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РЕЗЮМЕ
Методами мас-спектрометрії *(LA ICP-MS)* і електронного парамагнітного резонансу проведено дослідження розподілу елементів-домішок (Li, Al, Be, B, P, Ti, Mn, Fe, Ge) і парамагнітних центрів (Al-O$^-$, Ti^{3+}, Ge^{3+}) у зональному монокристалі кварцу з камерних пегматитів Волині. Проаналізовано можливості використання отриманої інформації для відновлення умов утворення кварцу.

SUMMARY
Mass-spectrometry (LA-ICP-MS) and electronic paramagnetic resonance (EPR) methods have been used for the study of distribution of impurities (Li, Al, Be, B, P, Ti, Mn, Fe, Ge) and paramagnetic centres (Al -O$^-$, Ti^{3+}, Ge^{3+}) in zonal single-crystal quartz from Volyn breast pegmatite. Application of the obtained information for decision of geological problems have been analysed.

Институт геохимии, минералогии и рудообразования им. Н.П. Семененко НАН Украины, г. Киев
e-mail: abrik@igmof.gov.ua

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A.B. BRIK, V.V. RADCHUK

STRUCTURE AND PROPERTIES OF BIOMINERALS LOCALIZED IN HUMAN ORGANISM

The properties of nanoscale solid-state particles localized into high- and weakly mineralized biological tissues are considered. For high-mineralized tissues (tooth enamel, bone) the problems, bound with hierarchy of an internal structure, anisotropy of their structure and impurity crystalline phases are discussed. For weakly mineralized tissues (brain tissues) the anomalous resonance signals (caused by particles with magnetic ordering), which have unique dynamic characteristics are described. The possible applications of the results for solution problems, connected with mineralogy, ecology and medicine are discussed.

INTRODUCTION

More than fifty minerals of different types have been discovered in human organism [1, 2]. The most widely spread biogenic minerals are calcium phosphates, carbonates and oxides, including ferric oxides. Inorganic solid-state particles are formed into organic matrix as a result of the biomineralization processes [1, 2]. Physiological (normal) and pathological mineralization takes place in human organism. Bones and teeth are the result of physiological mineralization. Different types of stones in kidney and other organs are the examples of pathological mineralization. Significant efforts were made for investigation of the biominerals and mineral inclusions into biological tissues [3-6]. Nevertheless, many important issues concerning the structure and properties of the nanoscale solid-state particles are still investigated insufficiently. In the present paper some general characteristics of biominerals as a special class of substances are described. Main attention in the paper devoted to data obtained by electron paramagnetic resonance. The possible using of the results for solving different type fundamental and applied problems is discussed.

INTERNAL CONSTRUCTION OF THE BIOMINERALS

The biominerals are complex multicomponent systems. The processes in the systems can be explained only with account of hierarchy of their internal construction. The tooth enamel is the most highly mineralized tissue of a human organism. Some peculiarities of the internal structure of tooth enamel are illustrated in Fig. 1. In the mineral component of tooth enamel one can identify enamel prism and nanocrystals, which immersed into organic matrix. The dimensions of nanocrystals fall into the intervals: length 100-200 nm and cross dimensions 15-20 nm.

The bone tissue has essential distinctions in comparison with enamel because bones have cells, nerves and blood vessels. Despite distinctions in the internal construction of bones and enamel, some essential peculiarities of their internal construction are similar. The mineral component of these biominerals is represented by small isolated solid-state particles with dimensions in the range of nanometers. The mineral solid-state particles of the tissues are immersed into water organic matrix, which operates their properties. Both tooth enamel and bones have a barrier layer, which control the mass transfer processes into the solid-state particles. The hierarchy of internal construction of the biominerals determines the local and macroscopic properties of the biological tissues.

The biominerals should be considered as mineral-organic nano-associated (MONA) systems. The role of structural units in the MONA system play nanocrystals (NCR), organic layers (ORG) and barrier layers (BL), located between the mineral and organic subsystems. The electrical charge of the subsystems can be varied in time due to chance of external conditions [3]. Just electrical charges of the nano-scale subsystems control the mass-transfer processes between an organic and mineral matter of biominerals. The organic matrix can effectively operate properties of nanocrystals (and biomineral as a whole) if the full energy of the mineral particles and their surface energy are commensurable.

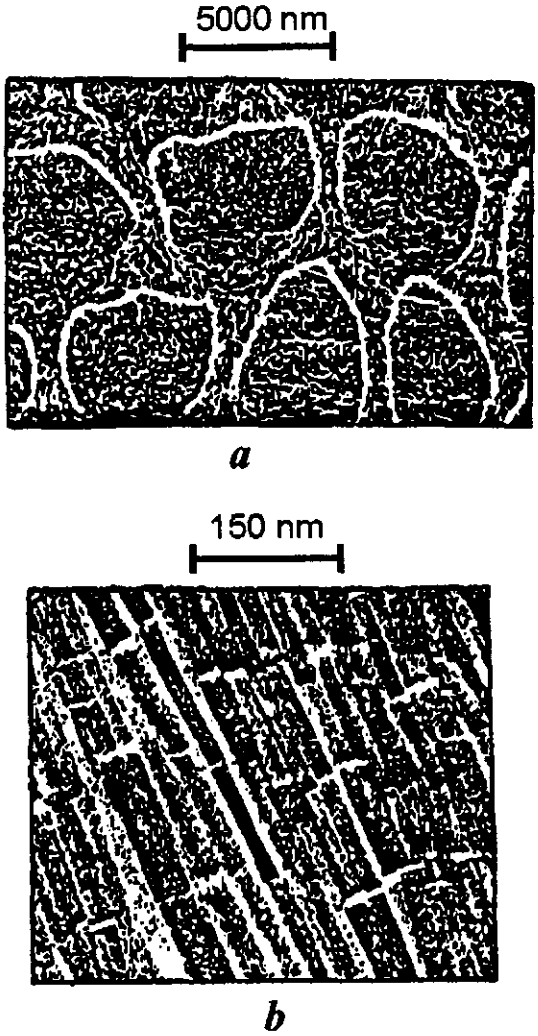

Fig. 1. **Electron micro photos of various sections of tooth enamel [3]. Photo *a* shows enamel prisms and photo *b* the hydroxylapatite nanocrystals filling the prisms**

ANISOTROPY OF TOOTH ENAMEL AND BONES

Tooth enamel and bones are highly textured systems. Accordingly EPR signals of enamel and bones display anisotropy when the plates manufactured from the biominerals, are rotated in magnetic field. The EPR signal anisotropy in biominerals is caused by anisotropy of the organic matrix and phenomenon of bioepitaxy. Due to bioepitaxy the organic matrix of the biominerals influence on orientation of the nanocrystals. Diseases of teeth and bones change properties of biominerals and change the anisotropy effects. EPR investigations open possibilities for study the changes caused by diseases of bones and teeth.

Fig. 2 illustrates the anisotropy of EPR signals caused by CO_2^- radicals. The figures have shown that the form of the signals change due to rotation of the enamel plate in the magnetic field and due to heating of the sample. The extrema of the curves located in magnetic fields B_1 and B_2 (see dashed arrows) correspond to $g_1 \cong 2.003$ and $g_2 \cong 1.997$. The intensities of the peaks are marked as $I_\perp$ and $I_\parallel$.

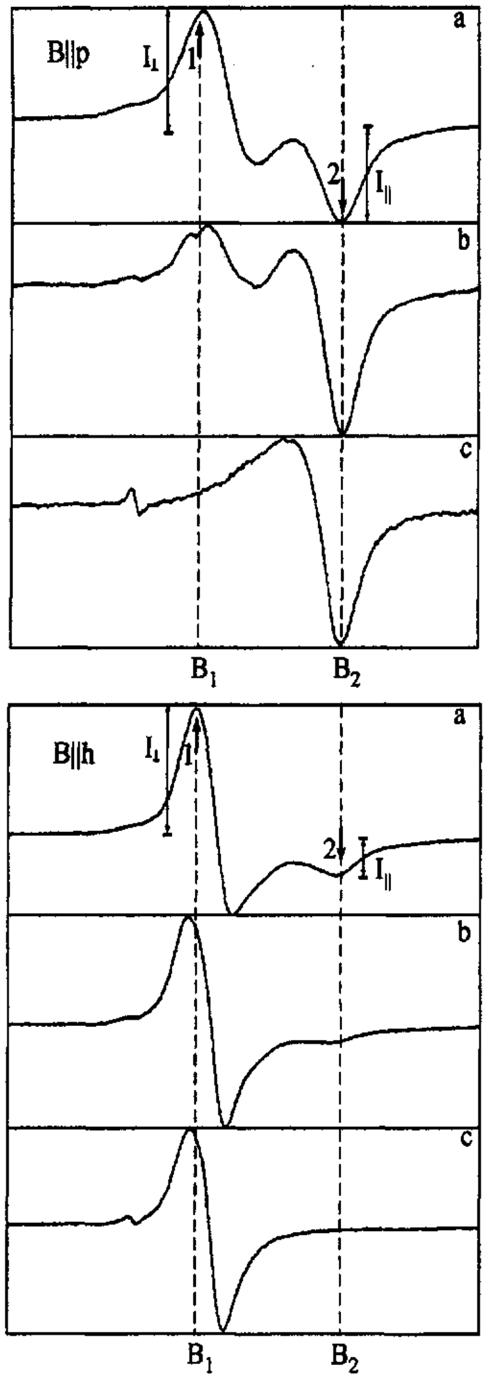

Fig. 2. **EPR spectra of tooth enamel plate for two orientation of magnetic field *B* (*B* is parallel to perpendicular *p* and horizontal *h* axis). The spectra *a*, *b*, *c* corresponds to plates heated one hour at temperature 75, 170 and 285 °C**

The anisotropy of the EPR signal of CO_2^- radicals in bones is similar to the anisotropy in enamel. The anisotropy of EPR signals in enamel and bones can be described by texture coefficients $k_1 = I_\perp,h \,/\, I_\parallel,h$ and $k_2 = I_\perp,p \,/\, I_\parallel,p$. In these formulas the values $I_\perp,h$ and $I_\parallel,h$ correspond to the plates with orientations $\mathbf{B}_0 \parallel h$, while the values $I_\perp,p$ and $I_\parallel,p$ correspond to the plates with orientations $\mathbf{B}_0 \parallel p$. The texture coefficients have been changed due to illness of enamel by caries and due to illness of bones by osteoporosis [3]. The coefficients change as well for rat bones after imitation of space flight conditions [4]. The texture coefficients open new possibilities for study of anisotropy and other properties of the high-mineralized biological tissues.

EPR OF THE IMPURITY CRYSTAL PHASES IN BIOMINERALS

Mineralized biological tissues have complicate phase composition. Most unequivocally the phase composition of biominerals can be determined the by means of the X-ray difraction. However possibilities of the X-ray phase analysis for study the mineral phases of biominerals are limited. Small sizes of particles, which form the mineral component of biominerals, and defectiveness of structure of the particles complicates research of biominerals by the X-ray phase analysis. Application of EPR for study of impurity crystal phases is based on the following factors [3]. Firstly, this method has high sensitivity, and, secondly, the EPR characteristics of paramagnetic ions (including Mn^{2+} and Cr^{3+}), located in different crystal lattices, are essentially different (Fig. 3-a). It gives possibilities to investigate the composition of impurity crystal phases by EPR in biominerals (Fig. 3-b).

The impurity crystal phases essentially influence on mineralization and demineralization of bones and teeth and reflect the changes of these tissues due to diseases. The information about phase composition of mineral component of biominerals and their synthetic analogues has great importance for solution different fundamental and applied problems. The phase composition of biominerals varies with age of biological objects and due to diseases of bones and teeth. A special interest to phase composition of biominerals is connected with study of osteoporosis and bone demineralization during space flight [4] and with application of synthetic hydroxylapatite for treatment of bone diseases.

ANOMALOUS SIGNALS IN SOLID-STATE PARTICLES LOCALIZED IN BRAIN TISSUE

Mineral particles (or mineral inclusions) are contained not only into highly mineralized tissues. The presence of mineral particles is common property of biological tissues [3]. Many biological tissues, including brain tissue, contain small amounts of mineral inclusions. EPR spectrometers are usually used to study the diamagnetic (or paramagnetic), which contain different types of paramagnetic centers and broken chemical bonds. As a rule, this class of objects has the "usual" EPR signals, i.e. signals with the usual form and dynamic characteristics. EPR spectrometers are also utilized for research of ferromagnetic and antiferromagnetic dielectric materials, semiconductors, metals and superconductors. In these types materials the "anomalous" signals, whose form and dynamic responses are unusual, can be observed. The presence of the anomalous signals indicates the existence of special properties of the researched objects and causes heightened interest in them. This interest is related to the search of new physical phenomena, and to search of new materials for solution of applied tasks with the help of non-traditional approaches.

We have registered the magnetic resonance signals in brain tissue that have anomalous dynamical characteristics [3, 5]. Additional coherent signals appear on the outline of resonance lines when the power of microwave field is greater that the critical value ($P > P_{cr}$). The critical value of the microwave field for different situations lies in the interval of 65-85 mW. We divide the signals in brain tissue in two groups: the narrow signals with $\Delta B \approx$ (5-8) mT and the broad signals with $\Delta B \approx$ (12-150) mT. Under high level of microwave power, parabolic zones, caused by manifestation of quantum oscillations, appeared on the outline of the narrow resonance signals.

On the basis of experimental results it is possible to make the conclusion that the brain tissues have both physiological and pathological biomineralization [3]. The mineral particles that have narrow resonance lines are the product of physiological mineralization, and the mineral particles that have broad resonance lines are the product of pathological mineralization. Different organic matrices can stimulate formation of different mineral

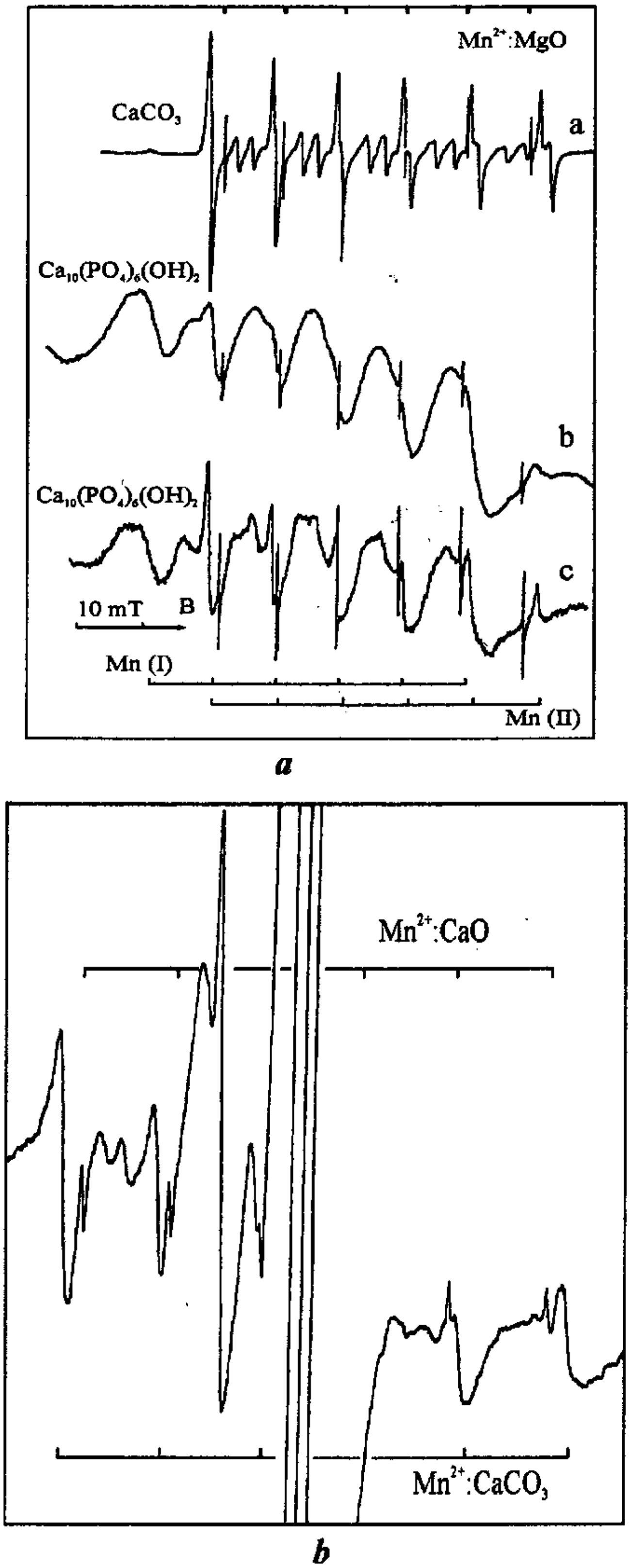

Fig. 3. **EPR of Mn^{2+} ions in different crystal lattices *(a)* and in bone tissue *(b)***

substances. The brain tissues promote deposition of oxides and hydroxides of iron. We believe that the mineral areas play an important role in processes related to functioning of the brain. We think that mineral particles formed due to physiological biomineralization play an important role in storage and processing of information, and pathological mineral particles can be a cause of various diseases of the brain.

CONCLUSION

The properties of mineral matter generated into biological tissues, and properties of appropriate synthetic substances or substances produced by "nonliving" Nature differ essentially. The mineral substance of biominerals consists of small solid-state particles that have dimensions in nanometer range. The nanoscale particles are immersed into organic matrix, which operate their properties. The surface properties of the mineral particles (the interface between mineral and organic substances) play an important role in formation of the biominerals. As the mineral particles grow on an organic substrate, the structure of the organic matrix substantially determines the properties of the mineral particles. The study of mineral particles localized into biological tissues uncovers new possibilities for clarification of co-evolution mechanisms of organic and mineral matter, and for solution of different type fundamental problems related to functioning of biological tissues, including brain tissues [3].

Study of nanoscale mineral particles of biological tissues serve for solution of different type applied problems. The applied problems related to field of mineralogy, ecology, biology and medicine. It is well known that demineralization of bone tissue takes place due to osteoporosis but most fast bone demineralization takes place under microgravity conditions during space flight. Information about properties and structure of bone and teeth play important role for treatment of the biological tissues damaged by different diseases. The information is important for manufacturing of synthetic materials, which are used as implants in orthopaedics, traumatology and stomatology. The study of tooth enamel properties is important for retrospective EPR dosimetry of population irradiated due to Chernobyl accident.

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РЕЗЮМЕ

Розглянуто властивості мінеральних нанорозмірних частинок твердого тіла, яки локалізовані в високо та слабо мінералізованих біологічних тканинах. Для високо мінералізованих тканин (емаль зубів, кістки) розглянуто проблеми, що пов'язані з ієрархією внутрішньої будови, анізотропією їх структури та з домішкорвими кристалічними фазами. Для слабо мінералізованих тканин (тканини мозку) розглянуто характеристики аномальних резонансних сигналів, яки обумовлені магнітно упорядкованими частиками. Проведено обговорення можливих застосувань отриманих результатів для вирішення проблем, пов'язаних з мінералогією, екологією та медициною.

РЕЗЮМЕ

Описаны свойства минеральных наноразмерных частиц твердого тела, которые локализованы в высоко и слабо минерализованных биологических тканях. Для высоко минерализованных тканей (эмаль зубов, кости) рассмотрены проблемы, которые связаны с иерархиею внутреннего строения, анизотропией их структуры и примесными кристаллическими фазами. Для слабо минерализованных тканей (ткани мозга) рассмотрены характеристики аномальных резонансных сигналов, которые обусловлены магнитоупорядоченными частицами. Проведено обсуждение возможных использований полученных результатов для решения проблем, связанных с минералогиею, экологиею и медициною.

M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine, Kiev

Institute of Telecommunications and Global Information Space of NAS of Ukraine, Kiev

e-mail: abrik@voliacable.com