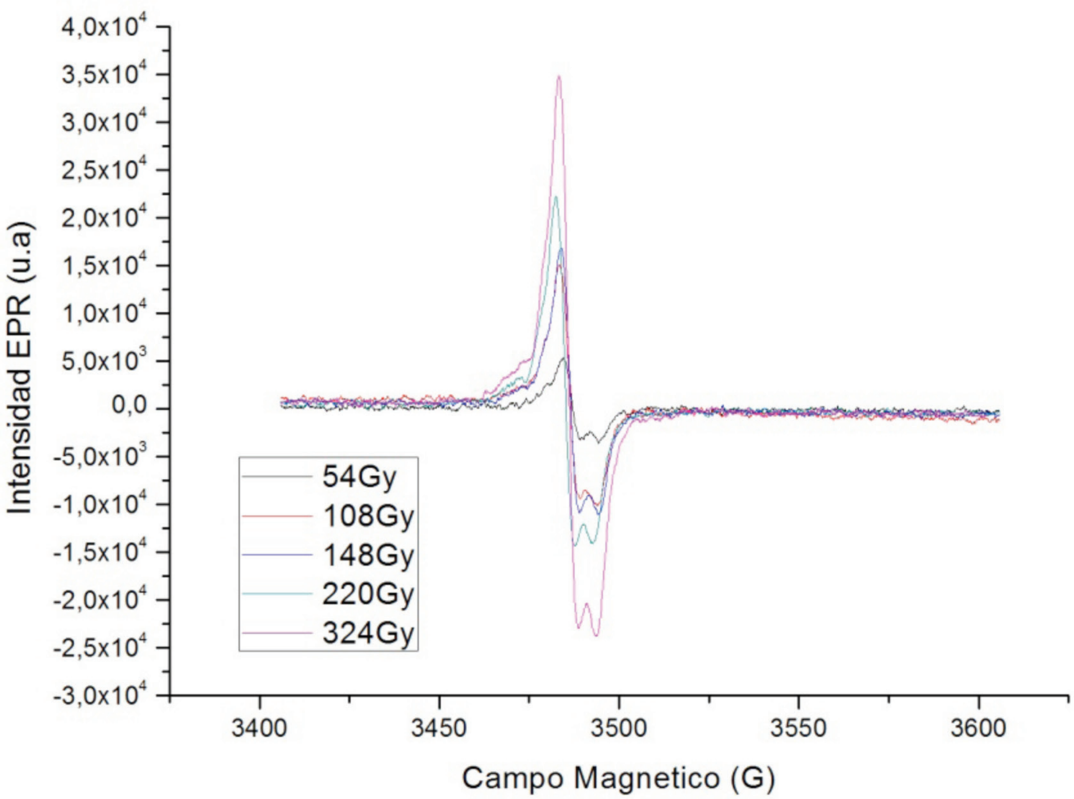

Figure 3. ESR spectra of tooth enamel AG-I in a range of 54 to 324 Gy.

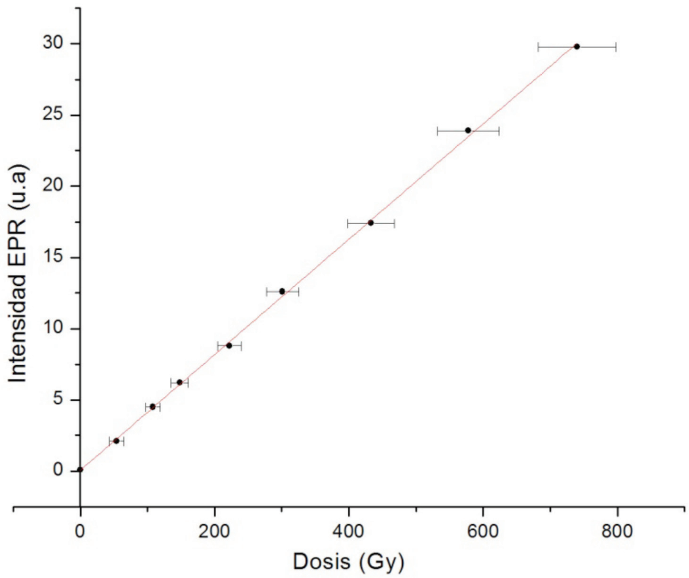

Figure 4. Signal versus dose growth showing the linear fitting used. Archaeological dose for AG-I was AD = 2.91 ± 0.14 Gy; correlation coefficient was 0.9937.

soil sample analysis and enamel (1.4 mm AG-I thickness and 5 mm dentine thickness) in sample. Soil water content was 12.1%. The software's default values were used for the remaining parameters. The cosmic radiation dose rate was obtained using the equation for luminescence and ESR dating (Prescott & Hutton 1994).

Finding the dose rate to convert D_A into an age is a crucial step after D_A has been found. ROSY software allows age to be calculated from an enamel sample by taking D_A due to radioisotopes from adjacent layers into account. The software computes age based on three uranium absorption models (linear, early uptake and a combination of both). Table 1 shows the soil analysis results. The present work did not determine U, Th and K concentration in enamel and dentine as their percentages have been negligible for calculating age in previous work, especially in dates for the Holocene period (Kinoshita *et al.*, 2008; Hefne *et al.*, 2002).

Typical soil density, enamel and dentine values were used for calculating age (2.00, 3.00 and 2.82 g/cm^3, respectively). The layer of enamel stripped off from each side by acid etching was about 50±5 mm; this prevented a possible contribution towards the dose having been made by alpha particles deposited in the sample. Using these values and the radioisotope concentrations listed in Table 1, ROSY software was used for obtaining the alpha, beta and gamma radiation dose rate contribution for each radioisotope in sediment (the results are listed in Table 2). These results were the same for any uranium absorption model. Considering a 251 ± 15 µGy/year dose rate for cosmic radiation, a 3,256 ± 190y before present (BP) age was thus found for the AG-I sample.

It should be noted that ROSY software calculates these ages using three uranium accumulation models: linear, early and a combination of both (Ikeya, 1993; Grun, 1989; Fattibene *et al.*, 2010). The way that uranium accumulates in a tooth is established by these models; accumulation increases at the same rate as time in the linear model and accumulation occurs in a short period of time in the early model, relative to a tooth's age and then remains constant after this short period of time. The tooth's age was the same when calculated by these three methods; this result was consistent if taken into account that the accumulation of radioactive elements inside the tooth was negligible.

Conclusions

Age determined at many countries' archaeological sites is the result of radiocarbon (^{14}C) analysis of particular items found around the burials and not direct dating of individuals found there. The results regarding either physical or geological phenomena may not be chronologically equal, hence the importance of having techniques like ESR which can directly

Table 1. Uranium, thorium and potassium concentration as determined by gamma spectrometry.

Sample	Concentration (ppm)		
	^{238}U	^{232}Th	^{40}K
Aguazuque	1.86 ± 0.19	3.72 ± 0.37	1.66 ± 0.09

Table 2. Dose rate obtained from radioisotope concentration, local cosmic radiation and total dose rate. Alpha radiation from sediment was not used in the calculation, as about 50 µm was removed from the outer side of the tooth.

	Alpha	Beta	Gamma	Cosmic	Gamma+Cosmic
Dentine	0.00	0.00	-	-	-
Enamel	0.00	0.00	-	-	-
Cementum	0.00	0.00	-	-	-
Sediment	0.00	46.55	347.31	-	-
Uranium	0.00	34.54	188.50	-	-
Thorium	0.00	12.01	158.81	-	-
Potassium	-	0.00	0.00	-	-
Total	0.00	46.55	347.31	251.00	598.31
(Alpha+beta) dose rate (µGy/y) = 46.55					
Total dose rate (µGy/y) = 644.86					

and absolutely determine the age of individuals of interest. The age of a human burial site found in Colombia was determined in this work from a single tooth, a mean age of 3,256 ± 190y BP being found. This result agreed with stratigraphic analysis at sites providing soil ages ranging from 2,800 to 3,500y BP for 50 and 80 cm depths (Correal, 1990). ESR dating accuracy was obtained relatively straightforwardly, using just a few grams of tooth enamel, thereby highlighting some of the advantages and characteristics of the ESR dating method.

The results so obtained have contributed towards joining links in the long chain of Colombian and American history (where there is still much to do, due to the rich pre-Hispanic and colonial past). This paper thus represents a pioneering effort aimed at promoting the dating of our ancestors.

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