THE STRUCTURE OF A DOSIMETRIC EPR SIGNAL IN APATITES OF BIOLOGICAL ORIGIN

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We investigate the electron paramagnetic resonance (EPR) spectrum close to $g = 2$ that is created by gamma radiation in apatites of biological origin: enamel, bone, and dentin. This signal is used in retrospective dosimetry for the determination of an irradiation dose. The form and structure of the radiation-induced EPR spectrum of the plates made of enamel and bone are described and interpreted for the first time. It is shown that the spectrum of the substances under investigation is mainly conditioned by the contribution of CO_2^- radicals of two kinds. One of these radicals represents an oriented center, while the other one is a disordered one. We also determined the relative contribution of oriented and disordered CO_2^- radicals to the EPR spectrum of bioapatites of various origins.

1. Introduction

The irradiation of apatites of biological origin (bioapatites) with ionizing radiation gives rise to an EPR spectrum appearing in them in the neighborhood of $g = 2$. The intensity of this signal depends linearly on the radiation dose, that's why it is widely used in retrospective EPR dosimetry for the determination of absorbed radiation doses [1—6]. Due to this fact, it is called a dosimetric EPR signal. The substance most widely used in dosimetry is enamel that consists of 95—98 % of a mineral matter (mainly hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$). The intensity of the EPR spectrum in enamel depends linearly on the radiation dose in a wide range of absorbed doses (from several cGy up to 100 kGy), which, together with its mechanical and thermal properties, makes enamel to be a unique dosimetric substance. Other biological and synthetic apatites, though of a similar composition, have a considerably lower sensitivity to radiation than that of enamel. The clarification of the processes and mechanisms of formation of radiation defects in bioapatites can be useful for the whole solid-state dosimetry.

In spite of the wide application of bioapatites in retrospective EPR dosimetry and in the EPR dating, the nature and structure of the radiation EPR spectrum in the mentioned substances cannot be explained unambiguously, being considered to be mainly conditioned by CO_2^- radicals [7,8]. It was recently shown that enamel includes two types of these radicals [9—11]. One of them is located in B position of the apatite lattice (substitution of a PO_4 tetrahedron) and, due to its fast rotation about the O—O axis that coincides with the c axis of crystallite, forms a paramagnetic center of axial symmetry. In enamel plates, these radicals cause the so-called anisotropy of the EPR spectrum [8], namely a variation of its form that accompanies the rotation of the sample in a magnetic field. If the rotation of a radical is hindered by defects of the crystal lattice, such a radical forms a paramagnetic center of orthorhombic symmetry [9]. At the expense of magnetically non-equivalent positions in the lattice and possible disorientations of the center axes, such radicals form a powder spectrum even in plates. The parameters describing EPR spectra of the both kinds of radicals are close, that's why it is practically impossible to separate their EPR spectra obtained with the use of powder samples. The given paper is devoted to the comparative investigation of the anisotropy of EPR spectra in the plates of enamel, dentin, and bone in order to describe the form of a dosimetric EPR signal and its components and to determine the relation between oriented and disordered CO_2^- radicals.

2. Materials and Methods

The samples of teeth and bone used for measurements were obtained from Kyiv clinics. An intact tooth with a clinically sound enamel was cleaned with the help of dental tools and a nonabrasive polishing paste. The enamel plate of approximately $1\times2\times3$ mm^3 in size was cut in such a way that it had its largest dimension along the axis of growth of the tooth and the minimal one along the normal to its surface. In a similar way, a plate of dentin was cut of a near-surface part of the tooth. A plate of bone of was $2\times3\times4$ mm^3 in size and had its maximal dimension along the axis of growth of a bone and the minimal one along the normal to the surface.

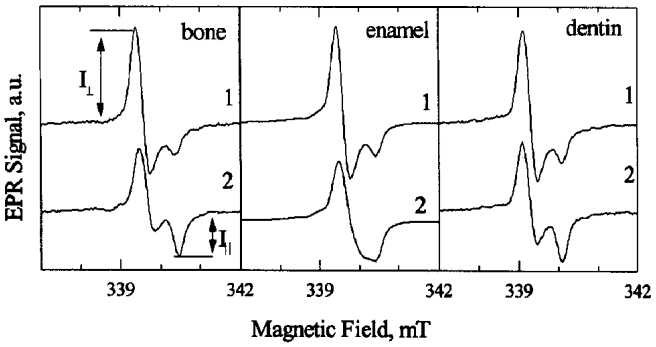

Fig. 1. Normalized EPR spectra of the plates of irradiated bioapatites for two orientations of the magnetic field that correspond to the maximal values of the amplitudes $I_\parallel$ (*1*) and $I_\perp$ (*2*)

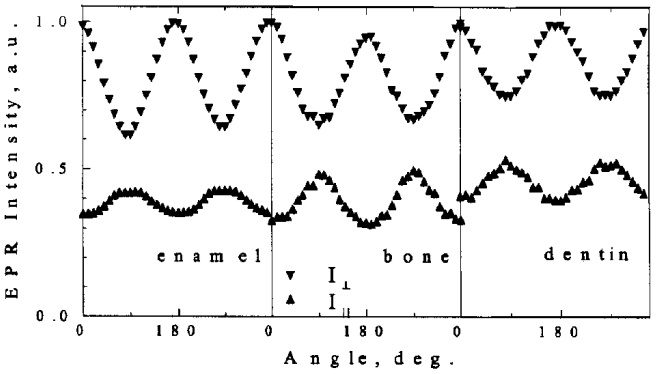

Fig. 2. Angular dependences of the amplitudes $I_\parallel$ and $I_\perp$ for the plates of bioapatites observed upon the rotation of a magnetic field in the plane of the maximal anisotropy. For each specimen, the maximal value of $I_\perp$ is taken as a unity

The samples were irradiated with gamma rays from a ^{60}Co source at a radiation power of 2.58×10^{-2} C kg^{-1}s^{-1} (100 R/s). The duration of irradiation amounted to 2.5 hours. The EPR spectra were recorded at room temperature using an X band EPR spectrometer. We registered the derivative of an absorption signal. The whole number of paramagnetic centers was determined with respect to the standard sample MgO:Cr^{3+} with a known number of spins. Experimental EPR spectra were normalized to the intensity of the standard sample.

3. Experimental Results and their Discussion

In order to investigate the anisotropy of EPR spectra of the plates of irradiated bioapatites, we used a technique proposed in [8] when studying enamel plates. We observed a variation of amplitudes in the maximum ($g \approx g_\perp$) and minimum ($g = g_\parallel$) of the EPR signal, where $g_\parallel$ and $g_\perp$ represent g-factors of an axial CO_2^- radical. The amplitudes $I_\perp$ and $I_\parallel$ were measured as the distance from the zero line of the spectrum (see Fig. 1). The rotation of the sample in an external magnetic field was accompanied with the redistribution of the absorption intensity in the EPR spectrum caused by the angular dependence of the line arising from oriented paramagnetic centers. Figure 2 shows the variations of $I_\perp$ and $I_\parallel$ observed as the sample was rotated in the plane where these variations were maximal. The earlier investigations of enamel plates [8, 11—13] have shown that apatite crystallites in enamel form two packets located in such a way that the c axes of crystallites make small angles $\pm\alpha$ with the normal to the tooth surface. That's why, in the case of an oriented sample in an external magnetic field being directed perpendicularly to this normal, the oriented centers contribute to the general EPR spectrum only in the neighborhood of $B_\perp = h\nu/\beta g_\perp$, where h is the Planck constant, ν stands for the frequency of a spectrometer, and β is the Bohr magneton. In this case, the amplitude of the spectrum at the point $B_\parallel = h\nu/\beta g_\parallel$ is determined solely by the disordered centers.

There exist X-ray data on the orientation of hydroxylapatite crystallites in bone (see, e.g., [14]), according to which the majority of them are oriented in such a way that their c axes are directed along the axis of growth of a bone. That's why one should expect that, when a bone sample rotates in a magnetic field about its axis of growth ($B\perp c$), the angular dependences of both $I_\parallel$ and $I_\perp$ are absent, which was also observed experimentally. The maximal variations of the amplitudes $I_\parallel$ and $I_\perp$ were observed as the plate was rotated about the normal to the bone surface. When a magnetic field is oriented in the plane that is normal to the axis of growth of a bone, the oriented centers contribute to the EPR spectrum only close to $B_\perp$, while the amplitude $I_\parallel$ is determined solely by disordered CO_2^- radicals just as in the case of enamel.

Thus, in enamel and bone plates, there exist such kinds of orientation that a contribution to $I_\parallel$ is determined only by disordered centers. It gives a possibility to make use of a high-field part of a signal for recovering the whole form of a "powder" EPR line which is conditioned by orthorhombic CO_2^- radicals. For this purpose, the EPR line of a powder with the known parameters of the g-tensor [9,11] was simulated in the first approximation (see, e.g., [15]). The variable parameters were the width and form of the envelope

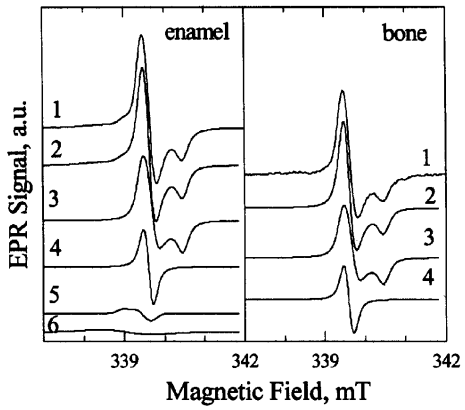

Fig. 3. Experimental EPR spectra of the irradiated plates of enamel and bone for the orientation of a magnetic field such that the oriented radicals CO_2^- give no contribution to $I_\parallel$ (*1*), model spectra (*2*) and their components conditioned by orthorhombic radicals CO_2^- (*3*), axial radicals CO_2^- (*4*), and radicals CO^- (*5*), as well as the spectrum similar to the so-called background signal (*6*)

line of spin packets; moreover, the parameters of the g-tensor were also changed within small limits. The best description of the whole EPR signal for both enamel and bone was obtained using the following parameters of orthorhombic centers: $g_x = 2.0017$, $g_y = 1.9972$, and $g_z = 2.0031$, which are close to those given in the literature for orthorhombic CO_2^- radicals in enamel [9,11]. In this case, we use the form of a Voigt line [16] with the contribution of homogeneous and nonhomogeneous broadenings being approximately equal (the widths of the lines used in the convolution were equal to 0.15 mT for a Gaussian and 0.2 mT for a Lorentzian). The EPR spectrum of oriented CO_2^- radicals was also simulated with the help of a Voigt line of the same width. Figure 3 shows the experimental EPR spectra obtained for enamel and bone samples oriented in such a way that oriented centers do not contribute to the EPR spectrum close to $B_\parallel$ (spectra *1*). We also present the overall model spectra corresponding to the experimental ones (spectra *2*) as well as their components (spectra *3*–*6*) which were used for description of the experimental data. For bone, a satisfactory description of the experimental EPR spectrum can be reached with the help of two centers: axial and orthorhombic CO_2^- radicals. In enamel, these centers make a dominant contribution to the dosimetric EPR signal but, for a complete description of the low-field part of the spectrum, we introduced additionally a CO^- radical ($g_x = 2.0061$, $g_y = 2.0033$, $g_z = 2.0018$) [17] and an isotropic line having 1.2 mT in width and g = 2.0055, which is similar to the so-called "background" EPR line [1].

The amplitude $I_\perp$ varied from 1 to 0.65 for both enamel and bone (here unity corresponds to the maximum value of $I_\perp$)). Thus, the variation of $I_\perp$ conditioned by oriented centers was equal to 35%. In this case, the relation of the number of axial centers to that of orthorhombic ones, which was determined as the relation of the areas under the corresponding curves, amounts to $N_{\rm ax}$: $N_{\rm rh} \approx 0.17$.

Dentine represents the least investigated substance, and there are no data on the orientation of crystallites in it. A variation of the amplitude $I_\perp$ observed for a sample rotating in the plane of the maximal anisotropy amounted to 25 %. It's worth noting that, in reality, the contribution of axial centers can be larger because a certain part of hydroxylapatite crystallites in dentin can be oriented chaotically. It is impossible to determine the accurate ratio $N_{\rm ax}$: $N_{\rm rh}$ for dentin due to the absence of the data on the spatial distribution of orientations of apatite crystallites in this substance.

Our experiments testify to the fact that, in all the investigated apatites of natural origin (enamel, bone, and dentin), there exist two kinds of CO_2^- radicals: disordered and oriented ones. Their contributions to the EPR spectra of gamma-irradiated enamel and bone are approximately equal and can amount to 35% with respect to the amplitude. In dentin, a contribution of oriented radicals is somewhat lower, but this fact can be conditioned by a worse ordering of the crystallites themselves. In other words, a part of axial centers in dentin can cause a powder-like EPR spectrum due to the disordering of crystallites rather than at the expense of the disorientation of radicals. It is possible that the ratio of the numbers of oriented and disordered radicals in apatites of biological origin represents a constant value.

Thus, in the present work, it is demonstrated for the first time that a dosimetric EPR signal in the plates of irradiated apatites of biological origin (enamel, bone, and dentin) can be mainly described in terms of two EPR lines. One of them represents a "powder" line and is conditioned by disordered orthorhombic CO_2^- radicals, whereas the other one is caused by oriented axial CO_2^- radicals. In bone, allowing for these radicals is sufficient for a satisfactory description of the experimental spectrum. In addition to CO_2^- lines, a complete description of the spectrum in enamel requires to take into account both the less essential contribution of CO^- radicals and the EPR line which is similar to the "background" line. We have determined the ratio of the numbers of oriented and disordered centers which turns out to be the same for enamel and bone and amounts to 0.17. In dentin, this ratio was lower, which is

conditioned, in our opinion, by a more essential disorder of hydroxylapatite crystallites than that in enamel and bone.

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СТРУКТУРА ДОЗИМЕТРИЧНОГО СИГНАЛУ ЕПР В АПАТИТАХ БІОЛОГІЧНОГО ПОХОДЖЕННЯ

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Р е з ю м е

Досліджено спектр електронного парамагнітного резонансу (ЕПР) поблизу $g = 2$ в апатитах біологічного походження: зубна емаль, кісткова тканина, дентин, — що сформувався після їхнього γ-опромінення. Цей сигнал використовується в ретроспективній дозиметрії для визначення дози опромінення. Вперше описано та пояснено форму і структуру радіаційно індукованого спектра ЕПР пластинок емалі та кісткової тканини. Показано, що у досліджених речовинах він зумовлений, головним чином, внеском двох типів радикалів CO_2^-. Один з цих радикалів є орієнтованим центром, в той час як інший — розупорядкованим. Визначено відносний внесок орієнтованих та розупорядкованих радикалів CO_2^- в спектр ЕПР біоапатитів різного походження.