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Studying of crystallization with participation synovial of the liquid of the person

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In live organisms of biological liquids are formed various органоминеральные units (a bone and tooth fabric, nephritic, salivary and scales in a human body etc.). It is known that the major property of any liquid is its viscosity. Viscosity renders a great influence for speed of movement of a liquid, resistance which it renders to particles at their moving, thereby defines a direction and intensity of many biochemical reactions, including processes of formation of mineral phases in vivo. Change is viscous – elastic properties influences a number of physical and chemical parametres of biological system, affects speed of the chemical reactions proceeding in bioliquids. Such bioliquid is synovial a liquid (SL, synovial) the person, it is one of the basic components of a joint and substantially defines its morfo-functional condition, carries out the important role in realisation of functions of a joint and maintenance of its communication with other fabrics. The key characteristic of the given bioliquid is its viscosity which provides normal mobility of a joint, reduces a friction and provides functional congruence. Viscosity синовии considerably fluctuates depending on pH, concentration of salts, temperatures. In comparison with other bioliquids viscosity synovial liquids is high enough [*Veresov, etc.,* 2004,], in communication, with what the purpose given work is the establishment of influence of viscosity of modelling solution synovial on processes of a bone mineralization. According to earlier spent thermodynamic calculation [*Lemeshev*, 2010], it is shown that within the limits of the chosen thermodynamic model in an investigated range pH in solutions probably formation of following substances (tab. 1): Ca_{10} (PO_4) $_6$ (IT) $_2$, β-Ca_3 (PO_4) $_2$, $MgHPO_4{\cdot}3H_2O$, $Ca_4H(PO_4)_3{\cdot}2.5H_2O$, $CaHPO_4{\cdot}2H_2O$, $CaCO_3$-kaltsit, $CaCO_3$-aragonite, α-Ca_3 (PO_4) $_2$. Thus for each system of value pH the sedimentation beginnings slightly soluble connections are various.

Table 1 Ranges of values pH, indexes пересыщения, energy of Gibbsa of crystallisation (kDg/mol) formations of firm phases in modelling solutions

No	Connection	Minimum concentration			Average concentration			Average concentration		
		pH	IS	-Δ*G*	pH	IS	-Δ*G*	pH	IS	-Δ*G*
1	$Ca_{10}(PO_4)_6(OH)_2$	7,00-8,00	0,80-1,36	4,17-7,11	7,00-8,00	0,89-1,45	4,66-7,60	7,00-8,00	0,95-1,51	4,93-7,90
2	β-$Ca_3(PO_4)_2$	7,00-8,00	0,21-0,75	1,07-3,90	7,00-8,00	0,32-0,86	1,65-4,48	7,00-8,00	0,39-0,93	2,01-4,84
3	$Ca_4H(PO_4)_3{\cdot}2.5H_2O$	7,10-8,00	0,01-0,34	0,02-1,8	7,00-8,00	0,06-0,45	0,33-2,33	7,00-8,00	0,13-0,51	0,65-2,65
4	$MgHPO_4{\cdot}3H_2O$	7,00-8,00	0,07-0,24	0,36-1,28	7,00-8,00	0,18-0,36	0,95-1,88	7,00-8,00	0,25-0,42	1,3-2,22
5	$CaHPO_4{\cdot}2H_2O$	7,15-8,00	0,01-0,14	0,01-7,10	7,00-8,00	0,10-0,28	0,52-1,44	7,00-8,00	0,19-0,36	0,97-1,90
6	$CaCO_3$ (kaltsit)	7,33-8,00	0,01-0,36	0,02-1,88	7,26-8,00	0,01-0,40	0,006-2,07	7,21-8,00	0,01-0,43	0,02-2,23
7	$CaCO_3$ (aragonite)	7,45-8,00	7,45-0,30	0,02-1,53	7,38-8,00	0,01-0,33	0,01-1,73	7,33-8,00	0,01-0,36	0,02-1,89
8	α-$Ca_3(PO_4)_2$	-	-	-	7,89-8,00	0,01-0,06	0,01-0,30	7,75-8,00	0,01-0,13	0,02-6,60

By comparison of values of their indexes supersaturate and energy Gibbsa of crystallisation for three values pH=7,4; pH=7,6; pH=7,8 it is revealed that the greatest thermodynamic probability of formation in modelling conditions is characteristic for hydroxyapatite. So, sizes of thermodynamic parametres (SI and ΔG) given slightly soluble phases differ from others in 1,6 and more times (fig. 1) that is in a greater degree shown at big value pH=7,8.

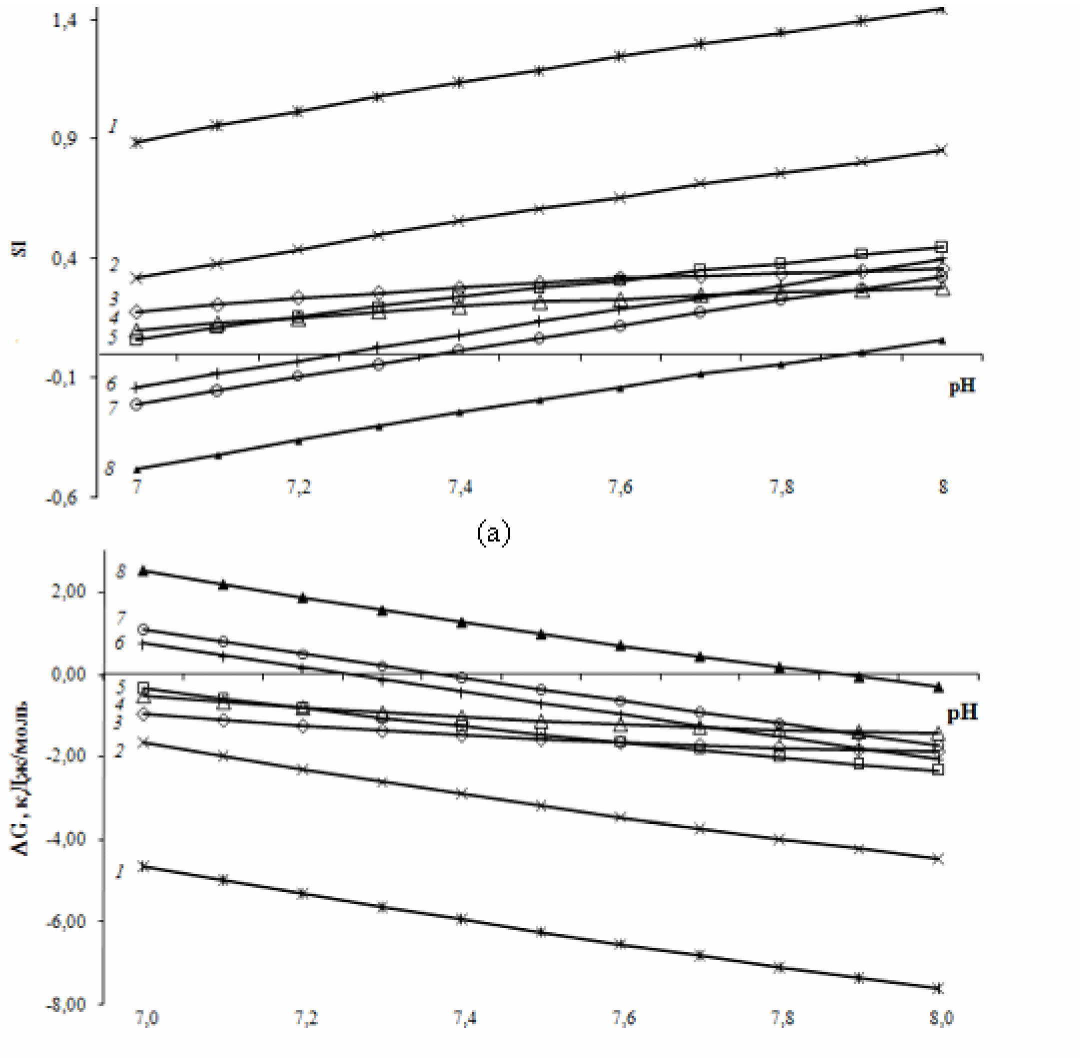

Fig. 1 Dependence of an index supersaturate (a) and energy of Gibbsa of crystallisation (b) from pH a solution for average values of a range of concentration synovial liquids for slightly soluble connections: $Ca_{10}(PO_4)_6(OH)_2$ (1); β-Ca_3 $(PO_4)_2$ (2); $MgHPO_4 \cdot 3H_2O$ (3); $CaHPO_4 \cdot 2H_2O$ (4); $Ca_4H(PO_4)_3 \cdot 2.5\ H_2O$ (5); $CaCO_3$ – kaltsit (6); $CaCO_3$ aragonite (7); α-Ca_3 $(PO_4)_2$ (8)

Besides, in modelling conditions a steady phase is β-Ca_3 $(PO_4)_2$. It is known, what exactly this phosphate acts initial amorphous компонентой of which as a result of recrystallization crystals гидроксилапатита bones are formed. For G (exception are marked, pHΔ7,8 negative values SI and positive >α-Ca_3 $(PO_4)_2$ at pH =7,75 at the maximum concentration of ions in a modelling solution), therefore within the limits of the given model its formation is improbable. Other connections possess intermediate stability (tab. 2), and, hence, their participation in formation of a bone fabric depends on concentration sedimentormation ions, ionic force, acidity of the modelled environment.

So, at pH=7,40±0,05 a modelling solution the thermodynamic probability of formation decreases among $MgHPO_4 \cdot 3H_2O$ > $Ca_4H(PO_4)_3 \cdot 2{,}5\ H_2O$ > $CaHPO_4 \cdot 2H_2O$ > $CaCO_3$-kaltsit> $CaCO_3$-aragonite and is similar for all considered range of concentration. It specifies, that at the given value pH environments can be neglected influence of ionic force. With increase pH solutions the greatest thermodynamic stability is got by phases, in anions which are absent or there are at smaller quantities hydrogen ions. So, at the minimum concentration of ions pH=7,60±0,05 a phase previous sedimentation newberyite is octacalcium phosphate, and brushite – kaltsit: $Ca_4H(PO_4)_3 \cdot 2.5\ H_2O$ > $MgHPO_4 \cdot 3H_2O$ > $CaCO_3$ (кальцит) > $CaHPO_4 \cdot 2H_2O$ > $CaCO_3$ (aragonite).

Table 2 Value of indexes supersaturate almost insoluble connections of modelling solutions at the minimum, average, maximum values of an interval pH and concentration of inorganic ions

№	pH	7,4			7,6			7,8		
	Concentration*	1	2	3	1	2	3	1	2	3
1	$Ca_{10}(PO_4)_6(OH)_2$	1,04	1,14	1,2	1,15	1,25	1,31	1,26	1,35	1,41
2	β-$Ca_3(PO_4)_2$	0,45	0,56	0,63	0,55	0,66	0,73	0,65	0,76	0,83
3	$Ca_4H(PO_4)_3\cdot 2,5H_2O$	0,14	0,24	0,3	0,21	0,31	0,38	0,28	0,38	0,44
4	$MgHPO_4\cdot 3H_2O$	0,17	0,28	0,35	0,2	0,32	0,38	0,23	0,34	0,41
5	$CaHPO_4\cdot 2H_2O$	0,06	0,2	0,29	0,09	0,23	0,32	0,12	0,26	0,35
6	$CaCO_3$ (kaltsit)	0,05	0,08	0,11	0,15	0,19	0,22	0,26	0,29	0,32
7	$CaCO_3$ (aragonite)	-0,02	0,02	0,05	0,09	0,12	0,16	0,19	0,23	0,26
8	α-$Ca_3(PO_4)_2$	-0,35	-0,24	-0,17	-0,25	-0,14	-0,07	-0,15	-0,04	0,03

Note* 1 – minimum; 2 averages; 3 - the maximum values of concentration.

At pH=7,80±0,05 the given law is traced more accurately. With increase in concentration of ions in both cases, forces of interionic pushing away that leads to reduction of factors activitts and to increase of probability of formation of the most soluble and thermodynamic an unstable phase increase. So, after sedimentation $Ca_4H(PO_4)_3\cdot 2.5H_2O$ consecutive formation of the connections which solubility decreases among is marked: $MgHPO_4\cdot 3H_2O$ > $Ca_4H(PO_4)_3\cdot 2,5H_2O$ > $CaHPO_4\cdot 2H_2O$ > $CaCO_3$ (kaltsit)> $CaCO_3$ (aragonite). Thus, the received results specify that optimum conditions of reception hydroxyapatite in modelling solutions synovial liquids is pH=7,8 (average, maximum concentration) where the basic dashy acts as a phase β-Ca3 (PO4) 2 and sedimentation of other almost insoluble connections thermodynamic is improbable. Sedimentormation synthesis reaction it is possible to present the basic as follows:

$10\ M_1X_2 + 6\ M_2HPO_4 + MOH \rightarrow Ca_{10}(PO_4)_6(OH)_2\downarrow + 20\ MX + 6\ H_2O$, where $M = Na^+, K^+$; $M_1 = Ca^{2+}, Mg^{2+}$; $X = Cl^-$.

For statement of modelling experiment in vitro, was the solution with the close mineral maintenance of the basic components to articulate synovial a liquid of the healthy adult average person (tab. 3) is taken. The structure of a modelling water solution was set on the basis of the minimum, average and maximum concentration of ions, the account of its ionic force, pH (7,0–8,0), temperature and viscosity which lies in an interval 26,3±3,13 mm2/with was spent. Thus in experiment viscosity equal 5,10,15,25,30 was created mm^2/with. Modelling synovial liquids created viscosity by means of a gelatin solution in water.

Table 3 Mineral structure synovial liquids of the person [*Matveeva, etc.*, 1999], mmol/l

Connection	Minimum concentration	Average concentration	Average concentration
Calcium	2,25	2,80	2,53
Sodium	130,00	150,00	140,00
Magnesium	0,70	1,50	1,10
Kaly	3,80	5,40	4,60
Chlorides	95,00	111,00	103,00
Carbonates	24,00	30,00	27,00
Phosphates	2,42	6,34	4,38
Sulfates	9,90	12,90	11,40

After necessary viscosity in a flask has been created added calcium and magnesium ions, lead up pH a solution to 7.4, tightly closed and left for 1 month for crystallisation of a firm phase from a solution. On the expiration it is specified term, a deposit strain and analyzed with the help X-ray photography the analysis (fig. 2). On the basis of data РФА in all range of the created viscosity the basic mineral phase is magnesium containing β-$Ca_3(PO_4)_2$ (whitlockite), and as it is known this mineral is initial amorphous multiplier from which as a result of recrystallization is formed crystals hydroxyapatite. On Ik-spectra of investigated tests (fig. 3) there are the strips of absorption corresponding to valency fluctuations of molecular water νH_2O - 3440 – 3400 sm^{-1} and to deformation fluctuations N-O-N in H_2O - 1680-1610 sm^{-1}; to asymmetric valency fluctuations $\upsilon 3$ P–O in PO_4^{3-} - 1090-1030 sm^{-1} and to deformation fluctuations υ_4 O-P-O the given group - 604 sm^{-1} and 546 sm^{-1}. Background signals in the field of frequencies can specify of 1560-1410 sm^{-1}, and also 900-600 sm^{-1} in impurity presence carbonate substitute hydroxyapatite. In our opinion, a limiting stage of sedimentation whitlockite is mass transfer particles in the viscous environment.

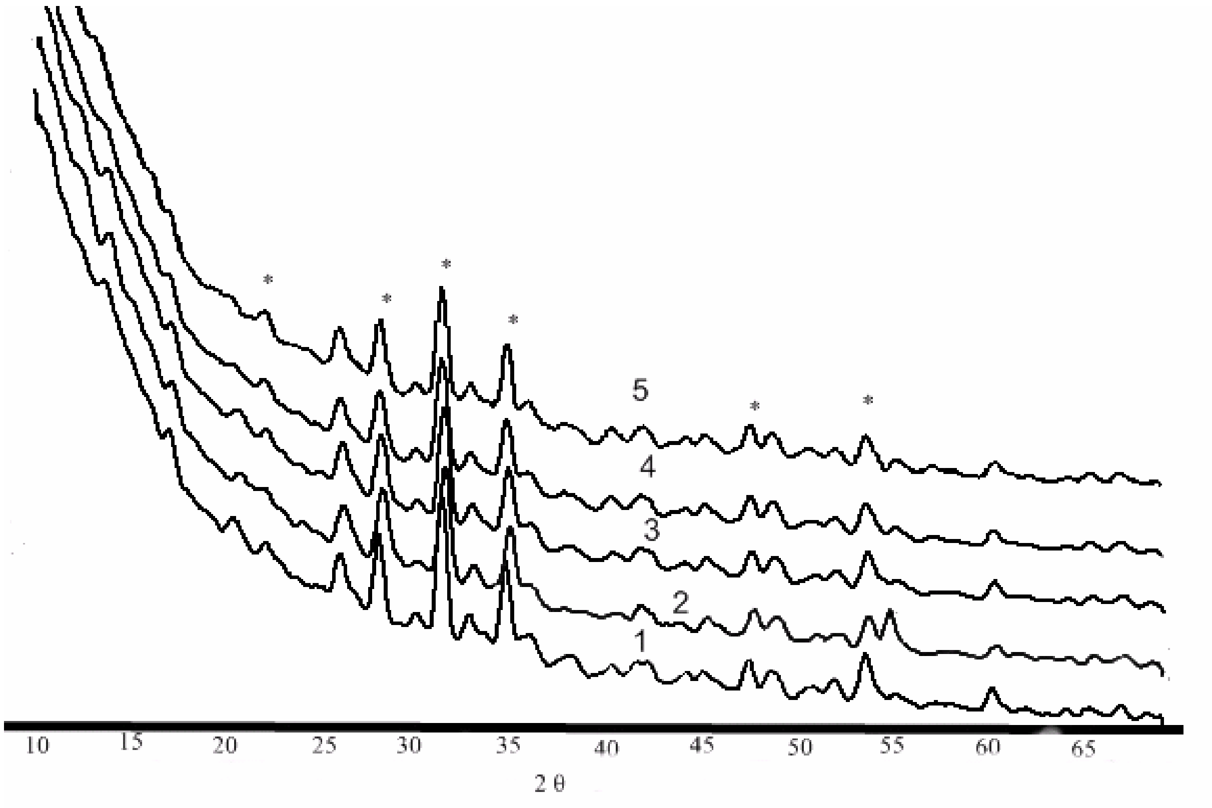

Fig. 2 Difraktograms the samples synthesised at viscosity 5 mm^2/with (1), 10 mm^2/with (2), 15 mm^2/with (3), 25 mm^2/with (4), 30 mm^2/with (5) *whitlockite.

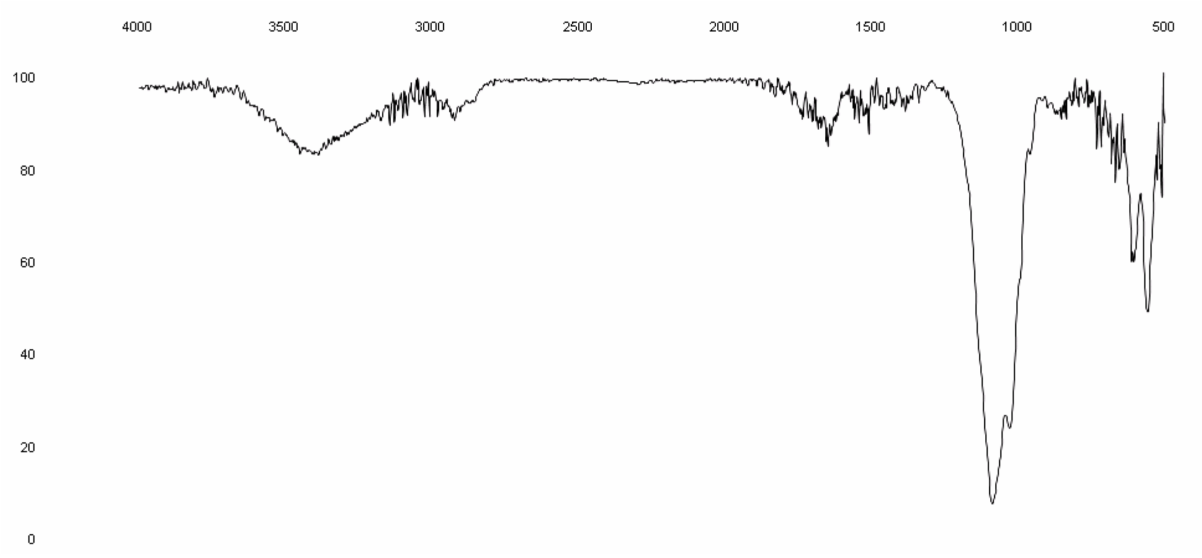

Fig. 3 IK - a spectrum of the sample synthesised at viscosity= 15 mm^2/with

Therefore in the absence of bone diseases of the further crystallisation hydroxyapatite with participation synovial liquids it is not observed and синовия together with the blood brought by blood capillaries from outside of a bone provide a food and functioning of an articulate cartilage, and, hence, mobility of the joint. Obviously, on character of a current of processes mineralformation besides viscosity of environment synovial liquids, influence value pH and change of the maintenance of some organic substances. This fact confirms earlier spent thermodynamic and experimental modelling without viscosity in which the basic formed mineral is hydroxyapatite, with impurity whitlockite, brushite, octacalcium phosphate. On the basis of the spent thermodynamic calculation the given connection is thermodynamic the steadiest.

Thus, it is possible to notice that in synovial liquids can be formed two basic minerals one of which is thermodynamic a steady product – hydroxyapatite, and another kinetic teady - magnesium containing β-Ca_3 $(PO_4)_2$ (whitlockite). Probably, it is formed at early stages diseases of oporno-impellent system of the person, then in hydroxyapatite which formation leads to infringement of many characteristics in a joint, first of all pH [*Larionov*, 2003] eventually passes, and it in the the turn influences viscosity synovial liquids, it decreases. It promotes abrasion hyaline a cartilage and to contact of a bone fabric of the person with synovial a liquid that leads to disease progressing.

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