## VARIATIONS OF ELEMENT STRUCTURE OF PATHOGENIC MINERALS IN AN ORAL CAVITY Belskaya L.V., Golovanova O.A. (chem. dep. OmSU) LudaB2005@mail.ru

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Studying of biominerals and process of their formation in a human body is the major direction of a science of biomineralogy. It is actual at the decision of the problems connected with formation of pathogenic minerals in a human body, leading to various diseases. A role of microelements including ions of metals, in the course of formation of pathogenic biominerals now up to the end it is not studied.

The particular interest represents the maintenance in biomineral formations of metals, including manganese and iron. So, manganese for live organisms has the vital value: it makes active many fermentative processes, is necessary for hemoglobin formation, stimulates synthesis of cholesterol and fat acids etc. Iron is a part of respiratory pigments, including hemoglobin, participates in processes of linkage and oxygen carrying over to fabrics; stimulates function blood-forming bodies; it is applied as a medical product at anemia and some other pathological conditions. However at adverse ecological situation elements arrive in a human body much, take calcium and magnesium positions in organic and inorganic structures, forming connections which can serve as germs of pathogenic mineral formations.

**The work purpose** – to reveal features of microelement structure of pathogenic formations of various localization and calculi-forming environments depending on local natural and technogenic factors of an inhabitancy on an example of Omsk region.

**Material and methods.** Object of research was the collection from 115 dental, 13 salivary stones and 120 samples of an oral liquid. All investigated samples of stones have been subjected the analysis at station of the power dispersive synchrotron X-Ray fluorescence spectrometry (Novosibirsk). Issue spectra of investigated tests were raised by a bunch polarized radiations by energy 25 kV. Samples prepared powder pressing in tablets is powerful 30 mg and in diameter 5 mm with superficial density 0.15 g/sm<sup>2</sup>. Were used two levels of energy of excitation:

– 22 kV for quantitative definition Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pb, Th, U;

- 42 kV for quantitative definition Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La and Ce.

Calculation of the maintenance of elements was spent by a method of the external standard. As samples of comparison standards of rocks served: CT-1a (трапп), CA-1 (aleurolite), CG-2 (granite), SI-1 (limestone), BCR-32 (phosphorite). Normalizing factors for calculation of maintenances of the elements which have been not certified in specified standards, have been received by interpolation of corresponding sizes for the next groups of elements. Limits of detection of elements at loading of a spectrometer path with frequency 10 kHertz and time of measurement of 1000 seconds make (0,1-2,0)  $\cdot 10^{-4}$ , %. Processing of issue spectra was made by means of the specialized program. At quantitative calculation the method of "the external standard" was used. The error of definitions of elements was in limits 2-5 %.

The element structure of samples of an oral liquid was defined by a method of atomic-issue spectroscopy with is inductive the connected plasma (AES-ISP). Measurements were spent on ISP-spectrometer OPTIMA 2000 DV (Perkin Elmer, Germany). Processing of results it was made with use of the software of a spectrometer.

**Results.** The analysis of the received results by definition of element structure of tooth and salivary stones (tab. 1, 2) shows that microelements K, Zn, Ba, Zr, Rb, Mn, Fe, Cu, Ti, V, Ni etc. concentrate in stones. The high maintenance of the listed elements in samples, probably, speaks their isomorphic introduction in apatite – the basic mineral to a component of dental and salivary stones of the person. Taking into account possible isomorphic replacements stoichiometric apatite it is possible to present the formula in a kind:  $Me_{10}(XO_4)_6Y_2$ , where  $Me = Ca^{2+}$ ,  $Mn^{2+}$ ,  $Mn^{3+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Na^+$ ,  $Rb^+$ ,  $Y^{3+}$ ;  $X = P^{5+}$ ,  $Si^{4+}$ ,  $S^{6+}$ ,  $Mn^{7+}$ ,  $As^{5+}$ ;  $Y = F^-$ ,  $CI^-$ ,  $OH^-$ ,  $O^{2-}$  thus for apatite it is characteristic both heterovalency, and isovalency isomorphism. Possibility of isomorphic introduction speaks affinity of ionic radiuses of elements:  $r(Ca^{2+}) = 0.106$ ,  $r(Sr^{2+}) = 0.127$ ,  $r(Ba^{2+}) = 0.143$ ,  $r(Mn^{2+}) = 0.091$ ,  $r(Zn^{2+}) = 0.083$ ,  $r(Na^+) = 0.098$ ,  $r(K^+) = 0.133$ ,  $r(Rb^+) = 0.149$ ,  $r(Ni^{2+}) = 0.078$ ,  $r(Cu^+) = 0.096$ ,  $r(Ag^{2+}) = 0.113$  nanometers and  $r(CI^-) = 0.181$ ,  $r(Br^-) = 0.196$ ,  $r(I^-) = 0.220$  nanometers [1].

## Table 1

Element	Experimental data	Literary data [2]
Fe	$(8.19\pm2.57)\cdot10^{-3}$	$(1.46\pm0.1)\cdot10^{-2}$
Ti	$(7.62\pm3.63)\cdot10^{-3}$	(6.4±3.3)·10 <sup>-3</sup>
Mn	$(2.41\pm0.73)\cdot10^{-3}$	(1.3±0.085)·10 <sup>-3</sup>
V	$(4.27\pm1.43)\cdot10^{-3}$	(2.4±0.16)·10 <sup>-5</sup>
Ni	$(1.60\pm0.59)\cdot10^{-3}$	$(0.3\pm0.016)\cdot10^{-3}$
Cu	$(1.53\pm0.61)\cdot10^{-3}$	$(1.6\pm0.078)\cdot10^{-4}$
Zn	$(2.52\pm0.53)\cdot10^{-2}$	$(1.6\pm0.11)\cdot10^{-3}$

The maintenance of microelements in dental calculi of inhabitants of Omsk region, wt%

Comparison of the received experimental data on scales with literary (tab. 1) allows to allocate the elements which maintenance is characteristic for Omsk region: Mn - on 46 %; Ni - on 81 % more than according to [2]. The maintenance V (in 178 times), Cu (in 95 times) and Zn (in 16 times) is considerably exceeded. In scales of inhabitants of Omsk are found out also Ag, Sn, I, Br and Rb.

## Table 2

The maintenand	ce of microeler	ments in salivary	v calculi of inhabitants of	of Omsk region. wt%

Element	Experimental data	Literary data [2]
Fe	$(7.37\pm2.63)\cdot10^{-3}$	$(1.00\pm0.09)\cdot10^{-2}$
Ti	$(5.65\pm2.82)\cdot10^{-2}$	$(1.30\pm0.13)\cdot10^{-3}$
Mn	-	$(2.30\pm0.13)\cdot10^{-5}$
V	$(1.71\pm0.72)\cdot10^{-2}$	$(1.30\pm0.34)\cdot10^{-3}$
Ni	$(1.18\pm0.61)\cdot10^{-3}$	$(2.60\pm0.18)\cdot10^{-4}$
Cu	$(1.84\pm0.88)\cdot10^{-3}$	$(1.50\pm0.08)\cdot10^{-4}$
Zn	$(1.28\pm0.76)\cdot10^{-2}$	$(1.4\pm0.1)\cdot10^{-3}$

It is necessary to notice that levels of the maintenance of elements depend on environment conditions and thereof the essential disorder of the sizes measured in various regions is marked. Thus, the raised maintenance of microelements in dental calculi, probably, is caused by specificity of Omsk region. Similar laws are received and for salivary stones of inhabitants of Omsk region (tab. 2): Fe – on 26 % it is less, and Ni – on 78 % more than according to [2]. Considerably exceeds literary values the maintenance V (in 43 times), Cu (in 12 times) and Zn (in 9 times).

A number of authors specify in the important role of saliva in scale formation. The mixed saliva represents the most probable source of receipt of mineral components, including microelements, in structure of tooth adjournment. For the purpose of an establishment of possibility of receipt of microelements definition of element structure of an oral liquid is spent to structure of stones by means of optical emission spectrometry with inductively coupled plasma (ISP-AES) (tab. 3).

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Element structure of a saliva in norm and in conditions of calculi-forming, mg/l

Element	Control group	Control group	Calculi in an oral
	(experimental data)	(literary data [3])	cavity
Fe	$0.278 \pm 0.041$	0.11-0.19	0.399±0.185
Mn	$0.050{\pm}0.014$	0.009-0.011	-
Zn	0.476±0.183	-	$1.082 \pm 1.010$
Cu	0.342±0.314	0.007-0.018	$0.054{\pm}0.033$

During research two groups have been allocated: group  $N \ge 1$  – the patients having tooth adjournment in an oral cavity (8 persons, 57 %); group  $N \ge 2$  – control (6 persons, 43 %). The group of persons taken as comparison, resistant (steady) against diseases, people with the identical somatic status "almost healthy", and also without parodontopathy and an oral cavity mucous membrane have made.

By results of the spent experiment microelements Zn and Cu are found out in all analyzed samples, and Fe, Mn, Ni and Al in the majority of samples. Thus the maintenance of the listed microelements increases in conditions камнеобразования in an oral cavity. By data Ob-Irtysh an inter-regional territorial administration on hydrometeorology and environment monitoring, at an estimation of quality of a surface water in territory of the Omsk region it is established that water of the river Irtysh in an alignment Omsk is characterized as "dirty" (a remote combinatory index of impurity of water – 3.66) [4]. In all alignments of Omsk a critical indicator of impurity of water are copper connections (12 – 14.7), and also gland (2.2), zinc (1 – 2.1), manganese (0.9 – 2.2 maximum concentration limits). For the river Om of size a remote combinatory index of impurity of water vary from 4.33 to 4.94, thus the maintenance of the basic polluting substances in controllable alignments of the river of Omi has made: Connections of iron 2.2 - 3.2, copper 13.3 - 19.3, zinc 1 - 1.9, manganese 8 - 19.9 maximum concentration limits. Also cases of extremely high pollution by connections of manganese 60.6 - 113.8 and copper 33 - 44 maximum concentration limits are noted.

In comparison of some average concentration of chemical elements in scales of inhabitants of Omsk: Zn > Fe > Cu > Ni > Mn c a number of average concentration of the given elements in an oral liquid: Zn > Fe > Cu > Mn > Ni it is visible that the sequence of an arrangement of elements in numbers is identical and, hence, a probable source of receipt of microelements in structure of tooth and salivary adjournment is the saliva of the person.

It is known that the saliva represents the structured biological liquid which all volume is distributed between micelles – colloid formations. Their kernels consist of molecules of phosphate of calcium and are surrounded by aqua-albuminous covers. Possibly, at superfluous receipt of microelements in structure of an oral liquid there is a formation of chelated complex connections with the amino acids which are a part of squirrel, and destruction of protective covers colloid micelles. As an example it is possible to result values of step constants of stability chelated complexes of nickel with glicine ( $K_1=1,4\cdot10^6$ ,  $K_2=8,9\cdot10^4$ ). At the raised concentration of ions of metals micelles lose stability and coagulate that leads to infringement structural and mineralizing properties of saliva and to formation of stones in a mouth of the person.

**The conclusion.** Thus, it is possible to assume that the microelement structure of dental and salivary stones is defined by a living environment of the patient and feature of exchange processes in its organism. Studying of formation and growth of minerals with accurately regulated conditions of a human body expands representation about genesis of minerals and promotes development of the general theory of mineral formation.

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