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AGE OF THE HARRISON STREET BEAST: ELECTRON PARAMAGNETIC RESONANCE SPECTRA FROM TOOTH ENAMEL

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Introduction

Workers doing road reconstruction in 1993 in Ft. Wayne, Indiana, uncovered remains of a large skeleton and contacted archaeologists for assessment prior to continuing work. The archaeologists excavated the remains which were located in a 19-cm thick layer of blue clay, a pedological deposit which forms from wet, anaerobic environments associated with bogs. This clay layer was located some 2 meters below the current ground level (Davenport 1996).

Subsequent morphometric analysis of the skeletal elements clearly suggested that it belonged to the genus *Equus* or horse. Additional, more extensive analyses indicated that the specimen was probably Pleistocene in age and was probably *Equus occidentalis*, a now extinct species of horse. Corroborating evidence supporting this conclusion included cut marks on a number of the bones, which are consistent with butchering patterns, and the recovery of *Mammuth americanum* (Mastodon) remains in a similar deposit from a nearby (≤ 1 mile) excavation. Furthermore, microscopic analysis of the cut marks suggests that they were made with stone tools, which implies butchering by prehistoric people (Davenport 1996).

This find, provisionally named the "Harrison Street Beast", is potentially of major archaeological significance. It may represent the only example of direct utilization of the horse by paleoindians, and it is one of very few such specimens recovered from contexts east of the Mississippi river (Davenport 1996). Because of the likely importance of this find, additional confirmation of the results was sought through use of chronometric dating methods. A date obtained by radiocarbon assay (Davenport, 1996; Sample Date no. Beta-80140) of bone collagen extracted from the surviving tibia suggested an age of 101 years. This raises the troubling possibility that the specimen may be modern, when the generally accepted date for the extinction of this species in North America is $11,300 \pm 1,200$ BP (Kurten and Andersen, 1980). In order to resolve this issue, an attempt was made to date some of the molar enamel using electron paramagnetic resonance (EPR).

In this paper, we present the results of an EPR analysis of tooth enamel (biogenic hydroxyapatite) from the Harrison Street Beast. The objectives of this study are: 1) determine an age for the specimen through EPR analysis of molar tooth enamel; 2) resolve and identify the radiation-sensitive EPR spectral components; and 3) develop a provisional model for the creation of radiation-sensitive components in the EPR spectra.

Grun *et al.* (1987) have described techniques for using the EPR spectra of tooth enamel to determine the age of a fossil. They show the spectra of the enamel before laboratory irradiation and then with subsequent laboratory irradiations with gamma-ray photons. They analyze the dependence on dose of various parts of the spectral component which they attribute to the enamel, and show that this component is a spin state with $S = \frac{1}{2}$ and with approximate axial symmetry, for which

$g_{\parallel} = 2.0018$ and $g_{\perp} = 1.9977$. Jonas (1995) has shown that Grun's component is not a single feature, but that it consists of three components each with $S = 1/2$, one with axial symmetry and two with g-tensors whose eigenvalues are degenerate. These are $g_{\parallel} = 1.99766 \pm 0.00003$ and $g_{\perp} = 2.00299 \pm 0.00003$ for the axial site, and $g = 2.00184 \pm 0.00034$ and $g = 2.0069 \pm 0.0006$ for the other two. (Note that $g_i = h_i / \beta H_i$, in which h_i , ν , β have their customary meaning and the H_i 's are the magnetic fields at which peaks in spectral components are observed.) The three components in Jonas' samples gave an A.D. (accumulated dose) which ranged from 105 to 212 Gy.

Methods

Sample preparation and analytical methods generally followed those suggested by Geyh and Schleicher (1990) and Grun *et al.* (1987). The details of these procedures are describe in the sections that follow. Samples were prepared by the University of Tennessee - Knoxville, Department of Anthropology. Radioisotopic analyses were performed at the Oak Ridge National Laboratory (ORNL) Dosimetry Applications Research (DOSAR) facility, and added radiation doses were provided at the ORNL Radiation Calibration Laboratory (RADCAL). Electron paramagnetic resonance (EPR) analyses were conducted by laboratories of the ORNL Solid State Division.

Sample Preparation

A sample of the interior enamel lamellae (Figure 1) was obtained by cutting away the exterior enamel casing with a diamond saw, following recommendations in Grun *et al.* (1987). Cement and dentine surrounding the interior enamel lamellae were ground away using a Dremel® tool fitted with a tungsten-carbide bit. The exterior enamel and a sample of the glay surrounding the skeleton were saved for isotopic analysis.

The interior enamel lamellae were broken into pieces and then hand-powdered in an agate mortar and pestle. The resulting powder was then passed through sieves with 125- μm and 98- μm openings. Powder that failed to pass through the sieves was re-ground and then re-sieved. This resulted in an enamel powder with grain sizes $\leq 98 \mu\text{m}$. The powdered enamel was then divided into fractions and each fraction washed in 10 mL of 10% HCl for 15 seconds. This was done to ensure that all remaining dentine and cement was removed. After 15 seconds had elapsed, the remaining HCl was decanted and the washed enamel rinsed in 100 mL of deionized, distilled water. The rinsing procedure was repeated five times to ensure that any remaining acid was neutralized. The cleaned enamel fractions were recombined and placed into a crucible and dried in a Transite® oven stabilized at 75 °C for 24 hours. A total of 5.2 g of cleaned enamel was obtained and this material was divided into aliquots weighing 100 - 125 mg.

Radioisotopic Analysis

Radioisotope activity concentrations in samples of tooth components and contextual material were determined by gamma-ray spectrometry. Contextual material was analyzed without treatment. Dentine and enamel components of a single tooth were analyzed separately, the enamel in small chunks and the dentine as a powder. The spectrometry system consisted of two p-type germanium

detectors operating in tandem, coupled for data acquisition to a personal computer through multi-channel analyzers and spectroscopic linear amplifiers. The gamma-ray spectra were collected for 72 hours over the energy range 0.05 - 1.8 MeV, and individual radioisotopes were identified using Genie[®] VMS, v. 4.0 (Canberra Nuclear Products), an automated peak-search routine.

Irradiation

Samples were mounted behind and in direct contact with a 1/8-inch quartz plate which was placed in the centerline of an X-ray beam filtered to produce the M150 beam code defined (Eisenhower, 1984) by the National Institute of Standards and Technology (NIST). The X-ray exposure rate at the sample position was determined by measurement using an ion chamber calibrated by NIST for response to the M150 beam code. The nominal dose (Gy) was determined from the exposure rate $\dot{E}$ (R/s) and the exposure time t (s) as $D \approx 0.01 \dot{E} t$, which is the approximate unattenuated dose rate in air. The nominal dose is reported here without correction for photon attenuation by the quartz plate or conversion from exposure (air) to sample dose. Exposure rates were between 185 R/h and 400 R/h. Samples were contained in small sealable plastic pouches for the early exposures, but were later irradiated inside quartz EPR sample tubes (4.00 mm outside diameter, 2.92 mm inside diameter). Both plastic pouches and quartz tubes containing sample material were mounted behind the quartz plate to assure electronic equilibrium during exposure.

Samples were divided into two groups. Samples in the first group, numbered HB01 through HB06, were given a single acute dose from 10 Gy to 80 Gy over a 1-week period, after which ESR analysis was performed. Those in the second group, HB07R (replacement for HB07, which was lost in analysis) through HB12, were provided fractionated doses in 5-Gy to 20-Gy increments over a period of about 3 months. ESR analysis was performed after each subsequent irradiation of the second group. Nominal delivered doses are presented with results of the EPR analysis in Table 1.

EPR Analysis

In our experiment we evaluated three spectral peaks at $g_A = 2.0063$, $g_{B/2} = 2.0038$, and $g_D = 1.9978$, all with random errors of ± 0.0003 (when measured on the same spectrum). Because of a systematic error, all g 's calculated from measurements of magnetic field and frequency are corrected, based on the g of the E' center in silica, by adding 0.0016 to that calculated. All of the samples were prepared from the enamel of the same tooth. Some samples were irradiated with increasing doses, as discussed above, so that we could determine the dose dependence of several individual samples and their intercepts on the amplitude axis. Data for all of the samples were then plotted on a master graph and a linear function fitted to each of the data sets, 'A', 'B/2', and 'D'.

The EPR spectra of our samples were measured at ~ 9.2 GHz, a microwave power of 2 mW, a field modulation frequency of 100 kHz, a field modulation amplitude of 0.1 mT, and at room temperature. The only spectrometer parameter that we changed was the receiver gain. The amplitudes of the spectral components were normalized to a receiver gain setting of 2×10^4 .

EPR sample tubes were filled with the powdered enamel to a height in the tube of ~ 12 mm. Sample masses were ~ 100 mg. Thus, the cavity filling factors were almost the same and no correction of component amplitudes was made for the filling factor. The method of inserting the

tubes into the cavity placed the tubes at the same position to within <0.5 mm in the vertical direction. The sample position in the horizontal plane was within 0.05 mm. For those measurements in which the signal-to-noise (S/N) ratio was >10 , the random errors in our amplitudes were within 10% of the measured value. For the smaller S/N ratios the error increased with decreasing ratio to $\pm 25\%$ at a ratio of 3.

The amplitudes of the various EPR spectral components were measured from a baseline that was drawn from one end of the 5-mT sweep to the other for each spectrum. These endpoints were determined by estimating the midpoint of the noise over 0.25 mT at each end of the spectrum.

Results

Radionuclide activity concentrations determined by gamma-ray spectrometry are shown in Table 2. The spectrum-analyzing software provides a radionuclide activity estimate and error bounds based on the intensity of each major peak in a particular isotope's spectrum. Sample means of activity concentration for a particular radioisotope were calculated as the average of concentrations reported by the software, weighted for the relative abundances of the photons on which the separate concentrations were based. These concentration means are reported in the table, along with the propagated errors.

Fig. 2 shows the EPR spectrum of an irradiated sample for two magnetic field sweep ranges, one of 0.5 T and the other of 5 mT, centered at ~ 0.33 T. In the 0.5-T sweep the most intense components are at $g = 4.26 \pm 0.1$ and $g = 2$. The $g = 4.26$ component is due to Fe^{+3} (Griscom, 1980). The components at $g = 2$ are composed of contributions of Mn^{+2} (Griscom, 1980); a component whose width is ~ 60 mT due to aggregations of Fe^{+3} and Fe^{+2} (Weeks *et al.*, 1973); a component whose width is greater than the 0.5-T sweep, also due to aggregations of Fe (Weeks, 1973); and a component at $g = 2$ whose width is of the order of 1.5 mT and which is produced by the irradiation, as seen in the portion of the spectrum for which the field sweep was 5 mT. We assume that this last component will be indicative of the A.D. of the unirradiated samples of the enamel. We have labeled various parts of this spectrum as 'A', 'B/2', and 'D'. In those samples which we irradiated in their sample tubes there are paramagnetic components in the spectra from the tube. These overlap part of the 'B' component, the larger field part; hence the part free of interference from the tube components was labeled 'B/2'. The tube components are due to E' centers (Weeks, 1956; Weeks and Nelson, 1960; Weeks, 1994). The E' center has $g_{\parallel} = 2.0018$ and $g_{\perp} = 2.0006$ at the maximum of the component's absorption (the baseline crossing in the derivative of the absorption spectrum, which is shown in our spectra).

The amplitudes of EPR spectral components and their corresponding nominal doses are summarized in Table 1. The nominal dose appears to be about half the actual delivered dose, based on a preliminary analysis of photon attenuation by the quartz and estimates of effective mass-energy attenuation coefficients for air, quartz, and tooth enamel for exposure to the M150 X-ray beam.

Discussion

EPR amplitudes of the iron and manganese components did not change, within errors of measurement, for any dose. The numbers of spins contributing to these components are more than

2 orders of magnitude greater than the radiation-produced components, 'A', 'B/2', and 'D'. We assume that the dose dependencies of the radiation-produced spectral components, shown in the 5-mT sweep of Fig. 2, are independent of the iron and manganese components.

In Fig. 3 we show the spectra of three samples: one without laboratory irradiation, one with a 5-Gy nominal radiation dose, and one with a 10-Gy nominal dose, with spectra of the empty microwave cavity shown in Fig. 4 for comparison. The 'A', 'B/2', and 'D' parts are resolved in the two irradiated samples, and are not resolved in the unirradiated sample. (There is a spectral feature in unirradiated samples in the same portion of the spectrum as our 'A', and its contribution is included in the dosimetric regression analysis of 'A', but its relationship to 'A' is unclear at this time.) There is a component observed in the unirradiated sample whose peaks are indicated by $g = 2.0079$ and $g = 2.0055$. Another component is indicated at $g = 2.0014$. The $g = 2.0055$ appears to be the zero-crossing point of the absorption at $g = 2.0079$. The peak occurring at $g = 2.0014$ marks a component whose width is much smaller than any other component in the spectrum. Because of its shape and appearance in the three spectra we assign it to a distinct paramagnetic state. A comparison of the spectra of the two irradiated samples shows that this component is not affected by the radiation. With the increasing amplitude of the 'B/2' component with increasing radiation dose and the invariance of the amplitude of this $g = 2.0014$ component with dose, it is not resolved in the spectra of samples with larger doses. The amplitude of the part of the component indicated by the $g = 2.0079$ peak increases, if it does, with a much slower rate than do the other three parts, 'A', 'B/2', and 'D'. In these samples there is no evidence for an A.D. producing either the 'B/2' or 'D' parts. There may be an indication of an A.D. in the case of the 'A' part, but this is difficult to assess, since 'A' is not resolved in the spectrum of the unirradiated sample.

We show in Figs. 5 and 6, in which the data have been fitted with linear functions of dose, that the dose dependencies of the radiation-sensitive spectral components differ. The differences in slopes and intercepts with the amplitude axis are proof that these components are independent and are not different parts of one or two components. Table 3 provides a comparison of the g 's of the various radiation-produced components in enamel observed by Grun, *et al.* (1987), those deconvoluted by Jonas (1995), and those identified in this work.

The three sets of data agree on one peak with $g = 1.9978$ in the powder patterns. We agree with Jonas that there is a peak at $g = 2.0037$ and at $g = 2.0069$ (within errors of measurement). Because of the interference of the sample tube components, we cannot resolve peaks at $g = 2.0018$, except in the spectra of the three samples shown in Fig. 3, as previously discussed. Because of their differing slopes and intercepts, our data do not show that the $g = 2.0038$ (our 'B/2') and $g = 1.9978$ (our 'D') peaks are due to a single component, as does the Jonas deconvolution. The 'B/2' part continues to a peak on the other side of the baseline which, from its appearance, is part of 'B/2'; the two parts appear to be an approximately isotropic component. The data of Grun, *et al.*, are consistent with the hypothesis that their $g = 2.0018$ and $g = 1.9977$ maxima are parts of the same component. There are two other independent components with peaks at $g = 2.0037$ and $g = 2.0069$, based both on their different dose dependence in our data (our 'B/2' and 'A') and on Jonas' deconvolution.

Intercepts, slopes, and regression coefficients are given in Table 4 for the ensemble of data and for individual samples. Only the 'A' part has an intercept that may indicate that the sample was exposed *in situ*, *i.e.*, that it might have an A.D. Linear least-squares regression of the 'B/2' and 'D' parts results in a positive intercept of the dose axis. Fitting the curves to a quadratic function, as in

Fig. 7, provides a slightly better fit of the data, is visually more gratifying, and results in intercepts at or near the origin for the 'B/2' and 'D' components. Supralinearity at low doses, such as that implied by Fig. 7, is also observed in thermoluminescence analysis of natural materials and has not been satisfactorily explained (Mejdahl and Wintle, 1984).

In the production of paramagnetic states by electron (hole) capture at some site in the material, there must also be a hole (electron) trapped at some other site. Absorbed radiation, in the simplest model of radiation effects, excites an electron from the valence band of a wide-band-gap material (such as tooth enamel) to the conduction band. The electron then moves through the material until it is captured by a site which has a binding energy to trap the electron for a time sufficient for it to be observed in our measurements. In the case of tooth enamel this time may be millions of years. The site from which the electron is excited is a 'hole', which can also move through the material until it also is trapped. Both the electron traps and the hole traps have energies that, in many cases, are both between the energies of the valence and conduction bands and are paramagnetic. The spectral components we observe in our experiments are clearly not due to the presence of trapped-electron/trapped-hole pairs, but belong to either trapped electrons or trapped holes because of the differing dependencies on dose.

If we assume that all of these components are due to trapped holes, then there is the question of the sites at which the electrons are trapped. In wide-band-gap materials in which both Fe^{2+} and Fe^{3+} are present it is possible to change the +3 state to the +2 state by capturing an electron. Thus the presence of Fe in our samples may provide trapping sites for electrons. The change in the number of Fe^{3+} ions would be a small fraction (<0.01) of the available Fe^{3+} ions, since the number of Fe ions contributing to the $g = 4.26$ component (not even considering the contribution due to Fe-ion aggregates) is more than 2 orders of magnitude (as shown in Fig. 2) greater than the number of radiation produced sites ('A', 'B/2', and 'D'). Thus, a change in the amplitude of the $g = 4.26$ component due to combination with radiation-generated electrons would not be detected.

The g 's of various components observed by Grun, *et al.*, Jonas, and in our work are shown in Table 3. From this table we see that Jonas identifies an isotropic component, G2, with the same g as our 'A' part. We also note that the $g_{\perp}$ of his 'A' component is, within the errors of measurement, the same as our 'B/2' part. We are all in agreement with respect to the $g_{\parallel}$ defined by Grun, *et al.*, Jonas, and our 'D' part. However, our data on the 'B/2' and 'D' parts of our spectra are consistent with a hypothesis that these two parts are independent paramagnetic states, while Jonas indicates that these are a single axially symmetric paramagnetic state.

Activity concentrations of radioactive elements present in the soil, enamel pieces, and dentine powder, given in Table 2, show that the naturally occurring series of ^{232}Th and ^{238}U are present in the soil and that the parent nuclides appear to be in approximate secular equilibrium with their progeny, including those from ^{220}Rn and ^{222}Rn . This conclusion is based on the relative abundances of ^{228}Ac and ^{208}Tl in the ^{232}Th series, and of ^{234}Th , ^{214}Pb , and ^{214}Bi in the ^{238}U series. (The parent ^{232}Th and ^{238}U were not quantifiable at these levels because of interference from actinidic contamination of the materials used in fabrication of the detectors.) It is evident from these data that the diffusion of radioactive elements into the enamel has been small, resulting in concentrations in the interior enamel that are only around 10% of those in the clay. Dose rate conversion factors from Mejdahl and Wintle (1984), shown in Table 5, were used with the observed radionuclide concentrations to estimate environmental effective dose rates to the enamel. An EPR efficiency of 0.15 was assumed

for α particles, based on reported efficiencies for α -produced thermoluminescence. Different assumptions about contributions from α -, β -, and γ -dose components were used to generate estimates of the lowest, highest, and most probable total environmental dose rates, which are found in Table 6. The lowest-dose-rate estimate assumes that, considering the large uncertainties in enamel radionuclide concentrations, the observed concentrations are not significantly different from zero (which is strictly true within the 95% confidence interval for ^{40}K and for radioisotopes in the ^{232}Th series). Environmental radiation dose is due solely to γ irradiation from the surrounding soil in this scenario, and the lowest reported values for radionuclides in the soil are used in arriving at a dose estimate of $1,227 \mu\text{Gy/a}$. The highest-dose-rate estimate uses the highest reported radionuclide concentrations in soil and enamel and assumes a rapid equilibration of radionuclides in the enamel, resulting in an estimated $1,763 \mu\text{Gy/a}$ dose rate. The most probable effective dose rate was derived using the mean of lowest and highest reported activity concentrations. This value was halved to estimate average concentrations in interior enamel, accounting for time required for diffusion from soil to teeth. The most probable environmental effective dose rate is $1,763 \mu\text{Gy/a}$.

An upper bound on the age of the Harrison Street Beast is found from an estimate of our critical level (the level below which an EPR signal is assumed to be not different from background, within the 95% confidence interval of background measurement results) and the environmental effective dose rate. We report a 25% uncertainty (1σ confidence interval) in the EPR result from sample HB07R with a nominal delivered dose of 5 Gy (actual dose of about 10 Gy). This corresponds to a critical level of about 5 Gy, actual delivered dose. The maximum age of the Harrison Street Beast, based on the EPR analysis, is then 2,800 - 4,100 y, with a most probable maximum age of 3,400 y.

Conclusions

We conclude that the enamel from the teeth of the Harrison Street Beast has an age that is less than 4,100 y, and is more probably less than 3,400 y. Potassium and uranium/thorium series concentrations were only about 10% of those observed in the surrounding soil, which is to be expected for a relatively young specimen. [Migration of uranium in enamel, for instance, is on the order of 1 -3 cm in 100,000 years (Grun *et al.*, 1987)].

The fact that both radiocarbon analysis and our results indicated that the specimen may be recent raises significant issues. Radiocarbon dates based on bone collagen are often unreliable (Bowman, 1990; Geyh and Schleicher, 1990) and the accuracy of EPR dates are affected by the accumulated radiation dose, which can depend significantly on uptake of contextual radionuclides. Nevertheless, the corroborating EPR and radioisotopic evidence (both bone collagen ^{14}C analysis and gamma-ray spectrometry of tooth and contextual materials) suggests that the specimen may be much younger than originally believed. Therefore, a radiocarbon date based on intact amino acids, and perhaps a reevaluation of the archaeological data, would be useful. In particular, reexamination of the morphology of these skeletal remains is strongly suggested.

It is evident from a comparison of our data with those of Grun *et al.* and Jonas that there is only limited agreement on the EPR components produced by irradiation of the enamel of the various specimens that have been investigated. We clearly show at least 3 independent paramagnetic components, based on the unique radiation dependence of our 'A', 'B/2', and 'D' spectral features.

Our 'D' component at 1.9978 corresponds with the $g_{||}$ of both Jonas and Grun, *et al.* We also find a peak at 2.0063 (our 'A') that corresponds with Jonas' 'G2', and one at 2.0038 that corresponds with Jonas' 2.0029 (within errors of measurement), but which have no correspondence with any of the features reported by Grun *et al.* Both Grun *et al.* and Jonas suggest that the feature at 1.9974 should change with irradiation with the same dependence as either that at 2.0029 (Jonas and this work) or 2.0018 (Grun, *et al.*), but our results indicate that this is not the case. Additional research is clearly needed to resolve the EPR spectral components of tooth enamel and their dependence on enamel composition.

There is not sufficient information at this time to present a fully developed model for the production of EPR features by irradiation. We suggest that the presence of Fe ions in the enamel provides a possible mechanism for trapping electrons, which would leave behind unpaired holes and give rise to the observed EPR spectra. The reduction of Fe^{3+} to Fe^{2+} , which would trap electrons and leave unpaired holes, should be reversible by thermal treatment and would result in the disappearance of the EPR features under such conditions. Oxidation of Fe^{2+} under these conditions would free the trapped electrons, allowing them to migrate in the enamel matrix and neutralize the unpaired holes. This proposed model, although provisional, can be tested and refined with additional appropriately designed experiments.

A degree of supralinearity in the radiation dependence of EPR spectral features is implied by the good quadratic fit of Fig. 7. Some supralinearity is expected, to the extent that EPR results mimic those of thermoluminescence; however, supralinearity gives way to linearity after fewer than 5 Gy of added dose in thermoluminescence results (Mejdahl and Wintle, 1984). Supralinearity is not well understood, and these observations indicate that the phenomenon may be a significant factor in correctly interpreting EPR data and should be studied further.

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Table 1. Nominal Delivered Doses¹ and Corresponding Amplitudes of EPR Spectral Components

Sample No.	Mass (mg)	Dose (Gy)	Mass-Normalized Response (mg ⁻¹)		
			'A'	'B/2'	'D'
PH02	111.9	0	0.0223	0.0000	0.0000
HB01	90	10	0.0278	0.0444	0.0389
HB02	90	20	0.0389	0.100	0.0556
HB03	70	35	0.0500	0.143	0.0857
HB04	160	50	0.0375	0.181	0.112
HB05	120	65	0.0667	0.308	0.200
HB06	110	80	0.0727	0.400	0.254
HB07R	117.5	5	0.0136	0.0272	0.0068
HB08	125	15	0.0200	0.0600	0.0400
HB09	127	30	0.0394	0.118	0.0787
HB10	128	30	0.0391	0.117	0.0781
HB11	98	45	0.0510	0.214	0.122
HB12	75	45	0.0533	0.160	0.107
HB07R	117.5	15	0.0213	0.0553	0.0383
HB08	125	25	0.0320	0.112	0.0800
HB09	127	60	0.0787	0.268	0.158
HB10	128	60	0.0625	0.266	0.188
HB11	98	75	0.102	0.408	0.245
HB12	75	75	0.0800	0.400	0.267
HB07R	117.5	25	0.0383	0.102	0.0511
HB08	125	35	0.0480	0.160	0.0960
HB09	127	90	0.0945	0.409	0.268
HB10	128	90	0.0938	0.406	0.266
HB11	98	105	0.122	0.582	0.357
HB12	75	105	0.107	0.560	0.373

¹Actual delivered doses to enamel are approximately twice the reported nominal doses.

Table 2. Gamma-ray Spectral Analysis of Teeth and Contextual Material

Radionuclide	Activity Concentration ¹ (pCi/g)			Decay Series (⁴⁰ K)	Parent Mass Concentration ² (ppm)		
	SOIL	DENTINE	ENAMEL		SOIL	DENTINE	ENAMEL
⁴⁰ K	15.34±1.20	0.59±2.23	--		2.19	0.08	--
²²⁸ Ac	0.77±0.03	0.17±0.80	0.07±0.11	²³² Th	7.0	1.6	0.64
²⁰⁸ Tl	0.71±0.07	0.37±0.50	0.03±0.11		6.5	3.4	0.27
²³⁴ Th	1.70±0.56	--	--		5.06	--	--
²¹⁴ Pb	1.31±0.09	0.23±1.38	0.13±0.06	²³⁸ U	3.90	0.68	0.39
²¹⁴ Bi	1.31±0.09	0.16±0.39	0.17±0.16		3.90	0.45	0.51

¹Estimates of activity concentration and the associated confidence interval are made at each photon energy for radionuclides with multiple photon emissions. Values given here are the concentration average (weighted for the photon abundances) ± twice the sample average standard deviation. Uncertainties in individual concentration estimates are propagated in calculating the sample average standard deviation. No shielding corrections for varying densities have been incorporated.

²Secular equilibrium is assumed in determining equivalent masses of the parent ²³²Th and ²³⁸U from the activities of progeny reported in the gamma spectrometry analysis and the specific activities of the parents. Confidence intervals, which are in the same ratios as those of activity concentrations, are not reported.

Table 3. g 's of Radiation-Produced Components in EPR Spectra of Horse Tooth Enamel

			$g_{\perp}$	$g_{\parallel}$	
Grun, <i>et al.</i> (1987)			2.0018	1.9977	
Jonas (1995)	A		2.0029	1.9977	
	G1	2.0018			
	G2	2.0069			
This Paper	A	2.0063			
	B/2	2.0038			
	D	1.9978			
Weltner (1983)	CO_3^-		2.0031	2.0013	In CaCO_3
			2.0083	2.0065	In KHCO_3

Table 4. Slopes¹ and Intercepts¹ for Individual Samples and Ensembles

Sample No.	Nominal Dose ¹ Range (Gy)	EPR 'A'		EPR 'B/2'		EPR 'D'	
		Slope (mg ⁻¹ Gy ⁻¹)	y-Int (mg ⁻¹)	Slope (mg ⁻¹ Gy ⁻¹)	y-Int (mg ⁻¹)	Slope (mg ⁻¹ Gy ⁻¹)	y-Int (mg ⁻¹)
		(×10 ³)	(×10 ³)	(×10 ³)	(×10 ³)	(×10 ³)	(×10 ³)
HB07R	5-25	1.2	6	3.7	5	2.2	-1
HB08	15-35	1.4	-2	5.0	-14	2.8	2
HB09	30-90	0.92	16	4.9	-26	3.2	-21
HB10	30-90	0.91	10	4.8	-26	3.1	-10
HB11	45-105	1.2	3	6.1	-58	3.9	-52
HB12	45-105	0.89	13	6.7	-127	4.4	-84
PH002, HB01-HB06	0-80	0.60	23	4.8	-10	3.0	-6
		$r^2 = 0.85$		$r^2 = 0.97$		$r^2 = 0.96$	
All Samples	0-105	0.92	13	5.3	-26	3.4	-19
		$r^2 = 0.92$		$r^2 = 0.97$		$r^2 = 0.97$	

¹Nominal doses are reported; slopes and intercepts were derived using the nominal doses. Actual delivered doses are approximately twice the nominal doses.

Table 5. Dose rate conversion values for the naturally occurring radionuclides (adapted from Mejdahl and Wintle, 1984)

Radionuclide	Concentration	Dose Rate ($\mu\text{Gy/a}$)		
		α	β	γ
Thorium series (No thoron loss)	1 ppm ^{232}Th	738	28.6	51.4
Uranium series (No radon loss)	1 ppm ^{238}U	2,783	146.2	114.8
Natural Potassium ¹	1 ppm ^{40}K		697.7	203

¹Based on Mejdahl and Wintle's values for 1% natural potassium;
1% $\text{K}_{\text{nat}} = 1.19 \text{ ppm } ^{40}\text{K}$.

Table 6. Effective dose rate to interior tooth enamel of the Harrison Street Beast

	Effective ¹ Dose Rate ($\mu\text{Gy/a}$)		
	Low ²	Probable ³	High ⁴
γ (from soil)			
^{40}K	445	445	445
^{232}Th	334	347	360
^{238}U	448	514	581
β (from interior enamel)			
^{40}K	--	--	--
^{232}Th	0	3	18
^{238}U	0	33	75
α (from interior enamel)			
^{232}Th	0	25	71
^{238}U	0	94	213
TOTAL	1,227	1,461	1,763

¹An EPR efficiency of 0.15 is applied to the α dose, with the assumption that α -particle efficiency in producing EPR signal is the same as for producing thermoluminescence (Mejdahl and Wintle, 1984).

²Assumes that reported activity concentrations in enamel are not different from zero (negligible α and β irradiation from radionuclides in the enamel); all dose is presumed due to γ radiation from soil. Values for γ -emitters in soil are the lowest reported.

³Assumes that an intermediate value between the lowest and highest reported represents the best estimate of current radionuclide concentration. Half this intermediate value is taken to be the mean concentration in the interior enamel, averaged from time zero to the present.

⁴Assumes the highest values reported. Values for α - and β -irradiation assume that activity concentrations from Table 2 equilibrated rapidly in the enamel.

Figure 1. Interior structure of a horse maxillary molar. The cement is denoted by *I* and *I'*. Interior enamel used in this study is denoted by the heavy black areas surrounding the cement. (Figure taken from Baker, 1972.)

First Derivative of Absorption

Figure 2. EPR spectrum of irradiated interior enamel from a horse tooth. Spectral components are seen for two magnetic field sweep ranges, S.R. = 0.5 T and S.R. = 5 mT. 'M.A.' is the microwave amplitude.

Figure 3. EPR spectra showing the growth of radiation-sensitive components in samples with 0 Gy, 5 Gy, and 10 Gy nominal added dose. 'A', 'B/2', and 'D' are the spectral regions identified in this study, as discussed in the text.

Figure 4. EPR spectra of the empty microwave cavity (for comparison with Fig. 5).

Figure 5. Linear regression of EPR spectral component response with dose for Sample HB09

Figure 6. Linear regression of EPR spectral component response with dose for all samples

Figure 7. Quadratic fits to the EPR data (all samples).

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