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EPR STUDY OF THE MODERN TOOTH ENAMEL

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Abstract: The current work is a comparison of the EPR signals obtained from three-year-old modern cow tooth enamel with the spectra of fossil tooth enamel that was irradiated by natural background radiation for a long period. The fossil tooth enamel spectrum exhibits some additional components not visible in the modern tooth enamel EPR spectra. In particular, the intensity of the septet signal, attributed to dimethyl radicals, does not change with the additional laboratory dose and it does not appear in EPR signals of modern tooth enamel when irradiated up to 1.3 kGy. It has been assumed that dimethyl radicals present in the fossil tooth enamel are not radiation-induced and result from the decomposition of the organic components of tooth enamel due to natural aging.

Keywords: EPR dating; Retrospective dosimetry; Fossil tooth enamel, modern toothenamel

1. Introduction

EPR dosimetry and dating are based on the detection and quantitative characterization of an EPR signal induced by ionizing radiation provided the signal intensity was settled to zero in the past. Implicit in this method is the assumption that there is a correlation between the intensity of the radiation-induced signal and absorbed radiation dose. This property lies on the base of EPR dosimetry and dating using tooth enamel [1]–[5] as a natural dosimeter. Irradiated tooth enamel exhibits a stable EPR signal, the intensity of which correlates with the absorbed dose [6]. At the same time, it has been well established that the EPR signal of the fossil tooth has a composite nature, thus creating the necessity for the isolation of a radiation-induced EPR signal from other paramagnetic signals[4], [5], [7]–[9]. Such a signal in tooth enamel or bone, which is suitable for dating, is a stable CO_2^- radical generated by radiation in hydroxyapatite.

Other radicals induced by irradiation, e.g., CO_3^{3-}, CO_3^- are not relevant for retrospective dosimetry or dating due to their instability [10]. Apart from that, the EPR spectrum of the tooth enamel contains a native signal as well, and it is present at the non-irradiated modern tooth enamel and naturally irradiated fossil tooth enamel. However, even the youngest tooth is not free from a small dose due to natural background irradiation. The subject of the current work is a comparison of the EPR signals obtained from three-year-old modern cow tooth enamel with the spectra of fossil tooth enamel that was irradiated by natural background radiation for a long period (approximately 300,000years, unpublished data).

2. Experimental

The investigated objects were the well-preserved fossil tooth of an elephant (*Palaeoloxodon antiquus*[1]) found in the Mingachevir district of Azerbaijan in 2010 and a three-

[1] The **straight-tusked elephant** (*Palaeoloxodon antiquus*) is an extinct species of elephant that inhabited Europe during the Middle and Late Pleistocene (781,000–50,000 years before present). It was formerly thought closely related to the living Asianelephant; however, in 2016, DNA sequence analysis showed that its closest extant relative is actually the African forest elephant, *Loxodonta cyclotis*. It is closer to *L. cyclotis* than *L. cyclotis* is to the African bush elephant, *L. africana*, thus invalidating the genus *Loxodonta* as currently recognized (E. Callaway, "Elephant history rewritten by ancient genomes", *Nature*, Sept. 2016.doi:10.1038/nature.2016.20622).

year-old modern cow tooth. Sample preparation and ESR measurement procedures were as follows. The enamel was initially removed from the teeth using a dental drill and water cooling. The 1.5-mm mean thickness enamel was then placed in a 30% NaOH solution for one day to disinfect it and separate any remaining dentine.

A dental drill was used to strip around 50±5 μm from inside and outside of the enamel surface to ensure the natural alpha radiation did not affect the fossil tooth enamel samples. In total, 2 g enamel was collected from both the fossil and modern tooth and it was air-dried at room temperature for three days. Half of the samples were powdered using agate mortar, and powder sized 100–50 μm was separated for further measurements. The other part was left as a single fragment of enamel with the size 4mm × 1mm × 1.5mm. Enamel powder (0.1 g) and single fragment (bulk) samples were separately placed inside glass tubes (Suprasil) for the measurements of EPR signals.

The ESR signal for the samples was measured with a Bruker EMXplus (X-band) spectrometer. The spectrometer parameters used were: 3,520G central field, 100 G scan range, 3 G amplitude modulation, 100kHz modulation frequency, 20.48 ms time constant, and 2.14 mW power if not especially emphasized in the text. The samples were then irradiated at ambient temperature using a ^{60}Co source with additional doses, and ESR signals were measured under the same conditions. The dose rate of the ^{60}Co source was determined using the Magnettech Miniscope MS400 EPR Spectrometer with individually wrapped barcode-labeled BioMax Alanine Dosimeter Films (developed by Eastman Kodak Company).

3. Results and Discussion

The ESR signal of fossil tooth enamel is an asymmetric signal defined by three peaks at g ~ 2.0043 (T1), g ~ 2.0013 (B1), and g ~ 1.9985 (B2) (Fig. 1).

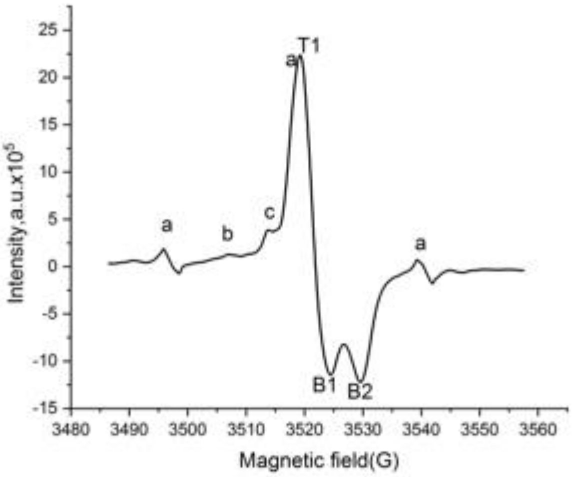

Fig. 1. ESR spectra of elephant fossil tooth enamel powder. Punctuation and attribution of ESR signals have been borrowed from [12]: (i) Signal labeled "a" is a septet centered on the main CO_2^- signal at g=2.0043 (only three lines are visible on that magnetic field range) formed by a free dimethyl radical; (ii) isotropic line (marked "b") at g=2.0114 might be attributed to CO_3^-; and the isotropic line at g=2.0075 (marked "c") is usually attributed to a free radical, likely SO_2^- . T1, B1, and B2 denote the positions of the main ESR signal.

A major contribution to this signal is attributed to CO_2^- radical[11], though some other radicals (mainly carbonate-derived radicals and some oxygen radicals[11]) are also suggested as minor contributors. Experimental separation of those signal is problematic, but the system is usually simplified by considering three main types of CO_2^-[11], one isotropic at g ~ 2.0006 and two anisotropic CO_2^-radicals, an axial ($g_\perp$~ 2.003; $g_\parallel$ ~ 1.997) and an orthorhombic (g_x ~ 2.003; g_y ~ 1.997 and g_z ~ 2.001). Due to the different characteristicsof these signals in terms of thermal stability or microwave saturation, their relative proportions in the ESR signal may not be the same in the natural and irradiated spectrum; hence, the different but close g values might be observed at the positions T_1, B_1, and B_2.

Laboratory irradiation leads to an increase in the ESR signal, and Fig. 2 illustrates the signal intensity at different doses. Peak increases are notable at the central part of the spectra and in the position of "b," whereas peaks attributed to dimethyl radicals remainunchanged (Fig 2. b).

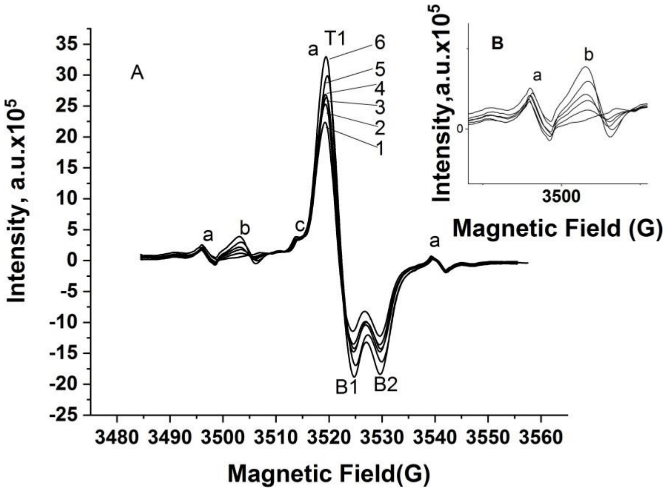

Fig. 2. Dose-response spectra of fossil tooth enamel powder: A: natural, no additional laboratory dose (1); irradiated at 44.7 Gy (2); 89.4 Gy (3); 114.1 (4); 178.8 Gy (5); 223.5 Gy (6). Dose rate 0.149Gy/s. B: represents an initial part of spectra around 3,500 G.

The same samples were measured after six months as well (Fig. 3). We have observed some decrease in the position of the central signal but the signal at position "b" droppeddown to its original position (Fig 3. B).

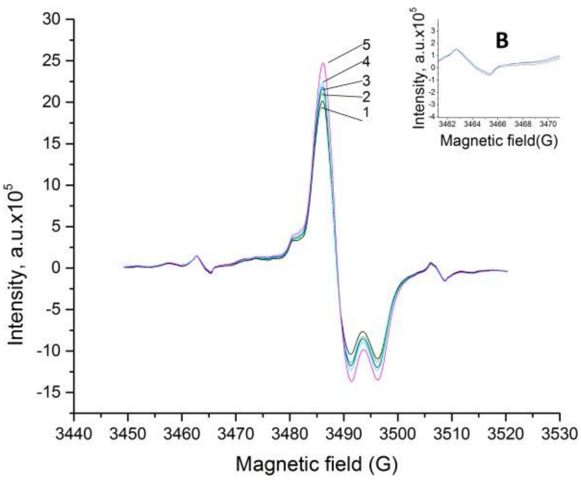

Fig. 3. Dose-response spectra of fossil tooth enamel powder six months later: irradiated at 44.7 Gy(1); 89.4 Gy (2); 114.1 (3); 178.8 Gy (4); 223.5 Gy (5). B: Part of the spectra around 3,470 G.The non-irradiated modern tooth sample does not show any significant ESR signal,which might be distinguished from the noise signal but with the observation of an additional laboratory irradiation typical tooth enamel signal.

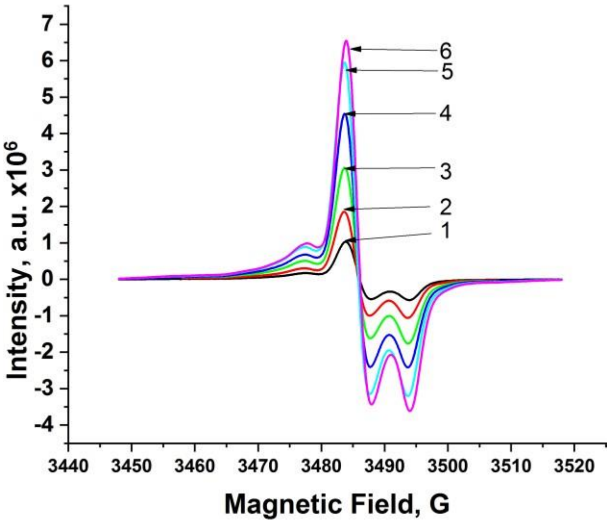

Fig. 4. Dose response spectra of modern cow tooth enamel powder: irradiated at 174 Gy (1); 348 Gy(2); 522 Gy (3); 783 Gy (4); 1,044 Gy (5); 1,305 Gy (6).

The dose-response ESR spectra of the modern tooth sample are depicted in Fig.4. Tooth samples were irradiated with ^{60}Co within the dose rate from 174 Gy to 1,305 Gy. The ESR signal of the modern cow tooth enamel is an asymmetric signal defined by three peaks at g ~ 2.0044 (T1), g ~ 2.0020 (B1), and g ~ 1.9987 (B2), and it does not show significant changes to compare with the fossil tooth enamel ESR signal. A distinguishing feature of the ESR spectra of the modern tooth is that neither the peak at position "a" nor the peak at position "b" is observable, and the peaks at positions "a" and "b" do not appear in the spectrum up to the irradiation dose of 1,305 Gy. The peak at position "a" (Fig.1) is attributed to the dimethyl radicals; hence, they are not produced during irradiation. Therefore, we assume the ESR signal of fossil tooth enamel at position "a" is not radiation-induced and results from the decomposition of the organic components of tooth enamel due to natural aging.

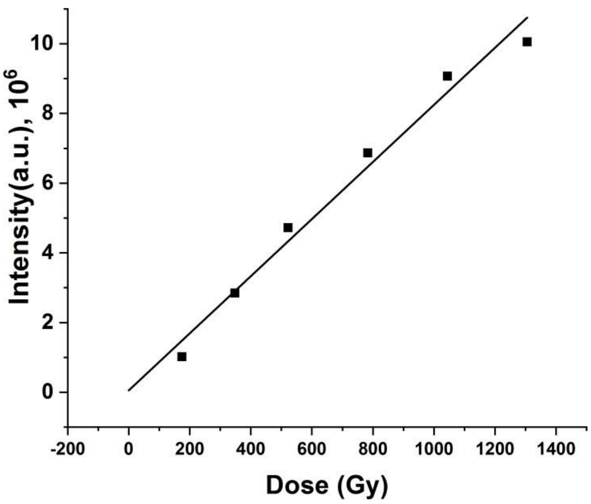

Fig. 5. Dose-response curve of the modern tooth ESR signal intensity at different laboratory irradiation doses

Figure 5 depicts the dose-response curve of the modern tooth EPR signal intensity at different laboratory irradiation doses. Data were fitted with the linear fitting function.

Extrapolation back to the zero intensity gives approximately zero doses, which is in good agreement with the experimental result.

4. Conclusion

The central part of the ESR signal of the modern cow tooth enamel is an asymmetric signal defined by three peaks at g ~ 2.0044 (T1), g ~ 2.0020 (B1), and g ~ 1.9987 (B2), and it does not show significant changes to compare with the fossil tooth enamel ESR signal.

The ESR signal of the fossil tooth enamel at position "a", which is attributed to the dimethyl radical, is not radiation-induced and most likely results from the decomposition of the organic component of tooth enamel due to natural aging.

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ЭПР ИССЛЕДОВАНИЕ СОВРЕМЕННОЙ ЗУБНОЙ ЭМАЛИ

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Резюме: Настоящая работа представляет собой сравнение сигналов ЭПР, полученных от эмали зубов современной трехлетней коровы, со спектрами ископаемой эмали зуба, которая подвергалась длительному облучению естественным радиационным фоном. Спектр ископаемой зубной эмали демонстрирует некоторые дополнительные компоненты, не видимые в современных спектрах ЭПР зубной эмали. В частности, интенсивность септетного сигнала, приписываемого диметильным радикалам, не меняется с дополнительной лабораторной дозой и не проявляется в сигналах ЭПР современной зубной эмали при облучении до 1,3 кГр. Было высказано предположение, что диметиловые радикалы, присутствующие в ископаемой зубной эмали, не индуцируются излучением и являются результатом разложения органических компонентов зубной эмали из-за естественного старения.

Ключевые слова: датирование методом ЭПР; Ретроспективная дозиметрия; Ископаемая зубная эмаль, современная зубная эмаль

MÜASİR DIŞ EMALININ EPR METODU İLƏ TƏDQİQİ

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Xülasə: Bu məqalədə, müasir diş emalından alınan EPR siqnallarının, uzun müddət təbii fon şüalanmasına məruz qalmış dişin emalının EPR spektrlərinin müqayisəli analizi verilmişdir. Uzun müddət təbii fon şüalanmasına məruz qalmış dişin emalının EPR spektri, müasir dişin EPR spektrlərində görünməyən bəzi əlavə komponentləri nümayiş etdirir. Xüsusilə, dimetil radikallarına aid edilən sep stet siqnalının intensivliyi əlavə laboratoriya dozası ilə dəyişmir və 1,3 kGy-yə qədər şüalanma altında müasir diş minasının EPR siqnallarında özünü göstərmir. Uzun müddət təbii fon şüalanmasına məruz qalmış dişin emalında mövcud olan dimetil radikallarının şüalanma təsiri ilə dəyişmədiyi göstərilmişdir. Belə fərz olunur ki, bu radikallar şüalanma nəticəsində deyil, diş emalının tırkibində olan üzvi maddələrin təbii parçalanması nəticəsində əmələ gəlir.

Açar sözlər: EPR üsulu ilə yaş təyini, Retrospektiv dozimetriya, Qazıntı zamanı tapılmış diş emalı, Müasir diş emalı