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ANISOTROPY OF THE EPR SPECTRA OF FOSSIL TOOTH ENAMEL PLATES

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Abstract: The current work has been presented a variation of the lineshape of the EPR spectrum of a fossil enamel plate as it is rotated in the magnetic field around the axis of tooth growth. The central part of the EPR spectra of a fossil enamel plate consists of oriented and disoriented asymmetric CO^-_2 signals with the occasional presence of the isotropic signal. The intensity of the central signal changes due to the different contributions of the oriented CO_2 signal. The estimated share of the oriented CO^-_2 radicals is 36±2%.

Keywords: anisotropy; fossil tooth enamel; hydroxyapatite, electron paramagnetic resonance

1. Introduction

Radiation-induced EPR signal in tooth enamel has been extensively used in retrospective EPR dosimetry [1] and EPR dating [2]. Tooth enamel consists of 94- 97% of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, the rest is accounted for by water or organic matter [3]. Carbonate impurities in the hydroxyapatite substitute some of the phosphates and/or OH anions. Ionizing radiation creates various types of radicals that are trapped in the crystal lattice such as CO^-_2, CO^{3-}_3 ,CO^- ,O^- etc. , and located at the proximity of g=2[4]. The CO^-_2 radicals give rise to an EPR signal that is proportional to the dose absorbed in the enamel.

It is well accepted that the radiation-induced EPR signal of tooth enamel consists of at least three paramagnetic centers related to CO^-_2 radicals which are experimentally proved [5]. The spectroscopic parameters of these radicals are very close to each other, and their EPR signals are indistinguishable in powder samples. However, the line shape of the EPR spectra of these radicals in enamel plates is different. This is because the CO^-_2 radicals of the axial type are uniformly oriented in the enamel plates, whereas the radicals of the orthorhombic type are disordered. The EPR spectrum of the orthorhombic type radicals does not depend on the sample orientation in the magnetic field. The orthorhombic paramagnetic center is responsible for the EPR spectrum with the parameters g_x =2.0017, g_y =1.9970, g_z = 2.0031. This center has been observed in synthetic and biological (tooth enamel and bone) hydroxyapatite (HAP) [6] and it is the main paramagnetic defect in the irradiated HAP- containing materials. This center is quite stable however it was recently shown that under thermal annealing this orthorhombic paramagnetic center can be transformed into the axial paramagnetic center [7].

The signal from the axial type of CO^-_2 radicals depends on the direction of the external magnetic field concerning the crystallographic axis of the hydroxyapatite crystallites and is responsible for the EPR spectrum with the parameters $g_\parallel$=1.9970, $g_\perp$ =2.0027. Therefore, the total EPR spectrum of an irradiated tooth enamel plate is anisotropic, i.e. it changes its shape as the sample is rotated in the external magnetic field [8].

The third center with g =2.0006 is related to the isotropic EPR line in both modern [9] and fossil enamels [4], as well as in synthetic HAP [10]. “Isotropy” of the paramagnetic center is caused by the rapid jumps of the radical and in the EPR spectrum is observed only under certain specific conditions.

In this work, we have studied the anisotropy of the EPR spectra of naturally irradiated fossil enamel plates.

2. Materials and methods

The investigated object was a fossil tooth of an elephant (*Palaeoloxodon antiquus*) found in Mingachevir district of Azerbaijan in 2010 with well-preserved teeth. Sample preparation and ESR measurement procedures followed standard techniques [11]. The enamel was initially removed from teeth using a dental drill and water cooling. The 2 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 that alpha radiation had no effect. In total 1.2 gr. enamel was collected and it was air-dried at room temperature for three days.

Small enamel pieces of approximately 1x2x3 mm, further indicated as “enamel blocks” or “enamel plates”, were cut from the tooth using the water-cooled dental saw.

ESR signal was measured with a Bruker EMXplus(X-band) spectrometer. The spectrometer parameters used were: 3484 G central field, 100 G scan range, 3,2 G amplitude modulation, 100kHz modulation frequency, 20.08 ms time constant, and 2.12 mW microwave power.

3. Results and discussions

Fig. 1 shows the EPR spectra of fossil enamel plates at four different orientations relative to the magnetic field. The main radiation-induced EPR signals (at the magnetic field B~3460 - 3510 G) in these samples are similar if we take into account the extreme points at the spectral line shape. However, there are obvious differences if we analyze the values I_1, I_2, and I_3 that correspond to the amplitudes of EPR signals in the extreme points (the notations I_1, I_2, and I_3 as they were introduced in the paper [5].

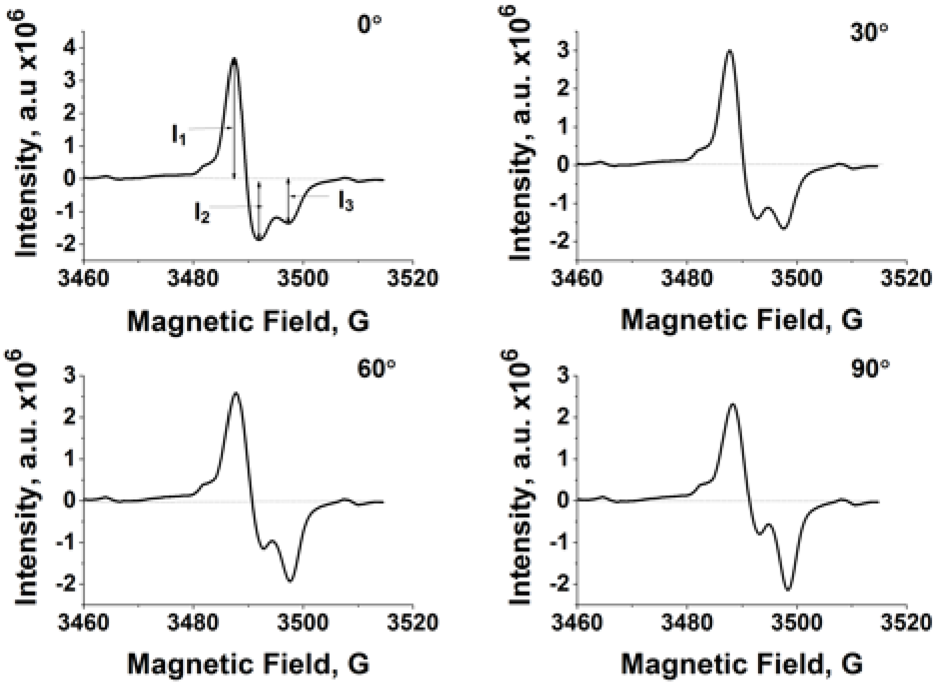

Fig. 1 Variation of the lineshape of the EPR spectrum of a fossil enamel plate as it is rotated in the magnetic field around the axis of tooth growth

The value of I_1 corresponds to the amplitude of the EPR signal near g=2 of the oriented centers (Fig. 1). EPR spectra of fossil enamel plates at four different orientations exhibit different ratios between I_1, I_2, and I_3.

The central part of this signal is formed mainly by the contributions of the axial and orthorhombic CO^-_2 centers [5]. Therefore, it is assumed that the differences in the values of I_1, I_2, and I_3 are caused by different contributions of the above-mentioned paramagnetic centers. Depending on the orientation of a sample, both oriented and disordered CO^-_2 radicals contribute to these values. The contribution of the oriented radicals depends on the sample orientation, while the contribution of the disordered radicals is constant.

Thus at the position when intensity I is minimal we observe the contribution of the disordered centers only. On the contrary, when the value of the I is a maximum then the contributions of both centers are maximum. It is seen from Fig.1 that, when a dental enamel plate is rotated in a magnetic field the amplitude I vary from the maximal value $I_{max} = I_{dis}+I_{or}$ to the minimal value $I_{min}=I_{dis}$. Conventionally, it is convenient to use the dimensionless value $\Delta=I/I_{max}$ and the changes of this value will determine the relative contribution of the oriented radicals to the amplitude I:

$$\mathbf{\Delta = (I_{1max}-I_{1min})/I_{max}= I_{or}/(I_{or} +I_{dis})}$$

Fig. 2 shows the variation of I_1/I_{1max} value (where I_{1max} is the maximum value of I_1; I_{or} and I_{dis} the EPR intensities of ordered and disordered CO^-_2 radicals respectively) at the sample rotation around the axis of maximum anisotropy in the magnetic field. It is seen that the ranges of I_1/I_{1max} value changes are different for the samples at different orientations. The maximum change, denoted as Δ, for the sample of fossil enamel it is equal to Δ= 0.36±0.02.

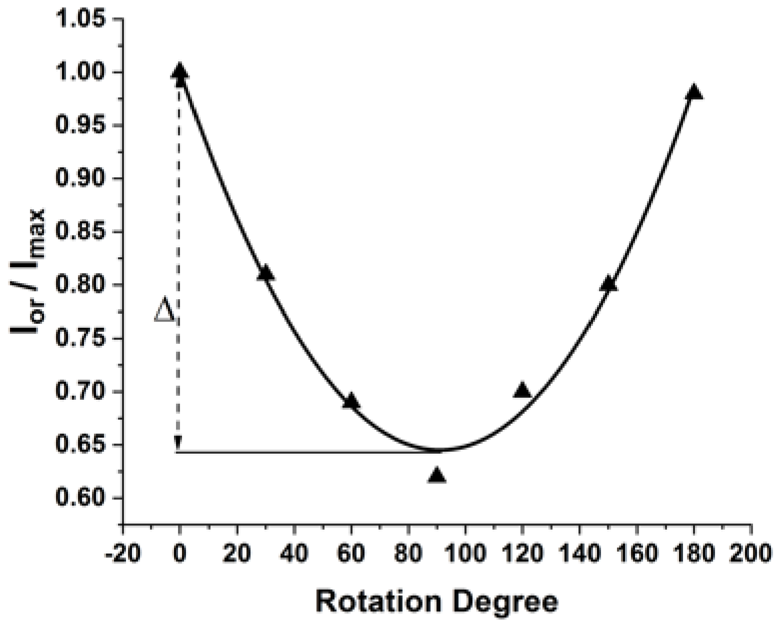

Fig. 2. EPR spectra anisotropy of fossil enamel plates.

Simulation of the powder spectra of the modern and fossil tooth enamel was carried out in [5] and it was found that the share of the axial centers in the total amount of CO^-_2 radicals is 20% in modern γ-irradiated enamel and 33% in the sample of fossil enamel. It was also reported that in the case of the enamel plates the share of the axial centers in the total amount of CO^-_2 radicals is 35% in modern γ-irradiated enamel and 40% in the sample of fossil enamel.

4. Conclusions

Unlike powder tooth enamel, anisotropy is observed in the EPR spectrum of fossil enamel plates when the plates rotate in a magnetic field. In this case, the intensity of the spectrum also changes depending on the fraction of the oriented anisotropic CO^-_2 spectrum in the central spectrum. The estimated share of this spectrum is 36±2%.

Measurements of the anisotropy of the EPR spectra of irradiated and/or fossil tooth enamel plates can be used for determining the real dose of γ-irradiation.

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АНИЗОТРОПИЯ СПЕКТРА ЭПР ПЛАСТИН ИЗ ЭМАЛИ ИСКОПАЕМЫХ ЗУБОВ

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Резюме: В данной работе было представлено изменение формы линии спектра ЭПР пластинки ископаемой эмали при ее вращении в магнитном поле вокруг оси роста зуба. Центральная часть спектров ЭПР пластинки ископаемой эмали состоит из ориентированного и дезориентированного асимметричного сигнала CO^-_2 с редким присутствием изотропного сигнала. Интенсивность центрального сигнала изменяется из-за разного вклада ориентированного сигнала CO^-_2. Расчетная доля ориентированных радикалов CO^-_2 составляет 36 ± 2%.

Ключевые слова: анизотропия; ископаемая зубная эмаль; гидроксиапатит, электронный парамагнитный резонанс

QƏDİM DİŞ EMALINI KRİSTAL LÖVHƏSİNİN ELEKTRON SPİN REZONANS SPEKTRİNDƏ ANİZOTROPİYA

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Xülasə: Bu işdə qədim dişin mina lövhəsinin EPR spektr xəttinin formasının dəyişməsini tədqiq edilmişdir. EPR spektr maqnit sahəsində dişin böyümə oxu ətrafında fırlamaqla ölçülmüşdür. Qədim dişin mina lövhəsinin EPR spektrinin mərkəzi hissəsi əsasən bir istiqamətlənmiş və bir istiqamətlənməmiş asimmetrik CO^-_2 siqnalından ibarətdir. Bu hissədə daha bir izotrop siqnalı da müşhidə oluna bilər, lakin bu həmişə baş vermir. Mərkəz siqnalının intensivliyi istiqamətlənmiş CO^-_2 siqnalının ümumi siqnalda payina uyğun olaraq dəyişir. Hesablamalara görə istiqamətlənmiş CO^-_2 siqnalının ümumi siqnalda payi 36 ± 2% təşkil edir.

Açar sözlər: anizotropiya; qədim diş emalı; hidroksiapatit; elektron paramaqnit rezonans.