THE MECHANISM OF CO_2^- RADICALS FORMATION IN BIOLOGICAL AND SYNTHETIC APATITES

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Biological and synthetic apatite dosimetry is an widely used method for dose evaluation. Dose reconstruction in irradiated apatites is based on the measurements of the EPR signal intensity. This signal is mainly caused by the CO_2^- radicals - axial and orthorhombic. Despite of wide use of this signal the mechanism of CO_2^- radicals formation and their localization are still under debate. At present several versions of CO_2^- radicals formation are discussed. CO_2 molecule in organic and on the surface of crystallites, fragments of organic molecules and molecular ion CO_3^{2-} located in phosphate or hydroxy site were proposed as a precursor of CO_2^- radicals. The main purpose of the present work is to study short-living radicals induced by irradiation and to find out the mechanism of CO_2^- formation.

The EPR spectra of powders and plates of tooth enamel and bone are investigated. The detailed comparative analysis of the spectra recorded immediately after $\gamma(^{60}Co)$- irradiation and after a 2-month storage at room temperature is carried out. The formation of CO_2^- radicals in powders of B-type synthetic apatites under annealing of samples is also studied.

It is found that: 1) the main short-lived (unstable) radicals in bioapatites are the CO_3^{3-} in B site, 2) the decay of CO_3^{3-} results in the increase of the intensity of CO_2^- EPR signal, mainly, due to the increase of axial CO_2^- amount, this points to the transformation $CO_3^{3-} \rightarrow CO_2^-$, 3) the thermal generation (TG) of CO_2^- radicals in unirradiated synthetic apatites is registered for the first time, 4) UV irradiation and TG create more axial centers than orthorhombic ones as compared to γ – irradiation.

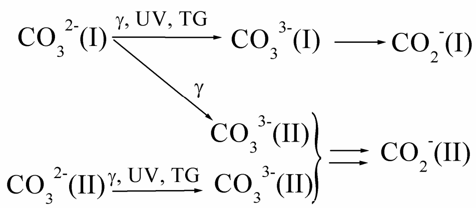

Fig.1. Scheme of CO_2^- radicals formation in apatite

The following conclusions are done. The precursors for CO_2^- radicals are the molecular ions CO_3^{2-}. The difference between the axial and orthorhombic radicals is caused by the center symmetry lowering due to the presence of a lattice defect in CO_2^- surroundings. Fig.1 shows the principal scheme of CO_2^- radicals formation. Here, I and II indicate the species in the defect-free area and with a defect nearby, correspondingly. The process of radicals formation is the following. At the capture of electron (either induced by radiation or released from a trap by thermal phonons at the annealing of synthetic apatites) the ion CO_3^{2-}(I or II) is transformed into a metastable CO_3^{3-} radical (I or II, respectively). Except for the above process, γ-irradiation also creates additional defects thus opening a new path for the formation of II-type defects, $CO_3^{2-}(I) \rightarrow CO_3^{3-}(II)$ (denoted by a tilted arrow in the Fig.1). Thus, γ-irradiation produces more precursors for orthorhombic CO_2^- radical than UV. Both $CO_3^{3-}(I)$ and $CO_3^{3-}(II)$ are unstable. They decompose into CO_2^- radicals by a process $CO_3^{3-} \rightarrow CO_2^-$ and form axial $CO_3^{3-}(I)$ and orthorhombic $CO_3^{3-}(II)$, correspondingly. Decay of $CO_3^{3-}(I)$ goes more slowly than the one of $CO_3^{3-}(II)$. The reason can be the potential barrier lowering by a neighboring defect. As the result only short-lived $CO_3^{3-}(I)$ radicals are observed in the experiment, and after two month storage they transform into $CO_2^-(I)$.