# Hydrothermal processes, fluid system, metasomatism

<sup>#</sup>Dadze T.P., Kashirtseva G.A., Akhmedzhanova G.M. Gold solubility in sulfide-bearing solutions depending on temperature and pressure (from experimental data).

Experimental study on gold solubility in sulfide-bearing solutions has been carried out. The data on gold solubility have been obtained at T=200, 250, 300,  $350^{\circ}$ C and a pressure along the saturation line of water vapor of 300 and 100 bar at different concentrations of sulfide sulfur in a solution.

The experiments were carried out in titanium autoclaves 20cm<sup>3</sup> in volume made of BT-8 alloy preliminary passivated by 20% nitric acid at 400°C for a day. The autoclaves were placed into a gradient-free zone of the resistance furnaces, the temperature being held within an accuracy of  $\pm 2^{\circ}$ C. Pressure in autoclaves was preset by the filling coefficient on P-V-T data for water. A gold plate was hung up on the obturator in the upper part of the autoclave. Thioacetamide (CH<sub>3</sub>CSNH<sub>2</sub>), which hydrolyzes in water solution to yield H<sub>2</sub>S in stoichiometric amounts, was used as a source of sulfide sulfur [1]. Run durations were 45 days at 200°C, 30 days at 250°C, 25 days at 300°C, 18 days at 350°C, which is according to literature data [2] quite enough to reach the equilibrium in the system. The autoclaves were quenched by cold running water for 5-7 min. Gold content in a solution has been determined by an atomic-absorbtion method in acetylene-air flame using an AAS-N apparatus at the wave length of 242.8mm.



**1.** Dependence of gold solubility on sulfide sulfur concentration in the solution at **300** kbar. 1- 200°C, 2-250°C, 3-300°C, 4- 350°C.



Fig.2. Temperature dependence of gold solubility at a pressure of 300 bar. The contents of sulfide sulfur in the solutions are: 1-0.5m, 2-0.3m, 3-0.05m.



Fig.3. Dependence of gold solubility on sulfide sulfur concentration in the solution at 300oC and pressures of: 1- $P_{sat.}$  2- 300bar, 3- 1000bar.

The experimental results obtained are given in tables 1-2 and figures 1-3. Presented in table 1 and fig.1 are the data on gold solubility depending on sulfide sulfur concentration in a solution in the temperature range 200-350°C. Fig. 2 presents the temperature dependence of gold solubility at sulfide sulfur concentrations 0.05, 0.3, and 0.5 m. As it is shown in fig. 1-2, gold solubility increases with decreasing temperature and increasing sulfide sulfur concentration in the solution. Presented in table 2 and fig. 3 are the data on gold solubility depending on sulfide sulfur concentration in the solution at T=300°C at various pressures (P<sub>sat.</sub> 300, and 1000bar). The obtained data show that gold solubility at low concentrations of sulfide sulfur decreases with pressure, which agrees with

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literature data [3]. In our experiment at sulfide sulfur concentration in the solution higher than 0.3m, gold content at 1000bar is higher than at 300bar, and at sulfide sulfur concentration in the solution up to 0.5m gold content approaches that at  $P_{sat}$ . This is likely to be related to changing the forms of existence of gold complexes in the solution.

#### References:

N	N of run	charge CH <sub>3</sub> CSNH <sub>2</sub> M	lgm <sub>H2S</sub>	lgm <sub>HS</sub> -	$m_{Au} \bullet 10^4$	lgm <sub>Au</sub>	pH calculated		
	iii								
1	Au-243	0.05	-1.414	-1.945	0.303	-4.520	5.986		
2	Au-244	0.1	-1.120	-1.624	0.865	-4.060	5.987		
3	Au-245	0.2	-0.834	-1.289	2.150	-3.660	6.000		
4	Au-246	0.3	-0.670	-1.088	4.510	-3.345	6.010		
5	Au-247	0.4	-0.554	-0.934	7.210	-3.140	6.019		
6	Au-248	0.5	-0.468	-0.832	10.700	-2.970	6.025		
	<u>i</u>			250°C	I				
7	Au-231	0.05	-1.337	-2.389	0.15	-4.82	5.789		
8	Au-232	0.1	-1.033	-2.116	0.22	-4.66	5.741		
9	Au-233	0.2	-0.736	-1.805	1.01	-3.99	5.727		
10	Au-234	0.3	-0.560	-1.610	1.34	-3.63	5.728		
11	Au-235	0.4	-0.438	-1.466	1.18	-3.74	5.732		
12	Au-236	0.5	-0.343	-1.351	1.99	-3.23	5.737		
				300°C*					
13		0.05	-1.311	-2.885	0.069	-5.16	5.740		
14		0.1	-1.008	-2.631	0.210	-4.68	5.679		
15		0.2	-0.705	-2.377	0.830	-4.08	5.614		
16		0.3	-0.527	-2.228	0.794	-4.10	5.573		
17		0.4	-0.402	-2.104	1.860	-3.73	5.562		
18		0.5	-0.307	-2.004	2.200	-3.66	5.556		
	i								
19	Au-255	0.05	-1.302	-3.552	0.023	-5.64	5.822		
20	Au-256	0.1	-1.000	-3.306	0.028	-5.55	5.758		
21	Au-258	0.3	-0.520	-2.917	0.222	-4.65	5.649		
22	Au-259	0.4	-0.394	-2.815	0.305	-4.52	5.619		
23	Au-260	0.5	-0.296	-2.735	0.662	-4.18	5.595		

Table 1. Experimental data on Au solubility at P=300bar.

<sup>#</sup> Averaged values of gold concentrations in the solution are given.

N	N of run	Charge CH <sub>3</sub> CSNH <sub>2</sub> M	Lgm <sub>H2S</sub>	Lgm <sub>HS-</sub>	M <sub>Au</sub> *10 4	lgm <sub>Au</sub>	PH calc.
			P of satu	rated water vapor	ā	k	
1	Au-127	0.107	-0.975	-2.808	0.762	-4.118	5.674
2	Au-128	0.214	-0.672	-2.558	2.034	-3.69	5.605
3	Au-129	0.321	-0.496	-2.389	3.405	-3.53	5.587
4	Au-130	0.428	-0.371	-2.259	5.117	-3.29	5.582
5	Au-131	0.536	-0.274	-2.153	9.330	-3.03	5.581
	<u></u>		<b>i</b>	300 bar*		L	
6		0.05	-1.311	-2.885	0.069	-5.160	5.740
7		0.1	-1.008	-2.631	0.210	-4.680	5.679
8		0.2	-0.705	-2.377	0.830	-4.080	5.614
9		0.3	-0.527	-2.228	0.794	-4.100	5.573
10		0.4	-0.402	-2.104	1.860	-3.730	5.562
11	-	0.5	-0.307	-2.004	2.200	-3.660	5.556
			i	1000 bar	<b>i</b>	i.	i
12	Au-137	0.089	-1.066	-2.465	0.076	-5.12	5.537
13	Au-138	0.179	-0.760	-2.204	0.538	-4.27	5.475
14	Au-139	0.268	-0.586	-2.026	1.148	-3.94	5.466
15	Au-140	0.357	-0.462	-1.895	1.65	-3.78	5.562
16	Au-141	0.446	-0.366	-1.789	3.49	-3.46	5.462

#### Table 2. Experimental data on Au solubility at T= 300°C.

<sup>#</sup>The averaged values of gold concentrations in the solution are given.

# <sup>#</sup>Khodorevskaya L.I. Magmatic replacement of amphibolite at high parameters. Experimental study.

#### key words [granite, amphobolite, migmatite, trondhjemite]

Granite formation by D.S. Korzhinskii can occur at interaction of trasmagmatic solutions with a high content of silica and alkalies with the enclosing rocks. As the simplest model of granitization of metamorphic rocks we studied amphibolite interaction with the preliminarily synthesized glass of gaplogranite composition at  $T= 800-950^{\circ}C$  and P=7 kbar in the presence of aqueous fluid.

The runs were conducted in a high gas pressure vessel with the internal heating by quenching technique. The starting materials were fine-ground / $\mu$ m/ amphibolite characterizing rocks of the basic composition of the Tavajarvinskii complex of Nothern Karelia and preliminarily synthesized gaplogranite. Hornblende, plagioclase and biotite , as well as sphen, magnetite mainly enter amphibolite composition. Amphibolite charge of 200-300 mg was ground and tightly packed into the capsule, then 0.04-0.05 ml H<sub>2</sub>O was added and granite charge of 100-200 mg, which was also densely packed there. The capsule was welded and kept in the regime of the runs for 3-5 days. After the run the sample was studied with the help of the microprobe "Camscan" in the laboratory of microanalysis of the petrology department of Moscow University and on the "Camebax", IEM. The determination of the bulk composition was made from the area of 0.1-0.25 mm<sup>2</sup> in each zone.

After the runs the samples 1D ( $800^{\circ}$ C) and 9D ( $950^{\circ}$ C) represented a dense partially melted rock , dark - grey , not fully coloured. The part of the sample where amphibolite was placed was dark- grey , but where the initial synthetic granite was put, there was formed a colourless, transparent glass, slightly coloured into grey in the vicinity of the contact.

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800°C



950°C



In sample 1D the basic minerals in the contact zone were represented by amphibole and biotite. In the third zone together with amphibole and biotite plagioclase appears whose alkalinity increases from  $Pl_{35}$  to  $Pl_{48}$  while removing from the contact. In sample 9D in zone 1 (Fig.1a) after homogeneous granite glass a layer of fine crystals of orthopyroxene with the iron content of f=27% appears. It is a narrow zone of 50-70 µm (zone 2). Towards amphibolite the zone practically disappears, being

replaced by the narrow band of 50-70  $\mu$ m of the quenching glass. Then ( in zone 4) among the glass large up to 100  $\mu$ m zonal crystals of amphibole and biotite appear. A bit further across the section crystals of clinopyroxenes can be seen. Approximately in 500  $\mu$ m from the contact zonal crystals of plagioclases with Ca enrichement of the edge zones of crystals from Pl <sub>31</sub> to Pl <sub>54</sub> occur.

In a general case the run products show two processes: partial melting of amphibolite and diffusional interaction of the melted granite with amphibolite in the contact zone. In that part of the samples where amphibolite was placed especially at 800°C practically no marked gain or loss of the components can be observed. Here a partial melting of the rock can be seen: a melt of the acidic composition while preserving amphibole and biotite is formed, amphibole is enriched in silica, plagioclase is preserved, at T=950 °C clinopyroxene is formed. In the contact zones with the partial melting amphibolite interaction with granite melt with the gain - loss of the components takes place. As a result of this, plagioclase disappears, it is possible, that newly-formed biotite appears. At T=950°C orthopyroxene is formed at the contact. The initial amphiboles refer to edenite hornblende. At a partial melting of amfibolite at 800 °C hornblende preserves, at T=950°C it transforms into ferropargaside hornblende. Due to the diffusion of the components, caused by the interaction of amphibolite with the granite melt in contract zones amphibole transforms into edenite at 800°C and ferro-pargasite at 950°C. In chemical composition biotite in the samples does not differ essentially. Clinopyrocxenes at the contact contain less Fe and somewhat more Al than the pyroxenes of the sample edge at a practically identical content of Mg.

A variable number of the quenching glass (from to 100 - 24 wt%) can be seen in all zones of one and the other sample. In glass composition of the initial granite the presence of ions of Ca , Mg , Fe in the very edge parts of the sample is fixed. Here a drop of alcali concentration can be seen. While recalculating chemical compositions of the quenching glasses in that or another sample for normative compositions it was found that at  $800^{\circ}$ C quenching glasses in contact zone represent trondhjemite, at  $950^{\circ}$ C - granites, at partial melting of the samples granodiorites are formed. Apparently, recrystallization of the quenching glass is to take place in accordance with the normative compositions. In such a case the experimental column formed at  $800^{\circ}$ C C will look as below :

recryst. melt min. in the run	Q+Ort+ +Pl <sub>10</sub>	Q+Ort+Pl <sub>17-35</sub> +Am+ Bt	$\begin{array}{l} Q+Ort+Pl_{17-35}+\\ +Am+Bt \end{array}$	$\begin{array}{c} Q + Ort + Pl_{35-50} \\ + Am + Bt \end{array}$	
rock	granite	migmatite of the trondhjemite		partially amphibolite	melted

The experimental column is comparable with the natural columns formed at feldspatization and the initial stage of melting of amphibolites : zones 1 and 2 can characterize "occurrence of drops of leucocrate composition in the rear zones of feldspatized rocks". The next two columns 3-4 represent migmatites close to trondhjemites in composition. Zone 5 represents enclosing rocks, in our case - amphibolite subjected to partial melting.

At recrystalization of quenching glasses obtained at 930°C the experimental column looks as follows.						
recryst.	melt	Q+Ort+	Q+Ort+	Q+Ort+	Q+Ort+Pl <sub>10-20</sub> +	Q+Ort+Pl <sub>25</sub> +
minerals	in the	+Pl <sub>до 10</sub>	Pl <sub>10</sub> +Opx	$+Pl_{10-20}$	+ Am+ Bt	+Am + Bt
run						
rock		charnokite		leucocrate	migmatite of	partially melted
				zone	granite composition	amphibolite

At recrystallization of quenching glasses obtained at 950°C the experimental column looks as follows :

The similar zoning is close to that pointed out at granitoid formation of charnokite series.

A comparison of the results of the runs with the natural objects is sure to be of a conventional character, since natural processes under lab conditions can not be reproduced. Together with that, the results of the runs show that at a magmatic replacement of metamorphic rocks as well as at metasomatism, zoning of a magmatic replacement is formed. Depending on temperaure mineral composition of such zoning can be represented either by amphibole assemblage with biotite, typical for granitized amphibolites, or by the formation of the assemblages with orthopyroxene, typical for charnokite complexes.

# <sup>#</sup>Kotelnikov A.R., Gurbanov A.A. Sulphatebearing sodalite stability under hydrothermal conditions.

<u>Introduction</u>. As it was shown in work [1], NaCl- bearing sodalite stability (relative to nepheline) at different temperature is dependent on NaCl concentration in a water solution.

The position of monovariant reaction:  $6 \text{ NaAlSiO}_4 + 2\text{NaCl} = \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$  (1) was determined in coordinates: temperature - NaCl- concentration.

The equilibrum concentration of NaCl in a solution (for reaction 1) at various temperatures is presented in Table 1. Sulfur plays an important role in mineral forming fluid. Therefore, the aims of this work were: (1) to study the stability of  $SO_4$ - bearing sodalite (nosean) depending on temperature and concentration of  $Na_2SO_4$  in a solution (at  $D_{fl} = 2kbar$ ); (2) to study the anion isomorphic replacement in the join NaCl-sodalite - nosean solid solutions.

*Experimental study.* 1. The runs on nosean stability were carried out by the capsule method in cold-seal hydrothermal vessels with external heating (accuracy of temperature control was  $\pm 5^{\circ}$ C; pressure  $\pm 50$ bar). The run duration was 4-21 days. The method of "the large ampoule" was used to control the Na<sub>2</sub>SO<sub>4</sub> - concentration in fluid: the ratio sample:fluid was 1:20.

<sup>#</sup> The work has been supported by the RFBR grant 00-05-64680.

Table 2. Unit cell parameters of sodalites solid solutions (NaCl- sodalite - nosean).

The analysis of the run products was carried out by the
immersion method and X-ray method. It was shown, that SO <sub>4</sub> -
sodalite is stable relative nepheline at Na <sub>2</sub> SO <sub>4</sub> concentration
(≥2 wt.% - 600°C; ≥1wt.% - 700°C; and ≥5wt.% - 800°C). Data
of nosean stability are listed in Table 1.

**Table 1.** Stability of NaCl- and Na<sub>2</sub>SO<sub>4</sub>- bearing sodalites depending on the salt concentration of the hydrothermal fluid at different temperatures ( $P_{\rm fl}$  = 2-3 kbar).

NaCl-	- sodalite	$Na_2SO_4$ - sodalite		
t, °C	Equilibrium concentration of NaCl (wt.%)	t, °C	Equilibrium concentration Na <sub>2</sub> SO <sub>4</sub> (wt.%)	of
600	17.5	600	2	
700	25	700	1	
800	37.5	800	5	

The refinement of the unit cell parameters of the  $Na_2SO_4$ bearing sodalites synthesized at various temperatures was caried out. It was shown, that they do not differ (within the limits of accuracy of calculation).

2. The runs on the synthesis of (Cl, SO<sub>4</sub>)- sodalites solid solutions were carried out under hydrothermal conditions at temperature 700°C and a fluid pressure of 3 kbar. Starting material for the sodalite solid solution synthesis was gel of NaAlSiO<sub>4</sub> composition. The composition of the synthesized sodalite solid solutions was set by a ratio (NaCl/Na<sub>2</sub>SO<sub>4</sub>) in an initial solution. Run duration was 15 days. The composition of sodalite solid solutions was determined by the microprobe method (accuracy not less than 2 mol.%); the X-ray study allowed to refine unit cell parameters of the synthesized sodalite solid solutions.

The data on microprobe and X-ray study of sodalite solid solutions have shown, that in the investigated join of solid solutions (NaCl- sodalite - nosean) there is an immiscibility gap at the composition  $X_s^{Sod} = 0.024(4) \div 0.71(7)$ . The unit cell parameters of synthesized solid solutions are listed in Table 2.

Run no	$X_S^{Sod}(I)^{1)}$	$X_{S}^{Sod}(II)$	a,[A] (I)	a,[A] (II)	$V,[A]^{3}(I)$	$V,[A]^{3}(II)$
4953	$0.024(9)^{2}$	0.67(6)	8.880(1)	9.048(1)	700.1(2)	740.7(1)
4954	0.022(6)	0.75(7)	8.879(2)	9.060(2)	700.0(2)	743.6(2)
4955	-	0.71(3)	-	9.047(1)	-	740.3(2)
4956	-	0.74(4)	-	9.053(1)	-	742.1(2)
4957	-	0.82(1)	-	9.060(2)	-	743.7(1)
4958	-	0.90(1)	-	9.065(1)	-	744.8(2)
4959	-	0.90(5)	-	9.068(2)	-	745.7(3)
4960	-	1.00	-	9.070(1)	-	746.2(1)

1) phases of sodalite solid solution coexisting in run products: (I) - chlorine sodalite, (II) sulphate- sodalite.

2) The errors of calculations are given in brackets and concern to last decimal place.

Conclusions.

1. The field of nosean stability is determined depending on temperature and  $Na_2SO_4$  concentration in hydrothermal solution.

2. The solid solutions chlorine sodalite - nosean are investigated. The existence of an extensive area of immiscibility of solid solutions is shown. The unit cell parameters of synthesized sodalite solid solutions are specified.

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<sup>#</sup>Redkin A.F. Experimental and thermodynamic evaluation of the congruent and incongruent dissolution of ferberite in the chloride solutions at

<sup>&</sup>lt;sup>#</sup> The research was supported by the Russian Foundation of Basic Research, grant № 99-05-64106.

# 500°C, 1 kbar under Kfsp-Ms-Qtz-Ni-NiO buffer assemblage.

According to [1, 2, 3, 4], ferberite solubility depends both on *m*KCl and *m*HCl. Thus, we carried out the experimental investigations in the Kfsp-Ms-Qtz buffered system to support a constant activity ratio of *m*KCl/*m*HCl. Taking in account that Fe and W are the elements of variable valence we used Ni-NiO buffer to keep a constant value of  $fO_2$  in the system. The runs duration was 14-28 days.

The experiments were performed in Pt capsules in 5,15, 25 and 40 wt. % KCl in 0.1-0.01 mHCl. The pure synthetic ferberite prepared by hydrothermal procedure from WO<sub>3</sub> and FeO was used in the runs. The solid (microcline+muscovite+quartz+ferberite) solution (KCl+(0.01-0.1))mHCl = 1:8. The results of quenched solution analyses were taken into account to make a decision about a mechanism of the dissolution and the concentrations of dissolved compounds. It has been found that the concentrations of W and Fe after runs were different (mKCl/mW/mFe: 0.706/0.0058/0.011, 0.706/0.011/0.0022, 2.367/0.016/0.053, 2.367/0.020/0.033, 4.471/0.021/0.10, 4.471/0.042/0.076, 8.942/0.021/0.15, 8.942/0.055/0.090), i.e. the incongruent dissolution of ferberite took place in the runs.

To estimate ferberite solubility and the degree of polymerization of aqueous tungsten species (it is known only monomer species of Fe(II)) in brines, we used  $S_{\text{FeWO}_4} = \alpha + \sqrt[1]{mW_T^{\alpha} \cdot mFe_T}$  equation in the analysis of the results of the similar runs. This equation involves the total molal concentrations of dissolved compounds  $mW_T$  and  $mFe_T$  with molar fraction  $\alpha_i$  of the species of different nucleation *i* ( $\alpha$ 

 $= \sum_{i} \frac{\alpha_{i}}{i} = \sum_{i} \frac{mW_{i}}{i \cdot mW_{T}}$ ). This equation gives a precise solution

in the case when the ratio of the monomers and polynuclear species changes inessentially. As a result, it was found that the monomer acidic species were predominant in 5 and 15 wt. % KCl solution whereas dimmer species producing neutralization of the quenched solutions were formed in 25 and 40 wt. % KCl.

The experimental results were used in the analysis of the tungsten complexing in HCl-KCl solution. For the purpose of solving the reverse thermodynamic task we used a method of numeric modeling by Gibbs [5] program. Except 4 known species of W(VI):  $H_2WO_4^{\circ}$ ,  $HWO_4^{-}$ ,  $KHWO_4^{\circ}$ , 10 species of W(V):  $WO_2^{+}$ ,  $H_3WO_4^{\circ}$ ,  $WO_2Cl^{\circ}$ ,  $WOCl_3^{\circ}$ ,  $W_2O_6^{-2}$ ,  $HW_2O_6^{-2}$ ,  $KW_2O_6^{-2}$ ,  $HW_2O_6^{\circ}$ ,  $KHW_2O_6^{\circ}$ ,  $K_2W_2O_6^{\circ}$  were considered. The thermodynamic analysis showed that the best coincidence between calculation and experiments at 500°C and 1 kbar can

be reached when the species  $H_3WO_4^{\circ}$  and  $K_2W_2O_6^{\circ}$  were taken in consideration. The dominant iron species was FeCl<sub>2</sub><sup>o</sup> according to the accepted thermodynamic properties. The results of ferberite solubility calculations based on experimental data and by the Gibbs program are shown in fig. 1. As we can see in fig. 1 the good fitting takes place between experimental and calculated estimations. The maximum divergence of solubility values does not exceed 20 %.

The solid phase investigation showed that among initial phases the potassium tungsten bronzes (PTB)  $K_xWO_3$  were observed in the run products. Using experimental data and thermodynamic properties of WO<sub>3</sub> we calculated the free energies of the PTB row from 0 to 0.5 mol of potassium.

Figs.2a,b show the effect of PTB of different composition and magnetite (Mag) on equilibrium  $mW_T$  and  $mFe_T$  in ferberite-bearing systems. One can see from fig. 2a that concentration of W becomes stable and slightly depends on *m*KCl when ferberite together with PTB are subjected to dissolution. In such systems the concentration of W depends on the composition of PTB and varies from 0.06-0.05 mole/kg H<sub>2</sub>O for K<sub>0.2</sub>WO<sub>3</sub> to 5·10<sup>-4</sup> for K<sub>0.5</sub>WO<sub>3</sub>. In our runs *m*W<sub>T</sub> was within the range from 0.005 to 0.05 mole/kg H<sub>2</sub>O that corresponds to x =0.21-0.31 in PTB. The iron concentration, on the contrary, is strongly dependent on *m*KCl (fig. 2b).



**Fig. 1**. Dependence of ferberite solubility on total *m*KCl in Kfsp-Ms-Qtz buffered system (solid line) at 500°C, 1 kb,  $fO_2=fO_2$ (Ni-NiO). 1-from authors experimental data, 2 - calculated for the conditions of the runs.



Fig. 2. The effect of mKCl on ferberite solubility and values of log mWT (fig. a) log mFeT (fig. b) of and ferberite-bearing assemblages (with PTB. KxWO3, of different composition (x=0.2-0.5) and with magnetite, Mag) in Kfsp-Ms-Qtz buffered system at 500°C, 1 kb and fO2=fO2(Ni-NiO).

The conducted investigation shows that the dominant aqueous species for transportation of tungsten in reduced conditions on the ferberite (wolframite) ore deposits could be the compounds of W(V) such as  $H_3WO_4^{\circ}$ ,  $K_2W_2O_6^{\circ}$ , and their concentrations in the hydrothermal solutions depending on the total iron in them.

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# <sup>#</sup>Orlov R.Yu. Water as an internal standard in the Raman study of hydrothermal systems

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The experimental study of hydrothermal systems by Raman spectroscopy is now broadly used. The highest temperatures and pressures are limited only by a firmness of the windows of the spectroscopic cell. In most cases the results of these study have a qualitative character.

But it turns to a quantitative tool if using the Raman scattering of water as an internal standard. In this case Raman cross section of the studied complex is assumed to be independent on temperature, and its concentration - to be proportional to Raman intensity.

Contrariwise, the integral intensity of the band of water stretch vibrations  $(3000-3700 \text{ cm}^{-1})$  decreases with temperature faster then the density of water as it depends also on the dielectric constant of the media  $n(T)^2$  and a Lorenz factor  $L(T) = [(n^2+2)/3]^4$ . The intensity also depends on the number of hydrogen bonds in the structure of water.

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The molal concentration of the i-th species in the solution at high temperature can be determined during the next procedure. At first the scaling constant  $A_i = (I^o_{\rm H2O} / I^o_i) \cdot m_i$ , where I is the intensity, mi is the concentration of i-th species in mol/kg\_{\rm H2O}, must be determined at room temperature. The normalized values of the density and the intensity of water as a function of temperature  $K(T) = (I^T/I^o) \cdot (\rho^o / \rho^T)$  are also required. The molal concentration of the i-th species is now expressed as:

$$\mathbf{m}_{i}^{\mathrm{T}} = \mathbf{A}_{i} \cdot (\mathbf{I}_{i}^{\mathrm{T}} / \mathbf{I}_{\mathrm{H2O}}^{\mathrm{T}}) \cdot \mathbf{K}(\mathrm{T})$$

The function K(T) is independent on the setup parameters, whereas the constant  $A_i$  depends on the scattering geometry, laser wavelength, spectral properties of the setup and thus is not a universal constant.

If the molal concentration of some volatile matter is being determined in a vapor phase then the calibration on the Raman line of water vapor should be used. The intensity of this line is proportional to vapor density up to  $360^{\circ}$ C, hence K(T) = 1. The constant A<sub>i</sub> can be determined using the Raman scattering cross section values published in [1] or by the calibration of the setup against the gas mixture including the water vapor of the known composition. For this purpose a solution with the known content of the studied component is placed into the autoclave and then is heated up to complete evaporation of the liquid phase. The scaling constant is defined from the relation of the Raman lines areas already in gas phase.

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# Khomyakov A.P. Superfast hydrolysis of natural Na,Ti,Zr silicates.

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Experimental evidence is presented for the ability of some hypersodic Ti,Zr silicates, which are indicators of maximally alkaline conditions of mineral formation in magmatic processes, to be spontaneously replaced by their low-alkaline hydrated analogues under atmospheric conditions. A special genetic group of transformation mineral species is distinguished; these minerals can only form by pseudomorphic alteration of hyperalkaline protophases, inheriting from the latter the main compositional and structural features. The unambiguous correspondence between the minerals in the evolutionary sequences of this type opens up great opportunities in solving various problems, in particular in reconstructing the primary mineral composition of rocks and ores from secondary products.

# Tikhomirova V.I., Desyatova T.A., Akhmedzhanova G.M. Palladium sorbtion on carbons modified by thiocarbamide from the solutions of nitric acid.

## key words [utilization high level wastes]

1. Utilization of high level wastes of AES is a burning problem. It is known that after dissolving tvells in 6N nitric acid the whole mass of elements is stored for a long time before a final utilization. The possibility of separating noble metals from the mass of radionuclides and construction materials has been studied on an example of palladium whose concentration in the wastes of radionuclides reaches up to 1.3% to the dry residue.

2. For this task to be completed the possibility of the selective sorbtion of Pd on activated carbon impregnated by thiocarbamide has been considered. Carbon is known by its sorbtion ability and possibility to accumulate noble metals (NM) both in natural conditions [1] and in applied processes, in particular for concentrating noble metals before the analysis [2]. The sorbtion is more selective if it is followed by the formation of surface complexes [3-4]. For Pd such active coordinated groups are those involving nitrogen and sulfur. For carbon such a modifier could be thiocarbamide  $(NH_2)_2=C=S$ , which could sorb itself on carbon. Moreover, the method of grouped concentration of noble metals from strong sulfate solutions by thiocarbamide is known and successfully used for the analysis of industrial and natural objects [2,5].

3. Used in the work was activated carbon of AP-3 grade of a certain fraction (from 0.2 to 0.4 mm or 1.0-1.6 mm) which was washed in saturated NaOH solution or alcohol solution of thiocarbamide. In case carbon was being saturated first with alkali and then thiocarbamide the "complex" modification took place. Then carbon was washed up to the neutral reaction in water, dried and was used for the static and dynamic sorbtion of palladium. Palladium solutions were prepared using nitric acid of various concentrations (from 0.06 to 6.0 N).

The solutions containing 1000, 100, and 20 mkg/ml Pd were prepared for sorbtion, sorbent weight being from 100 mg up to 1 g. After filtration of carbon the solutions were analyzed for Pd presence by the atomic-absorbtion method with flameless atomization using an AA-670G apparatus produced by Shimadzu company. Pd sensitivity of the method was 0.01mkg/ml in the 2N HCl solution where small (microgram) Pd contents are more stable.

Table 1 presents the data on the static Pd sorbtion (starting content was 1000mkg in 50ml) on three types of carbon (fractions 1-1.6 mm): A- impregnated by NaOH, B- by alcohol solution of thiocarbamide, and C- by "complex solution" (NaOH + thiocarbamide mixture) from nitric acid. Duration time was 1 day.

The table shows that after a day adsorbtion on the carbon of C type from the acids of all concentrations, a 100% Pd sorbtion is observed. Changing the sorbent amount up to 100 mg we determined Pd sorbtion capacity on the carbon treated by a "complex mixture" of alkali and thiocarbamide.

Table 1. Pd sorbtion in mkg to 1g of carbon

HNO <sub>3</sub> conc., n		Type of sorbent	
	А	В	С
0,6	100	639	1000
1,0	515	880	1000
2,0	528	885	1000

**Table 2.** Sorbtion capacity of the "complex" carbon by Pd

HNO <sub>3</sub> conc., N	mg /1 g	mmol/1g	
0,6	6,0	5,64*10 <sup>-2</sup>	
1,0	5,0	4,70*10 <sup>-2</sup>	
2,0	3,5	3,30*10 <sup>-2</sup>	

**Table 3.** Static sorbtion of Pd from nitric acid of different concentration on various sorbents (fractions 1-1.6 mm): 1- carbon preliminarily treated by alkali and thiocarbamide ("complex") and 2- carbon (100mg) and thiocarbamide (100mg) mixed mechanically ("mixture"). Duration time of the contact of Pd solution ( total content 1000mkg in 50ml of the solution) with the sorbent was 1 day.

HNO <sub>3,</sub> conc. N	Sorbent	Pd, mkg/V=50	Pd, mkg on sorbent	Capacity by Pd mg/ 1g
0,6	"complex"	400	600	6,0
1,0	·· _"	500	500	5,0
2,0	·· - ··	650	350	3,5
2,0	"mixture"	575	425	4,25
4,0	·· - ··	276	724	7,24
6,0	·· - ··	0,0	1000	10,00

A regular decrease of sorbtion with increasing acidity is related to the possible Pd complexation in the nitric acid solutions with the concentration below 2 N.

4. Pd sorbtion from the solution of nitric acid of higher concentration proceeds in a different way which is shown in table 3.

As it is seen in the table, the character of the dependence of sorbtion vs acid concentration changes. So, in the modified carbon each gram accounts for 0.016 g of thiocarbamide (independent investigation) and in the "mixture" each gram of carbon accounts for 1 g of thiocarbamide. This is evidently an excess compared to the first part of the table.

5. An excess of thiocarbamide makes it possible the complexation of Pd and thiocarbamide which yields soluble compounds. So the composition of the known complexes in hydrochloric acid solutions is  $Pd\{[(NH_2)_2CS]_4\}Cl_2$  with the stability constant for 25°C, pK=31.9 [6].

The investigation of Pd complexation with thiocarbamide (TC) in nitric acid is necessary for understanding the mechanism of Pd sorbtion in strong solutions of nitric acid and for solving applied problems. The spectra were taken using the solutions with Pd concentration from 10 to 1000mkg/ml. The spectra of molecular absorbtion of Pd with (TC) complexes at different HNO<sub>3</sub> acidity (up to 1N) and depending on the (TC) and Pd ratio were taken using an UV-VIS spectrophotometer in the range 250-800  $\eta$ m. The analysis showed that as contrasted from the sorbtion of a simple Pd ion (max. at 456nm) its complex with thiocarbamide gives a blurred absorbtion spectrum with three ranges: up to 265  $\eta$ m is due to the effect of thiocarbamide itself; if TC is dissolved in nitric acid, so in the region of 290-310 nm the spectrum is superimposed by the absorbtion produced by the oscillations of nitric acid ion. Herewith, the association of thiocarbamide with nitric acid is shown up. In the same range the absorbtion produced by the Pd with (TC) complex superimposes inadditively. This region of the spectrum is likely to be related with the triple complex of palladium, thiocarbamide, and nitric acid ion. The composition of the Pd with TC complex which gives the absorbtion effect at 340  $\eta$ m was determined by the method of isomolar series. By contrast to the above composition for hydrochloric acid solutions [6], the Pd to TC ratio in HNO<sub>3</sub> appeared to be 1:3. An excess of thiocarbamide lowers the absorbtion maximum and its deficiency yields the brown residue, whose composition was not clearly determined.

The sorbtion of the complex (1:3) on the activated carbon proceeds slowly: in the nitric acid medium (from 0.04 to 1n) light absorbtion regularly decreases in all the spectrum ranges. After carbon addition light absorbtion decreases by 60% in 48 hours.

6. In HNO<sub>3</sub> solutions of higher concentration the processes follow another mechanism. Just 4N HNO<sub>3</sub> begins distracting palladium-with-thiocarbamide complexes. The process of distracting the complex proceeds in the following way: first the traces of precipitate appear, yellow coloration disappears in 30 min. after adding concentrated acid. Yellow residue precipitated in biacid after a day duration at room temperature, and upon boiling it occurs in an hour (or even less). If carbon is present in the solution as a sorbent, the residue precipitates on carbon and could be filtrated together with the sorbent. When further calcination at T=600°C, sorbed palladium sulfide precipitates on the carbon. This has been proved by X-ray phase analysis.

A detailed analysis of the transformations of precipitated on the carbon palladium compound showed that in an excess of thiocarbamide and nitric acid concentration above 6 N the oxidation of amine components of TC to nitrite form takes place which could dissolve the residue again with the formation of palladium complex of  $[Pd(NO_2)_4]^{-2}$  type.

For this reason for Pd sorbtion on the mixture of carbon and thiocarbamide from 6N HNO<sub>3</sub> one should select the concentration of thiocarbamide. The amount of precipitate

depending on the excess of added thiocarbamide is given in table 4.

**Table 4.** Residual Pd concentrations after its sorbtion from 6N solution of  $HNO_3$  on activated carbon mixed with different amounts of thiocarbamide (starting Pd content was 1 mg). Carbon mass is 100mg, fractions - 1-1.6 mm. A- after a day contact with carbon, B- after a 5 day contact.

Ν	TC amount, mg	A, mkg/ml	B, mkg/ml
1	Pure carbon, without TC	75.6	65.2
2	50 (TM)+NaOH	17.3	0.6
3	50 " - "	6.6	0.4
4	20 " - "	0.8	0.0
5	10 " - "	0.0	0.5
6	3 " - "	2.5	3.6

The table shows that an excess of thiocarbamide should not exceed three-fold amount necessary for bonding Pd (1:3) so that the residual amount of palladium in the solution will equal 0 just in a day. Other noble metals present in the wastes (for example ruthenium) are likely to be extracted selectively as it was shown for sulfate solutions, decomposing thiocarbamide upon heating  $(230^{\circ}C)$  [5].

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# <sup>#</sup>Savenko A.V. Sorption of UO<sub>2</sub><sup>2+</sup> on calcium carbonate

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Uranium migrates in biosphere mainly in aqueous medium. It is present there in the form of  $UO_2^{2^+}$  ion and its complex compounds, with except for anaerobic conditions. Sorption processes are the main factor, that controls uranium content in natural waters. A large number of researches considered sorption of uranium(VI) on various natural materials. Besides that, many problems require further investigation. In particular, it relates to the sorption of uranium (IV) on calcium carbonate – one of the major rock-forming mineral in the Earth's crust. Reference [1] notes, that sorption of uranium(VI) on calcium carbonate depends linearly upon the value of ratio between activities of  $UO_2^{2^+}$  and  $Ca^{2^+}$  in solution according to the reaction, which proceeds on a solid phase surface:

 $UO_2^{2^+} + CaCO_{3 \text{ (solid)}} = >UO_2CO_3 + Ca^{2^+}$ , (1) where a ">" symbol designates surface complex, that hosts sorbed uranium. However, the reaction (1) equilibrium constant was determined by the authors [1] with insufficient accuracy (lg  $K_{U(VI)} = 5.12 \pm 0.53$ ), that confines application of the obtained results to applied research in uranium geochemistry and environmental science.

The proposed paper is aimed at specifying the value of equilibrium constant for the reaction of  $UO_2^{2+}$  sorption on calcium carbonate. It also includes recognizing of how relation between masses of solid phase and solution affects the reaction. Some data [2] indicate, that characteristics of sorption equilibrium depend on this relation.

Calcium carbonate (calcite) of high purity with specific surface of 0.0235 m<sup>2</sup>/g was used in experiments. Experiments embraced two runs with different concentrations of dissolved calcium. The first run was performed on initial solutions, which contained 2 mM of HNO<sub>3</sub> and 2-10  $\mu$ M of uranium(VI). The second run operated with initial solutions, in which calcium nitrate was additionally introduced at 20 mM level of concentrations. Each run consisted of experiments performed under two values of mass ratio solid/solution: 1 to 67, and 1 to 200, respectively.

Weighted samples of calcium carbonate (1-3 g) were placed into cone flasks. After that 200 ml of initial solution were added to each flask. Open samples were intensively mixed during 4-6 hours for the complete removal of excess CO<sub>2</sub>, that originates due to CaCO<sub>3</sub> reaction with nitric acid. Removal of CO<sub>2</sub> was controlled via solution pH transition to a steady value. with  $HNO_3$  increased  $Ca(NO_3)_2$ Reaction of CaCO<sub>3</sub> concentrations by 1 mM. As a result, the total content of dissolved calcium amounted for the first run and for the second run 1 and 21 mM, correspondingly. Simultaneously, mass of CaCO3 after its partial dissolution decreased in all experiments by 0.02 g, i.e. not more than by 2% from the initial sample weight (1-3 g). After removal of CO<sub>2</sub> samples were closed, and were intensively mixed during two months. Preliminary kinetic experiments showed, that sorption attained equilibrium in 1-2 weeks. After exposition time finished, samples were filtered through dense paper filter. Values of pH and residual concentration of uranium(VI) were determined in filtrate applying potentiometry and colorimetry with arsenazo III, correspondingly.

Experimental results indicate, that the values of specific sorption ( $\Gamma_{U(VI)}$ , µmol U / g) rise linearly with an increase in equilibrium concentration of dissolved uranium ([U(VI)], mM), and do not depend on mass relation between solid phase and solution. Herewith, proportional coefficient *k* for the regularity  $\Gamma_{U(VI)} = k$  [U(VI)], (2) decreases with the growth of calcium contents in a solution: when each provide the solution of the solution of the result of the solution of the so

when calcium concentration is equal to 1 mM k=0.0066, but when calcium concentration is equal to 21 mM k=0.0053.

<sup>&</sup>lt;sup>#</sup>The research was performed under the support from Ministry of Science and Technologies of Russian Federation for the Program "Global Changes of Environment and Climate".

Dependence of uranium(VI) sorption on calcium concentration in a solution was recognized as well in [1]. According to the results presented there, the value of specific sorption is a function of the ratio between activities of  $UO_2^{2+}$  and  $Ca^{2+}$  ions.



**Fig. 1.**,Dependence of uranium(VI) specific sorption on the ratio between activities of  $UO_2^{2^+}$  and  $Ca^{2^+}$  ions. *1* is 1 mM  $Ca(NO_3)_2$ , solid / solution ratio 1: 200; 2 is 21 mM  $Ca(NO_3)_2$ , solid / solution ratio 1: 200; 3 is 1 mM  $Ca(NO_3)_2$ , solid / solution ratio 1: 67; 4 is 21 mM  $Ca(NO_3)_2$ , solid / solution ratio 1: 67.

Based on our experimental data, linear increase of uranium(VI) specific sorption with the growth of the ratio between activities of  $UO_2^{2+}$  and  $Ca^{2+}$  ions in a solution was established (fig. 1). The increase is described by the common equation for all experiments:

$$\Gamma_{U(VT)} = K \frac{a_{UO_2^{2+}}}{a_{Ca^{2+}}},$$
(3)

where  $\Gamma_{U(VI)}$  is a specific sorption for a unit of sorbite mass, mol U / g CaCO<sub>3</sub>;  $\alpha_{UO_2}^{2+}$  and  $\alpha_{Ca}^{2+}$  are activities of UO<sub>2</sub><sup>2+</sup> and Ca<sup>2+</sup> ions, respectively; *K* is proportional coefficient, equal to 0.0401  $\pm$  0.0039 mol / g. If sorption is referred to a unit of sorbite surface, equation of dependence looks as follows:

$$\Gamma'_{U(VT)} = K' \frac{a_{UO_2^{2+}}}{a_{Ca^{2+}}},$$
(4)

where  $\Gamma'_{U(VI)} = \Gamma / S$  is a specific sorption for a unit of sorbite surface, mol·U/m<sup>2</sup>, S is a specific surface of CaCO<sub>3</sub>, equal to 0.0235 m<sup>2</sup>/g, K' is proportional coefficient, equal to 1.71 ± 0.16 mol / m<sup>2</sup>.

The sorption value was determined in [1] as mol fraction of uranium in a surface phase:

$$\chi_{U(VT)} = \frac{[>UO_2CO_3]}{[>UO_2CO_3] + [>CaCO_3]} \approx \frac{[>UO_2CO_3]}{[>CaCO_3]} = K_{U(VT)} \frac{a_{UO_2^{2+}}}{a_{Ca^{2+}}}, (5)$$

where  $K_{U(VI)}$  is sorption equilibrium constant, equal to  $10^{5.12\pm0.53}$ . According to [1], for pure calcite [>*CaCO*<sub>3</sub>] = 8.31·10<sup>-6</sup> mol / m<sup>2</sup>. When uranium(VI) concentrations in solution are at low level, [>*UO*<sub>2</sub>*CO*<sub>3</sub>]<<[>*CaCO*<sub>3</sub>], so the  $\Gamma'_{U(VI)}$  value in equation (4) may be expressed in terms of the parameters for equation (5):

$$\Gamma'_{U(VI)} = [>CaCO_3]K_{U(VI)}\frac{a_{UO_2^{2+}}}{a_{Ca^{2+}}} = (0.32 \div 3.71)\frac{a_{UO_2^{2+}}}{a_{Ca^{2+}}}.$$
 (6)

Comparison of equations (4) and (6) shows, that the value of proportional coefficient K', that was obtained in our experiments  $(1.71 \pm 0.16 \text{ mol} / \text{m}^2)$ , is in a good agreement with the value range  $0.32 \div 3.71 \text{ mol} / \text{m}^2$  referenced by [1].

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# <sup>#</sup>Ezhov S.V. Feldspathoid mineralization in experimenal skarn columns

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Feldspathoid mineralization (nepheline, sodalite, cancrinite) in former experimental bimetasomatic columns was marked in two conditions: 1) when albite (or its mixture with quartz) was used as a silicate rock, and CaO+MgO as a carbonate one, in the presence of NaCl solution, and 2) on the granodiorite and limestone (or dolomite) contacts in cases of using alcaline Na (NaOH, NaF, NaCO<sub>3</sub>) solutions [1]. Only NaCl or NaCl+KCl solutions were used in our experiments. The specific feature of the experiments was the presence of sulphides (galena, sphalerite and others) or calcium sulphate. Feldspathoids have been developed at the temperatures not lower than 550-600°C.

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Fig.1. Ratio of Na, K and Ca, Cl and S contents (in formulae indexes) in feldspatoids. 1 - sodalites, 2 - hauynes.



**Fig. 2.** Different positions of feldspathoid mineralization in the specimens structure. Temperature of the experiments:  $550^{\circ}$ C (a),  $600^{\circ}$ C (b,c,d); pressure 1 kbar. Solutions: a – 1,5 m NaCl+KCl (with admixture KF), b, c – 1m NaCl, c – 1m NaCl+KCl. Granodiorite-porphyry was used as an initial silicate rock, limestone (a, c), dolomite (b) and anhidrite-contained limestone (d) as a carbonate one. Minerals' indexes: Bus – bustamite, Cc – calcite, Cpx – clinopyroxene, Fo – forsterite, Gr – garnet, Hn – hauyne, Ksp – potash feldspar, Mtc – monticellite,  $Pl_{50}$  – plagioclase (lower index – per cent of anortite), Sod – sodalite, Wo – wollastonite

Feldspathoids always develop as very large idiomorphic crystals or in their compact growths, that outstand among finegrained and usually "friable" aggregate of other minerals of endomorphic zones of the column. Sodalite or hauyne formed in different experiments (fig.1). Sodalite more often appeared when NaCl solution was used, hauyne – in cases of NaCl+KCl solutions. Both these feldspatoids could develop simultaneously in the same experiment, though in different parts of the specimen.

Feldspathoids appeared at three different structural positions: 1) at endomorphic parts of bimetasomatic skarn columns – as a rule on the border between potashfeldsparbearing and plagioclase-bearing zones (fig. 2 a, c). A "lateral" unsteadiness of feldspathoid zone (as well as other ones) was clearly manifested: this zone can be completly vanished (feldspatoids developed only at the certain distance both from

sulphide components source and the open edge of the ampule), 2) as isolated metacrystals or vein-shaped concentrations parallel to zones borders (fig. 2 b, d), 3) at an open edge of the ampule where interaction between silicate rock and free solution took place (fig. 2 c, d).

Localization in the 1-st position as a rule occured when mixtured NaCl+KCl solutions were used; in the 2-nd and 3-rd ones – only with NaCl solution. Composition of initial rocks had no noticeable importance – feldspathoids could appear in cases of using either granodiorite-porphyry or artificial potash feldspar -quartz mixture (where complete replacement of potash feldspar by albite took place). Limestone as well as dolomite can be used as a carbonate rock (pure or with anhydrite admixture).

Feldspathoid zone formation within endomorphic part of columns is a clear example of components differentiation under

bimetasomatism (space division of potassium, sodium and calcium and concentration of these components in piroxene-potashfeldpar, piroxene-sodalite and piroxene-plagioclase zones, accordingly). Metacrystals in altered granitoid developed where the composition of plagioclase is rather acid, so the process signifies the culmination of sodium concentration.

The obtained results clearly demonstrate sulpher presence (equally sulphide or sulphate forms) as a favour condition for feldspatiod development.

The appearing mineralisation can be represented by either hauyne ( sulpher-contained form) or sodalite ( quite almost sulpher-free form).

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# <sup>#</sup>Ezhov S.V. Experimental simulation of the mineralization mechanism inside open cavities

key words [veins cavities experiments diffusion mineralization]

Mineral filling of open crack cavities may be caused by two main mechanisms: sedimentation of matter from hydrothermal solutions entering given crack from the outside (hydrothermal veins), or using matter from the country rock (Alpine vein). The carried out experiments are to understand the particularities of the second mechanism.

The initial specimens had complex structure: intervals of different composition imitated carbonaceous (limestone, dolomite) and silicate (granodiorite-porphyry, hornfels) rocks, as well as sourses of ore components (the pulverized mixtures of ore minerals). 1 m solutions of NaCl, NaCl+KCl at a temperature of 550°C were used.

During the experimental procedure the split-shaped cavities were formed in three cases: 1) within forming bimetasomatic columns (because of the dissolution of country rock minerals and their redeposition at wollastonite, garnet or pyroxene compact zones, fig. 1, cavities  $Cv_1$ , 2) because of total dissolution of thin intervals of quartz among granitoid rock, fig. 2, and 3) variously oriented crack-like cavities because of ejection of matter (fig. 1, cavities  $Cv_2$ ). The new mineral formations, including ore, arises in cavities of all these three types. Ore deposition in the first type cavities ("hollow" zones of bimetasomatic columns) can be explained by the reduction in solubility of ore components as a result of silicate and carbonaceous rock pores solution mixture. This process is a special case of bimetasomatic interaction and is not discussed here. The two other processes are more interesting in the framework of this study.

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**Fig.1.** Two types of experimental cavities :  $Cv_1$  - in the neighborhood of bbimetasomatic column,  $Cv_2$  - in the neighborhood of endomorphic contact of grano-diorite-porphyry changing. Nomenclature of minerals: Gr - garnet, Ksp - potash feldspar, Sch - scheelite, Wo - wollastonite. Experiment AT-113. Sketch of the part of specimen.



**Fig.2.** The cavity (Cv) mineralization arisen because of quartz band leaching amongst the granodorite-porphyry. Sketch of the part of specimen. Cpx – clinopiroxene. Txperiment AT-109. Sketch of the part of specimen.

The cavity among changed granodiorite-porphyry (that is transformed into potash feldspar rock with small admixture of clinopyroxene) was arisen as a result of total dissolution of quartz and has thin finest clinopyroxene crystals edging (fig. 2). This clinopyroxene noticeably differs from the initial one: it contains 32-36% of hedenbergite against 28% of the country rock and johannsenite - 10-12% against 8% accordingly. In the other cases in addition to pyroxene the edging contains wollastonite and garnet similar to grossular (15% of andradite). The smallest gold granules in the area of pyroxene edging and at the its border with country rock are noticed.

The experimental conditions exclude the possibility of infiltration import of the matter. It is to suggest that mineral formation takes place because of diffusion import of matter. This process directs strictly axipetal: from the country rock to the open cavity, from both its boards equally.

The diffusion is possible only if the gradient of concentration exists. It means, that solubility of minerals in the pore solution is lower than in the pore channels of the country rock. It can be explained by the fact that the main part of the fluid volume is in close contact with crystalline phases and thus surface effects take place. The directed diffusion leads to the mineral deposition in the cavity, so the vein body is forming.

In various cases (in temperature, salt concentration, mineral composition of enclosing rocks, their porosity and shape, composition of ore components in situ) various proportion among components' solubility are possible. It is the reason for multiplicity of veins composition. They may contain (in addition to vein minerals such as quartz, calcite etc.) rare ore minerals though their constituent elements are present in the surrounding rock in small amounts. An allocation of gold is indicative (fig. 2): the initial matter contained an insignificant impurity of gold (small charges of sulfide minerals of Darasun gold deposit were used). It is to note, that in the neighborhood within the skarn column no gold is detected although active deposition of sulfides (galena, sphalerite, covellite et cet.) takes place.

The effect of cavity filling becomes most intensive if the ore mixture contains wolframite. Scheelite deposition takes place both in the skarn columns area and in the outer space within the endomorphic potassium feldspar rock (fig. 2). In the last case the veinshape cavities become points of scheelite deposition. These cavities as usual are close to limestone and are the result of the ejection of the matter while skarn column formation. Many of them are oriented prallel to the contact, but some of them are perpendicular or diagonal to the contact. The scheelite deposition is caused by two effects: cross diffusion of tungsten and calcium and the described above effect that leads to the deposition of scheelite in the open cavities.

## <sup>#</sup>Kotelnikova Z.A. Healing of cracks in quartz.

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Introduction. Formation of fluid inclusions is connected with the healing of cracks. Besides, elastic and other physical properties of breeds, the possibility of mass transport, are connected to geometry of porous space, both common porosity and permeability. The processes causing changes in the morphology of cracks, can also have an effect and on these characteristics. The experimental study of cracks healing in salt crystals, Lemmlein [1] has shown, that cracks healing occurs by dissolution and precipitation of the substance of cracks walls in case a fluid gets in a crack and the solution is saturated relative to walls and supersaturated relative to the faces growing across a crack. Smith & Evans, [2], Kotelnikova, [3] have shown, that healing depends on temperature, fluid nature and orientation of a crack.

Cracks healing can occur by means of diffusion through a lattice and transport of the material of a matrix along a surface solid-fluid or directly through fluid and does not require involving of the new matrix material. Thus the morphology of a crack changes. There is a difference of chemical potential between the moving end of a crack and its walls owing to roughness of the crack surface [2]:

## $\Delta \mu = \gamma (C_e - C_m) \Omega$

where  $\gamma$ -is superficial energy;  $\Omega$ - molecular volume;  $C_e$ ,  $C_m$  - curvature of the surface at excesses and in the middle part accordingly.

The analysis of the equation shows, that the substance transport occurs from the convex or concave sites of high curvature of the surface to the convex parts with low curvature.

Different density of dislocations on walls also is the reason of a difference in chemical potential (Geguzin et al, [4]). Geguzin [4] has shown, that the size of narrowed pore in the thermogradient field decreases up to the critical meaning:

### $Y_{D}^{*} \sim (\nabla T)^{-1/2}$

In case of healing  $(\Delta \mu)$  this dependence shows a limit in relation to the dissolution of lateral walls of cracks. Practically it follows from this dependence, that the more roughnesses in a crack, the finer the inclusions formed.

If the density of dislocations is low  $(10^5-10^6 \text{ cm}^{-2})$ , they practically do not influence moving of a step of dissolution. In case of a crystal with the high density of dislocations the dislocations are likely to be distributed along the surface in regular intervals. The steps of dissolution (growth) then are formed by the outputs of dislocations and these steps can move, if the distance between dislocations is not less than a diameter of a critical germ.

Nichols & Mullins [5] have shown, that at cracks healing with formation of inclusions from the ratio of the disstance between inclusions to their radius  $\lambda/R$  one can conclude about the form of mass transport: at  $\lambda/R=12.96$  diffusion through a crystal lattice takes place, if the relation is equal 9,02 - diffusion is through pore solution, at  $\lambda/R=$  8,89 an exchange surface - fluid prevails.

Experimental technique . The prisms cut from a quartz monocrystal and subjected to thermoshock to obtain a network of cracks, were placed in a platinum ampoule together with fluid mix and were maintained at high temperature and pressure for 2-900 hours. Length of the healed region was determined from the distance from the smallest inclusions up to the open part of a crack. We also measured the diameter of the smallest inclusions and the distance between them. The mistake in the calculation of an average length of healing was not less than 50%. The average value  $\lambda/R$  for 600°C was 9.0, that corresponds to mass transport through fluid.

<u>Results.</u> The gaugings of lengths of healing have shown, that the velocity of healing is directly connected to temperature. For convenience the results were recalculated to time necessary to reduce a crack 100 mcm in length in the run with 1Ì the solution NaCl. At  $500^{\circ}$ C this takes about 28 days. At  $700^{\circ}$ C - about 2 hours. As the mass transport proceeded through pore fluid, for the description of this phenomena the modified circuit offered by Geguzin et al. [4] can be used, for the estimation of the velocity of inclusions moving upon thermogradient conditions, and complemented by the equations of Smith & Evans[2] for definition of time of formation of the first inclusions at crack healing. Length of the healed site L can be determined by:

#### $L=\Lambda[(t \exp(-Q/kT))/T],$

where: A and  $\omega$ - constants dependent on the initial geometry of a crack, Q- the activation energy, for quartzes by estimations of Smith & Evans, [2] is equal 50kJ/mole; T- absolute temperature, k- Boltsmann constant, t- time. Then the speed of moving of short circuit of a crack (v) is:

### $v = \Lambda[(Q/kT)/T] = \beta \omega(Y - Y^*)(\partial c/\partial T)\Delta T,$

where:  $\beta$ - factor determined experimentally by inclination angle on the diagram v-R. The analysis of these dependencies suggests that: the speed of moving of short circuit of a crack (actually velocity of healing) linearly depends on the crack width. Geguzin et al.[4] have shown, that the factor  $\beta$  directly depends on the density of dislocations in a crystal. Healing in crystals with high density of dislocations occurs faster. The velocity of healing is a function of temperature, time and concentration of a solution.

Conclusions.

 $<sup>^{\#}</sup>$  The work has been supported by the RBRF (grant N 99-05-65225)

(1) In natural objects at elevated temperatures (more 400°C) the velocity of cracks healing in the presence of fluid is very high. Apparently, to maintain porosity and permeability of breeds it is necessary to assume reverse process of the formation of new cracks (for example, owing to different factor of expansion of minerals and related with this tension).

(2) Mass transport, basically proceeds through the fluid phase.

(3)The higher temperature, concentration of salt in pore solution and density of crystal dislocations, the faster crack healing.

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# <sup>#</sup> \*Kotelnikova Z.A, <sup>\*\*</sup>Kotelnikov A.R. Study of naf-h<sub>2</sub>o system by the synthetic fluid inclusions method.

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Introduction. The system NaF-H<sub>2</sub>O was not investigated at high temperatures and pressures before. The solubility of NaF has been studied up to 100°C; it equals 3.7% for 20°C and increases up to about 4.9% for 100°C. Sole definition of solubility at temperature near 300°C (Ravitch, 1974 [1]) has shown that it is close to zero. So phase diagram of this system is of the P-Q type, which means that critical and solubility curves have two crossing points, named P and Q.

This is the first experience of studying the P-Q type system by the synthetic fluid inclusions method, so the analysis of opportunities of this method is necessary. The coordinates of point P lay close to critical parameters of pure water for the water-salt systems with low salt solubility, as in the case with NaF. Biphase area (vapor + solution) should exist at vapor pressures below saturation pressure. If fluid inclusions were synthesized, it would be possible to study the vapor composition by measurements of cryometric temperatures. To analyze the composition of equilibrium liquid phase, one should know the solubility of NaF at high temperatures, but such data are absent.

It is important to consider the area between P and Q points. Neither critical phenomena, nor three-phase balance (vapor+solution+solid salt), can occur in interval P-Q. Critical phenomena should take place in supersaturated solutions, which cannot be obtained. On the other hand, since vapor and liquid do not exist simultaneously under supercritical conditions, three-phase equilibrium is impossible too. Only pure supercritical fluid or supercritical fluid+solid salt can exist in this area. Corresponding types of synthetic fluid inclusions should exist (vapor+ liquid or vapor+ liquid+solid).

The second critical point Q is low temperature limit of the upper biphase area. It is possible to find the border of biphase area position by condensing a grid of runs. The analysis of the immiscible phases has the same features as for lower biphase area. The accurate definition of coordinates of point Q is imposible.

From the above said, it is clear that for the investigation of synthetic inclusions, it is necessary to provide measurements under both negative and positive temperatures. Temperature and composition of eutectic mixture are known. Unfortunately, the eutectic temperature of the system NaF-H<sub>2</sub>O is very high (- $3.5^{\circ}$ C). That inevitably increases a mistake of definition of salt concentration in a vapor. The curve of NaF solubility is unknown at temperatures above 100°C. Using the method of synthetic fluid inclusions one can estimate the solubility of NaF under homogeneous conditions. Ampoules should be loaded in accordance with the given weights of NaF and H<sub>2</sub>O. If solubility of NaF decreased or remains constant with growth of temperature, the concentration of salt may be estimated by cryometry. If solubility grows, condensing of grids of runs should be useful to determine the first solid NaF in inclusions.

Experimental. Synthesis of fluid inclusions have been realized at 400-800°C and 500-2000 bars in 0.5M solution of NaF. As expected, the pressure of 500 bar appeared above critical for point P. All inclusions contained a solution corresponding to the initial one for each run. The geterogenization of the solution occurred only at pressures of 1000 bar at temperature close to 700°C, so we can say that the point Q lays between 1000 and 2000 bar and 650-700°C.

Inclusions of liquid phase contain large quantity of small crystals of NaF. The equilibrum vapor phase contains about 0.02% NaF. So villiaumite can be crystallazed as a mineral phase from rather low concentration, undersaturated NaF solution by heterogenization.

All inclusions in the interval 400-700°C have no solid phase: it means that supercritical fluid without salt crystal occurs at temperatures between points P-Q.

The attempt was made to estimate solubility of NaF at 400-700°C in homogeneous fluid. The 5, 10 and 15 weight % of solid NaF and pure water was loaded in the capsules. After the run no solid phase were found in inclusions. It means that solubility was not more than that of saturated solution at room temperature.

The study of the system with NaF is complicated because of the possibility of interaction of NaF and quartz at high parameters. The formation of compound similar to Na<sub>2</sub>SiF<sub>6</sub> is possible. At 700°C, 2 kbar the samples of quartz after run have on their surfase a thick layer of quenched phase and appear to be covered by glass. Below this «glass» layer the belt of the spherical gas inclusions with tiny solid occur. This inclusions are quite different from those in healed cracks and were trapped at the time of quenching. Such phenomena are connected with high solubility of quartz in NaF fluid. Rough estimate of the solubility of quartz by the measurements of thickness of quenched layer gives about 70 kg/m<sup>3</sup>.

<sup>&</sup>lt;sup>#</sup> The work has been supported by the RBRF (grant N 99-05-65225)

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# <sup>#</sup>Kurovskaya N.A., <u>Malinin S.D.</u> Experimental study of sheelite and fluorite solubility in the NaCl-H<sub>2</sub>O system at 800°C and 0.5-2 kbar.

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In addition to previous studies at 600°C [1], sheelite solubility in 1 and 5m NaCl solutions at 800°C and 0.5-2 kbar pressures in homogenous and heterogeneous regions has been studied. The fluorite solubility measurements at 800°C were also performed (1 and 5m NaCl solutions and 0.5, 1.6 and 1.8 kbar pressures) to improve the experimental data obtained earlier [2,3].

The experiments were carried out in two chamber bombs with external heating. using the rapid isobaric quenching method. Sealed platinum capsules were used.. Synthetic fluorite and sheelite monocrystals were used as starting materials. The method of monocrystal weight loss for the solubility determination was used. The weighing was done to  $\pm 0.005$  mg with a Sartorius 4503MP6 electronic microbalance.

It was found that at  $800^{\circ}$ C, in the same manner as at  $600^{\circ}$ C, the pressure dependence of the sheelite solubility had a minimum (fig).





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As it was shown earlier [1,3] the minimum corresponds to the point of fluid disintegration. The sheelite solubility in 1m NaCl solution sharply increases with pressure decrease in heterogenous region (more than one order of magnitude). This effect appears more slightly in 5m NaCl solutions. According to the H<sub>2</sub>O-NaCl phase diagram [4] the fluid disintegration of 1m NaCl (5.52 wt. %) and 5m NaCl (22.6 wt.%) takes place at about 1.3 and 1.4 kbar pressures, correspondly. The obtained experimental data show that this happens at about 1.4 and 1.6 kbar pressures correspondly. It could be suggested that this discrepancy is due to the experimental error. The same dependencies were found earlier for fluorite under similar conditions. It could be assumed that the obtained effect of the sharp increase of the mineral solubility at 600 and 800°C in the NaCl-H<sub>2</sub>O system at the fluid heterogenization is common for other sparingly soluble minerals.

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# <sup>#</sup>Vigasina M.F.<sup>\*</sup>, Ermilov A.Yu.<sup>\*\*</sup>, Orlov R.Yu.<sup>\*</sup>, Yakushevich A.N.<sup>\*\*</sup> Raman-spectroscopy and abinitio calculations of the oxycomplexes of tungsten from Na<sub>2</sub>WO<sub>4</sub>-HCl-H<sub>2</sub>O system.

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The vibrational spectrometric methods are of great importance at the hydrothermal investigations. The existence and the concentrations of some tungsten complexes in the water solution of Na<sub>2</sub>WO<sub>4</sub>.·H<sub>2</sub>O was obtained by the Raman spectrometric study at room temperature. The known frequencies of the aquacomplex WO<sub>4</sub><sup>-2</sup> (931cm<sup>-1</sup> [1]) and data of our quantum-chemical calculations were used for their identification.

The Raman lines at the frequencies 931, 960 and 980 cm<sup>-1</sup> were observed during the lowering pH of the solution from 9 to 4. The line 960cm<sup>-1</sup> was assigned to the HWO<sub>4</sub><sup>-</sup> complex owing to the experiment in which the solutions at pH=7.4 and three initial concentrations of the salt equal to 0.1, 0.05 and 0.025 mol/l were studied. It was observed that the relatition of intensity of the line at 960cm<sup>-1</sup> to the intensity of the line at 931cm<sup>-1</sup> remained constant. So, the conclusion was done that both lines belong to the tungsten monomers.

The equilibrium  $WO_4^{-2^-} + H^+ = HWO_4^-$  (1) was studied also at different value of pH. In the range pH=7.95-7.05 the linear dependence  $lg(I_{960}/I_{931}) = -pH+$  Const with the angle of incidence nearly 45° was observed. It confirms the assignment of the line at 980cm<sup>-1</sup> to the HWO<sub>4</sub><sup>-</sup>-complex.

The equality of the concentrations of  $WO_4^{-2}$  and  $HWO_4^{-2}$  species was obtained at pH=7.3±0.1, hence logarithm of the equilibrium quotient is  $lgK_1 \approx 7.3\pm0.2$  At the same manner

<sup>#</sup> This work was supported by Russian Fund of Fundamental Investigations (grant N 00-05-64132).

the line 980cm<sup>-1</sup> was attributed to  $H_2WO_4$  species and  $lgK_2 *= 4.6\pm0.2$  was obtained for the equilibrium  $HWO_4 + H = H_2WO_4(2)$ .

The activity coefficients of the tunsten complexes in the second approximation of the Debye-Hückel theory are:  $lg\gamma(WO_4^{-2})=-0.53$ ,  $lg\gamma(HWO_4^{-})=-0.13$ . Hence the equilibrium constants are:  $lgK_1=7.7\pm0.2$  è  $lgK_2=4.7\pm0.2$ . Applying the known value of the Gibbs free energy of formation of the species  $WO_4^{-2}$  in water solution  $\Delta G_f^{0}_{298,15}=-916$  kJ/mol [2], and our values of  $lgK_1$  and  $lgK_2$  we obtained the Gibbs free energy of formation for the studied aquacomplexes:

 $\Delta G_{f\ 298.15}^{o}(HWO_{4}^{-}) = \Delta G_{f\ 298.15}^{o}(WO_{4}^{-2}) - R \cdot T \cdot lnK_{1} = - (916+44) kJ/mol = -960 kJ/mol$ 

 $\Delta G_{f\ 298.15}^{\ o}(H_2WO_4){=}\Delta G_{f\ 298.15}^{\ o}(HWO_4^{\ -})$  -  $R{\cdot}T{\cdot}lnK_2$  = - (958+27)kJ/mol= -987 kJ/mol .

The calculations of the equilibrium geometries, vibrational frequencies and thermodynamic properties of free complexes  $WO_4^{-2}$ ,  $HWO_4^{-}$  and  $H_2WO_4$  were carried out for the interpretation of the experimental results. Our calculations were made at the restricted Hartree-Fock level. For tungsten we used SBK effective core potential. The atoms of oxygen, chlorine and hydrogen were calculated with the triple zeta valence basis sets with adjusted the polarization orbitals d-type at oxygen and chlorine and p-type at hydrogen. Theoretical equilibrium structures and vibrational frequencies for this complexes were also obtained using the second order of Möller-Plesset pertubation theory.

Vibrational frequencies( $\times 0.89$ ) of WO<sub>4</sub> -frame accumulated in the table (\*-experiment):

WO <sub>4</sub> <sup>-2</sup>	HWO <sub>4</sub>	$H_2WO_4$
883 / 931*	958 / 960*	1026 / 980*
763(3)	869	962
	866	695
	573	690
301(3)	315	350
	303	264
	271	241
296(2)	235	231
	224	193

The assignment of the lines at 960cm<sup>-1</sup> and 980cm<sup>-1</sup> to the protonated species is confirmed by our calculations which show that the highest vibrational frequency of the W-O bond increases with the increasing the number of the protons as 1:1.07:1.16.

The equilibrium structure of  $WO_4^{-2}$  is related to the  $T_d$  - symmetry point group with the bond lengths r(W-O)=1.77Å.

The structure of WO<sub>2</sub>(OH)<sub>2</sub> may be with equal correctness related to point groupes C<sub>3</sub> and C<sub>2</sub> due to existence of the isomers. In both cases two hydrogen atoms are attached to different oxygen atoms O<sub>1</sub> and O<sub>2</sub>. Bond lengths and angles of this isomeres are:  $r(H_1-O_1)=0.94$ Å,  $r(W-O_1)=1.86$ Å,  $r(W-O_3)=1.68$ Å,  $\angle O_1$ -W-O<sub>2</sub> $\cong 110^\circ$ ,  $\angle O_3$ -W-O<sub>4</sub> $\cong 108^\circ$ ,  $\angle O_1$ -W-O<sub>3</sub> $\cong 110^\circ$ ,  $\angle O_1$ -W-O<sub>4</sub> $\cong 110^\circ$ ,  $\angle W$ -O<sub>1</sub>-H<sub>1</sub> $\cong 137^\circ$ .

The equilibrium structure of HWO<sub>4</sub><sup>-</sup> is related to C<sub>s</sub> point group and may be described as deformed tetrahedron with bond lengths r(W-OH)=1.94Å, r(W-O)=1.72Å. and r(W-O<sup>1</sup>)=0.94Å. The hydrogen atom is placed at cis-form with respect to one of three non-bonded oxygens (O<sup>1</sup>) with the bond angle equal to  $\angle O^1$ -W-OH= $\cong$ 107°, the other bond angles are

 $\angle$ W-O-H $\cong$ 122°,  $\angle$ O-W-O $\cong$ 111° and two angles equal to  $\angle$ HO-W-O $\cong$ 109°.

The absolute entropy  $S^{\circ}_{298,15}$  calculated for the free complex HWO<sub>4</sub><sup>-</sup> is equal to 355 kJ/mol·K. The tabulated values for entropies of related substances [3] were used for the entropy of formation of HWO<sub>4</sub><sup>-</sup> calculatied according to the reaction  $1/2 \cdot H_2 + 2O_2 + W_{crys} = HWO_4^- : \Delta S_{f^{\circ}298,15}^{\circ}$  (HWO<sub>4</sub><sup>-</sup>)= -156 J/mol·K. Then, using the experimental enthalpy of formation [4], we calculated the free Gibbs energy of formation for the free complex:  $\Delta G_{f^{\circ}298,15}^{\circ}$ (HWO<sub>4</sub><sup>-</sup>)= -1093 kJ/mol.

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## Terentyev A.V. Recrystallization of carbonate mineral aggregates under hydrothermal conditions

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Recrystallization with grain size enlargement is common in the zones of pre-ore alteration of a number of hydrothermal stratiform deposits hosted by sedimentary carbonates. This phenomenon takes place at high temperatures and pressures and consists in redeposition of substance from one grains to others, which leads to enlargement of individuals and reduction of their number.

We have carried out experimental modeling of recrystallization of calcite and dolomite aggregates under hydrothermal conditions at temperature  $20-400^{\circ}$ C and pressure 0 - 1000 kgf/cm<sup>2</sup>. An attempt was made to determine the relationship between the grain size of the mineral aggregates and temperature and pressure on the basis of measuring the grain areas in cross-sections (checkered method).

Grain size data did not show any strict dependence of the grain size on temperature and pressure. Interpretation of the results was complicated by the fact that we were not dealing with the real structure of the rock, but with the structure revealed by the petrographic microsection. The latter, however, gives a direct and clear idea about the microscopic structure of the mineral aggregates. The maximal mean value for the cross-sectional area of calcite grains was observed at  $P=1000 \text{ kgf/cm}^2$ ,  $T=350^{\circ}$ C, of dolomite grains - when no pressure was applied and  $T=300^{\circ}$ C (Table).

Histograms of the variation of calcite and dolomite grain size give a more demonstrative picture of the mineral aggregate recrystallization (Fig 1, 2). The histograms clearly show

patterns in the enlargement of the grains, which at first are of a larger size at the expense of dissolution of smaller grains. Thus the number of calcite grains with cross-sectional area less than  $0,033 \text{ mm}^2$  decreases in the hydrothermal process. On the contrary, the number of the grains over  $0,033-0,726 \text{ mm}^2$  in size increases, grains more than  $0,726 \text{ mm}^2$  in size appear.

The grain size of a rock bears information about recrystallization, indicates the character and degree of the

variation of such properties as porosity, density, strength, permiability for hydrothermal solutions.

It is exactly in recrystallization of mineral aggregates of the source rock that the main role of the thermal influence in hydrothermal - metasomatic processes of mineral and ore formations is manifested.

	The mean cross-sectional area of grains, mm <sup>2</sup>						
Т, <sup>0</sup> С	Calcite				Dolomite		
	without	P=500,	P=1000,	without	P=500,	P=1000,	
	external	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	external	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	
	pressure			pressure			
20	0.086	0.121	0.114	0.0127	0.0161	0.0154	
	(initial)			(initial)			
100	0.129	0.128	0.126	0.0149	0.0156	0.0152	
150	0.104	0.117	0.151	0.0132	0.0166	0.0192	
200	0.138	0.166	0.152	0.0160	0.0166	0.0170	
250	0.136	0.135	0.124	0.0149	0.0186	0.0199	
300	0.112	0.130	0.159	0.0245	0.0200	0.0204	
350	0.141	0.141	0.225	0.0143	0.0190	0.0155	
400	0.140	0.141	0.184	0.0175	0.0203	0.0145	

Table. Variation of the mean cross-sectional area of calcite and dolomite grains in relation to P-T conditions



egate in relation to P-T conditions

# <sup>#</sup>Vigasina M.F., Orlov R.Yu., Tamm V.E. Raman spectroscopy of the [SiMo<sub>12</sub>O<sub>40</sub>]-complex in the high temperature solution.

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Heteropolyacid  $H_4[SiMo_{12}O_{40}]$  is supposed to be one of the most stable compounds in a broad range of temperatures and pH values[1].

The water solution of the acid was studied by the Raman spectroscopy at the initial value pH=1.2. The solution with the concentration 0.002 mol/l was placed into autoclave with sapphire windows. The filling coefficient was 0.5, the air was displaced by the gaseous argon.

The characteristic vibrational frequencies of the studied complex 982 cm<sup>-1</sup> and 960 cm<sup>-1</sup> [2] were observed up to  $230^{\circ}$ C without any significant change of their intensities. But in the range 230-240°C a fast destruction of the complex was found out. The same result was observed for the solution with the 0.2 mol/l concentration of NaCl. The complex Na<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] is even more unstable and undergoes destruction at 150-160°C. These experiments confirm the opinion that molybdenum heterocomplexes do not participate in the real geochemical process [3].

The behaviour of the tungsten-phosphate  $Na_3[PMo_{12}O_{40}]$  is quite different. Its characteristic frequencies at 1011 cm<sup>-1</sup> and 996 cm<sup>-1</sup> were observed in a high temperature solution up to 360°C [4]. The less stability of the crystalline molybdenum geteropolyanions with respect to tungsten ones was pointed out [5].

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# <sup>#</sup>Kolonin G.R.\*, Shironosova G.P.,\* Sushchevskaya T.M.\*\* Thermodynamic evaluation of

# possible REE concentrations in the fluoridesolution of complex composition during its geochemical evolution

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The given report is the first attempt of revealing the possible REE and Y concentrations in the model chloridecarbonate- fluoride fluid after its interaction with the mixture of quantitatively prevailing fluorite with REE and Y solid fluorides. The thermodynamic description of hydrothermal reactions with REE participation theoretically proves the possibility of their use as markers of both geochemical and technological processes. The stability constants of the main types of REE inorganic complexes in the wide range of temperatures and pressures have been recently calculated [1] using HKF equation [2]. At the same time Y, closely related to lanthanoides, remained outside systematic study. We have made this work using the same equation. The initial values of the constants for  $YF^{+2}$ ,  $YF^{2+}$ ,  $YF^{30}$  and  $YCl^{+2}$  at 25°C are taken from [3,4] and for  $YCO_3^+$  and  $YHCO_3^{+2}$  from [5]. Subsequent to the last-named and other authors, it is expected that Y constants bear close similarity to the middle (mean-numbered) REE due to their greatest similarity to the ion radii and other Y properties. At the same time the change of stability constants of halogenide and carbonate Y complexes is acceptable at 25-500°C within the range of variations of the constants for the whole group of REE. This is related to the fact that on the one hand Y is an electronic analogy of La, but on the other one it is close to Lu, the finite member of REE row, which has a complete electronic f-subshell. Besides, the similar change of Y position in the lanthanoide series, depending on the temperature, is revealed for its hydroxide complexes in accordance with their HKF parameters given in [6].

The thermodynamic modeling of the scales and peculiarities of the solubility of REE and Y fluorides in the oreforming fluid of the complex composition has been carried out with the help of the "HCh" software package [7]. At the first stage, the influence on the final results of deviations in the initial constants of the solid REE fluorides (presented both in [8] and [9]) has been evaluated. It is found out, that the total REE concentrations for Nd and Eu differ no more than by 0.1-0.2 log. units, and for La and Y they are about 0.3-0.4 log. units. Because the deviation reaches 1.5 order of magnitude for Ce, this requires additional thermodynamic analysis of the possible reasons and the choice of the most justified values of the initial constants.

The second stage of modeling reveals the influence of the change of natural fluid on solubility of the mixture of fluorite and eleven selected fluorides of REE and Y, including those which are usually analytically determined in geochemical objects, using the method of neutron activation [10]. In this case the initial constants for solid phases are taken from [8], where the complete set of needed information for all REE-Y fluorides is presented. The composition and P-T parameters of the evolving model fluid are selected on the basis of the generalized results of the study of gas-fluid inclusions in vein quartz of different stages of formation of Iultin, Khingan (Far East, Russia), Akchatau (Kazakhstan) and other REE deposits

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Fig. 1. The dependency of solubility of Ca, Y and REE fluorides on the composition and P-T parameters of the developing fluid.

The following main conclusions can be made based on this Figure: 1) the closeness of total fluorine concentration, obtained as a result of dissolution of the model fluoride mixture (the upper curve), to both the results of investigations of fluid inclusions in quartz [11] and to the evaluations, presented in [12]; 2) the drawing together of CaF2 solubility with the solubility of REE-Y fluorides during temperature decrease and chemical evolution of ore-forming fluid; 3) the most high and close to CaF<sub>2</sub> level of solubility for fluorides of Eu, Yb, Sm, which can be present in natural fluid in both three- and twovalence forms [13]; 4) the minimum solubility of Y and Tb fluorides, which is by 4-5 orders of magnitude lower than CaF<sub>2</sub> solubility; 5) the sparing and sufficiently close (within one order of magnitude) solubility of fluorides of the mixed REE group (light La, Pr and Nd, intermediate Ho, heavy Lu); 6) the conditional position of solubility curve for CeF3, related to mentioned above divergence of literature data on its thermodynamic constants. On the whole, the obtained results should be very useful for further development of physicochemical principles of the use of REE-Y as the markers of their fractionation in the processes of hydrothermal formation.

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## Kunts A.F. Hydrothermal-metasomatic barite formation in carbonate rocks (experimental models)

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The largest commercial barite concentrations occur in hydrothermal-metasomatic deposits confined to sedimentary rocks (first of all, carbonate rocks). The ore is formed chiefly at the expense of Ba<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> supplied to the metasomatic zones by strongly mineralised fluids. Barite is deposited when these fluids react with the carbonate rock horizons favourable for the ore accumulation at temperatures within the 100-300°C range.

The purpose of our experiments was to model formation of barite (Bar) and accompanying minerals - fluorite (Flu) and quartz (Q), and to find out the most favourable conditions for the formation of different types of barite ore. The experiments involved fluids of different compositions and pH factors and were conducted at temperatures from 150 to  $350^{\circ}$ C.

At the first steps of the experiments, we mostly used mixtures of  $Na_2SO_4$  and  $BaCl_2$  solutions with concentrations close to those of barite-forming fluids. At 250°C, we obtained a

metasomatic column with two zones, a barite zone and a transient one (Fig. 1).



**Fig. 1**. Barite-fluorite-quartz metasomatic zoning in carbonate rocks. Zones: I - barite; II - barite-quartz- fluorite; III - quartz-calcite; IV - unaltered limestone.

The former consisted of barite with some quartz which content reached its maximum at the zone boundary. In the transient zone, barite filled the intergranular spaces and voids in calcite (Calc). Interaction of Ba- and SO<sub>4</sub>-bearing acid chloride solutions with limestones produced barite mineralisation at  $t=150-300^{\circ}$ C; at higher temperatures, no barite was observed (Fig. 2). The interaction of carbonate rocks with neutral barium-bearing solutions (H<sub>2</sub>O) did not produce barite, the transformation being expressed in the washout of Si and Fe and a weak calcite recrystallisation (Fig. 2).

In the barite-bearing zones, barite occurs in the impregnated form. At the front of metasomatism, the rocks are strongly corroded, calcite recrystallised. Four zones have been recognised within the metasomatic column: barite, barite-quartz with pyrite (Pyr), barite-quartz-calcite, and barite-quartz-calcite-pyrite. The major role in the formation of the metasomatic columns is played by the opposed diffusion of barium, calcium, silicon, and iron. Barium is supplied by the fluid, and all other components are washed out from the carbonate. The ability of Ba and Si to migrate falls with rising temperature, while that of iron increases. The metasomatic columns become thinner with temperature (1.8 times from 150 to 200°C).

The Flu-Bar association is formed when the carbonate rock comes into contact with moderately acid  $Ba^{2+}$  and  $SO_4^{2-}$  bearing fluoride solutions throughout the entire temperature range (150-350°C); this process is particularly active at temperatures below 200°C, while higher temperatures stimulate active fluorite formation.

The Flu-Bar-Q mineralisation is produced by the interaction of carbonate with  $Ba^{2+}$  and  $SO_4^{2-}$ -bearing silicon-fluoride fluids. The metasomatic columns are thin (0.25-0.50 mm),with one or two zones. In contrast to the experiments with purely fluoride solutions, a rise in the temperature brings about an increase in the Bar content in the metasomatic columns. Silicon, barium, and iron are supplied to the front of metasomatism at t=150-250°C, giving rise to a peculiar zone of pre-ore alteration of the host rock, thickness of the zone falling with increasing temperature.



t=350<sup>0</sup>C 80 Са 40 Si мм 0 -3× -40 Fe -80 -120 Calc Cal Pyr 0 BaSO<sub>4</sub>-HCI-H<sub>2</sub>O t=250°C 80 Вa (Ci-Cx), % 0

BaSO<sub>4</sub>-HCI-H<sub>2</sub>O

(Ci-C<sub>x</sub>), %





Fig. 2. Metasomatic alteration of limestones under the action of  $Ba^{2+}$  and  $SO_4^{2-}$ -bearing hydrothermal fluids.

# Plyusnina L.P., Kuz'mina T.V., Nekrasov I.Ya. Experimental modeling of gold sorption on organic matter at 20-500°C, 1 kbar

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Over the past decades interest has been increased in Cbearing rocks enriched in noble metals. An ability of carbonaceous matter (CM) to accumulate noble metals was usually connected with the chemical sorption of metals onto CM [1, 2]. However, a metamorphic effect on its sorption activity is discussed hitherto. Experimental study of Au sorption on bitumens at 200-300°C and  $P_{tot} = 1$  kb marked an increase in sorption capacity with temperature [1]. On the contrary, G. M. Varshal with co-authors [2] using empirical data had concluded that the sorption capacity of coals in relation to the noble metals decreases with increasing degree of their metamorphism. Besides, an effect of Cl presence in a metamorphic fluid on the sorption ability of CM in relation to Au is also problematic [3].

Thus, the goal of the paper was experimental study of the Au sorption on CM in water and 1mNaCl solution at 20-500°C and 1 kb. Asphaltenes (As) and asphaltenic acids (Ac) composing about 80% of fractionated coals were chosen as model CM. Hydrothermal experiments were conducted in externally heated Ti or Ni autoclaves. Solution and 50 mg of the dry As (or Ac) were placed in Au ampoules, which also served as a source of Au for dissolution. In the system, the reaction C + 2H<sub>2</sub>O = CH<sub>4</sub>(g) + O<sub>2</sub>(g) is the principal redoxcontrolling one [4], that is why inorganic solid buffers were not used in the runs. After each run, CM precipitated on the filters was fractionated at 50°C with an alcohol-benzene (1:2) mixture for 12-20 hours. Thus, organic soluble fraction (SF) and solid residue (R) were derived. The Au content in both fractions was analyzed by AAS with about 20% accuracy, and IRspectroscopy of starting As and Ac and run products (SF and R) was performed. The X-ray analysis of R was used to control the beginning of CM graphitization, fixed at  $T = 500^{\circ}C$ . Experimental results are shown in Table 1.

t°C	СМ	log C <sub>Au</sub> in SF		log C <sub>Au</sub> in R		τ, hrs	Ls
		H <sub>2</sub> O	1mNaCl	H <sub>2</sub> O	1mNaCl		
20	Ac	-5.37	-	-	-	816	6
20	As	-5.58	-	-	-	816	2
200	Ac	-4.30	-4.69	-3.78	-4.55	624	33
300	Ac	-3.84	-3.29	-2.34	-3.04	336	45
400	Ac	-4.23	-4.60	-2.29	-2.67	240	74
400	As	-4.25	-	-2.44	-	240	55
500	Ac	-3.89	-	-1.72	-	168	92
500	Ac	-3.79	-	-1.82	-	24	90

Table 1. Au content (mole per 1 kg of dry matter) in the soluble fraction (SF) and solid residue (R)

CM - carbonaceous matter; Ls – weight loss of CM (%);  $\tau$  - run duration.

It turns out, that abundance of SF and R in the run products varies depending on both T and runs duration. As a rule, with an increase in either of these variables the R/SF ratio grows, indicating the enhanced degree of aromatic condensation. The measured Au contents ( $C_{Au}$ ) show that most of gold was sorbed on R in direct dependence on T ( $\geq 200^{\circ}$ C), while  $C_{Au}$  in the SF does not depend on T. It may be connected with different character of gold complexation in the fractions. In the SF, where aliphatic CM is predominant, the complexation of Au with CO and COOH functional groups is typical. In the R, with

prevailing aromatic CM content, the more stable Au-C connections are leading. It is followed by the increase in sorption capacity of R up to  $n \cdot 10^{-2}$  mole Au per kg of dry CM at 400-500°C. It is known that thermal destruction of hydrocarbons results in the formation of activated free radicals favorable for the reactions of metal addition [5]. The high sorption capacity of the CM in relation to Au, revealed in the study at T > 400°C, is accompanied by its destruction, dissolution and gas exsolution that tends to decrease total organic mass. Thus, the Au sorption on activated CM may be

an effective mechanism of gold accumulation in the C-bearing rocks even at their metamorphic alteration.

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# Golubev S.V., Savenko V.S. Solubility of CaF<sub>2</sub> in seawater and interstitial waters of marine sediments.

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In spite of poverty of information on the presence of fluorite in marine phosphorites its concentration can reach high Table 1

amounts - 2-3% [Krasilnikova et al, 1961]. It is known that accumulation of fluoride occurs in interstitial waters of marine sediments containing phosphate material in zones with high biological productivity: at the shelves of South America and South-West Africa [Shishkina, 1972; Baturin, 1978], however the conditions of CaF<sub>2</sub> formation remain unclear.

The average concentration of fluoride in interstitial waters is near 2.7 mg/l: it is twice as high as in seawater. In interstitial waters of marine sediments in the zones with high biological productivity concentration of fluoride can increase up to 8-11 mg/l [Shishkina et al, 1972].

Solubility of CaF<sub>2</sub> is defined not only from the total concentrations of calcium and fluoride, but by the concentration of magnesium due to its complexation with fluoride. Concentration of calcium and fluoride can vary in a wide interval changing the saturation state of solution with respect to CaF<sub>2</sub>. The aim of this study is experimental investigation of CaF<sub>2</sub> solubility in the solution imitating seawater and interstitial waters of marine sediments.

Reagent grade chemicals and distilled water were used to prepare solutions with different concentration of calcium and magnesium containing all other components found in natural seawater. All solutions after the addition of solid phase (CaF<sub>2</sub>) were stirred many times. After 6 mounts all solutions were filtered through a membrane filter. Solutions were analysed for dissolved Ca and Mg by titration. Fluoride-ion was analysed using fluoride-electrode; total concentration of soluble F was determined using a "method of addition". The results of all experiments are presented in table 1.

N⁰	[∑F], mkM	$[\Sigma Mg], mM$	[∑Ca], mM
1	89.5	0	39.75
2	107.9	6.40	33.40
3	139.2	15.10	23.85
4	184.4	23.60	15.70
5	277.2	31.10	7.75
6	726.8	37.35	0.95
7	194.9	0	10.43
8	236.8	12.55	8.15
9	314.9	23.95	6.05
10	430.3	35.35	4.30
11	598.5	45.75	2.40
12	969.9	57.23	0.90

Total concentration of fluoride  $[\Sigma F]$ :

 $[\Sigma F] = [F^{-}] + [CaF^{+}] + [MgF^{+}] = [F^{-}] \{1 + K_{CaF}^{+} [Ca^{2^{+}}] + K_{MgF}^{+} [Mg^{2^{+}}]\},$ 

where  $K_{CaF}^{+}$   $\mu K_{MgF}^{+}$  -the constants of stability of complexes CaF<sup>+</sup> and MgF<sup>+</sup>.

Using the equation for solubility  $L_{CaF^2}=[Ca^{2+}][F^-]^2$  we can write the next equation:  $[\sum F][Ca^{2+}]^{0.5}=L_{CaF^2}^{0.5}\{1+K_{CaF}+[Ca^{2+}]+K_{MgF}+[Mg^{2+}]\}, ,,(1)$ 

and for constant of sum of calcium and magnesium concentration:

 $\sum_{F} [Ca^{2+}]^{0.5} = L_{CaF^2}^{0.5} \{1 + K_{CaF}^{-+} [Me^{2+}] + K_{MgF}^{++} (1 - K_{CaF}^{-+}) [Mg^{2+}]\}, (2)$ where  $[Me^{2+}] = [Ca^{2+}] + [Mg^{2+}].$ 

Equations (1) and (2) we can write like y=a+b\*x, where for (1):  $y=[\sum F][Ca^{2+}]^{0.5}/(1+K_{CaF}^{+}[Ca^{2+}]); a=L_{CaF^2}^{0.5}; x=[Mg^{2+}]/(1+K_{CaF}^{+}[Ca^{2+}]); b=K_{MgF}^{+}L_{CaF^2}^{0.5}, and for (2): <math>y=[\sum F][Ca^{2+}]^{0.5}; a=L_{CaF^2}^{0.5}(1+K_{CaF}^{+}[Me^{2+}]); x=[Mg^{2+}]; b=K_{MgF}^{+}(1-K_{CaF}^{+}).$ Figures 1 and 2 show conformity of our experimental data with the equation  $y*10^{-5}=a+bx*10^{-3}$ .



Fig.1.

According to our experimental data  $L_{CaF2}=2.90*10^{-10}$ . Conversion to termodynamical solubility gives  $L^0=3.05*10^{-11}$ , (p $L^0=10.52$ ). This value is in a good agreement with the reference data (p $L^0=10.40$  [Lurie, 1971]). Using experimental results the diagram of correlation between concentration of equilibrium with CaF<sub>2</sub> fluoride and concentration of magnesium in seawater can be plotted (fig. 3).



Fig. 3.

As it is seen from fig.3, the solubility of  $CaF_2$  in magnesium-free seawater is by 1.5 times lower than in normal seawater. Interstitial waters of marine sediments (with normal concentration of magnesium – 53 mM) in the zones with high biological productivity containing 8-11 mg F/l can be supersaturated with respect to  $CaF_2$ .

As a result of changing of magnesium concentration in interstitial waters of marine sediments due to formation of dolomite or magnesium silicates [Initial reports of the deep sea drilling project, 1978, 1979, 1980, 1981] the saturation state of solutions with respect to  $CaF_2$  decreases. On the base of our experimental data we can conclude that precipitation of  $CaF_2$  can take place not only in interstitial waters of marine sediments in the zones with high biological productivity but due to the extraction of magnesium in marine sediments.

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Fig. 2.

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<sup>#</sup>Varshal G.M., Velyukhanova T.K., Chkhetia D.N., Kholin Yu.V.<sup>2</sup>, Shumskaya T.V., Tyutyunnik O.A., Korochantsev A.V., Koshcheeva I.Ya., **Bykov** I.V., Galuzinskava A.Kh. Experimental study the of processes of concentration of gold and platinum group elements in black shales

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A carbonaceous substance of black shales is a result of diagenetic and metamorphic transformations of humic acids (HA), which are the main constituents of organic substance of fluvial and marine sediments, soils, and aqueous suspensions. In order to find out a mechanism of accumulation of gold and platinum group elements (PGE) in black shales and qualitatively estimate the strength of chemical bonding of the elements with the carbonaceous matrix, data on nature and protolithic features of oxygen-bearing functional groups HA and data on sorption capacity of HA with respect of rare metals are necessary. HA, extracted from peat, as well as from marine sediments of the Peru oceanic shelf, were chosen as objects for the present study. HA properties were studied by the methods of IR-spectroscopy, potentiometric titration, CHNS analysis, and x-ray. The infrared spectra of HA from peat are very similar to that of HA from marine sediments. They show an intensive absorption peak at 1605-1630 cm<sup>-1</sup>, which corresponds to valent asymmetric oscillations of ionized carboxyl groups; distinct absorption peak at 1700-1720 cm<sup>-1</sup> corresponding to valent asymmetric non-ionized carboxyl groups; and absorption peak at 1040-1050 cm<sup>-1</sup>, which is characteristic of oxygen groups. The presence in the structure of HA of carboxyl groups and phenol oxygroups provides a

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possibility for formation of strong complex compounds with ions of rare and other metals.

The potentiometric titration of ashless samples of HA was performed by the method of separate charges with KOH aqueous solution, purified from carbon dioxide. Three distinct peaks were found on the differential curves of the potentiometric titration of HA from peat, two peaks were studied on the titration curve of HA from marine deposits. Values of dissociation constants for the functional groups HA  $(pK_a)$  were measured from the data on the pH-metric titration using the quantitative physico-chemical analysis (QPCA) [1]. A transformed Langmuir equation with isothermal parameters, calculated by the least square method using the CLINP 1.0 program, was used for calculations. It is found, that values of dissociation constants for carboxyl groups from both HA vary in a wide intervals: 5-7 at mean value  $pK_a=6.1$  for peat, 6-8 at mean value  $pK_a=7$  for marine sediments. Distribution of the functional groups by dissociation constants agrees with the Gauss distribution law.

Contribution of aliphatic and aromatic complexes into the structure of HA was estimated using the data on x-ray analysis by means of splitting experimental diffraction patterns of HA into individual peaks [2]. This contribution into peat HA is 77.2 % and 22.8 %, respectively, and 66.0 and 34.0 for marine sediments.

Sorption of ions Au(III), Pt(IV), Pd(II) Rh(III), Ru(IV), Os(IV) as their chloride complexes on ashless charges of acids, extracted from peat and marine sediments, was studied in the model experiments. It is shown that an equilibrium in the system HA-PGE is reached in 2-24 hours, whereas an equilibrium in the system Au(III)-HA is observed in 7 days. It is found that HA from peat and marine sediments have a relatively high and similar for the both types sorptive capacity with respect to ions Au(III), Pd (II), and Rh(III). The sorptive capacity for HA from peat is 320 mg/g for Au, 100 mg/g for Pd, 11 mg/g for Rh, 16-19 mg/g for Ru, 23 mg/g for Os. The sorptive capacity for HA from marine sediments is 351 mg/g for Au, 110 mg/g for Pd, 11.6 mg/g for Rh.

An interesting phenomenon was found for sorption of platinum (IV). It is found that HA from peat and marine sediments, in contrast to other carbonaceous compounds, i.e. coals, carbonaceous particles in rocks, bitumen [2], does not sorb Pt(IV). The reason for that is very important for understanding genetic features of rare ore formation in black shales.

Treatment of data on sorption of gold ions and PGE by the QPCA methods allows to estimate a strength of chemical bonding of the ions with the sorption centers of HA. It is shown that sorption of gold(III), palladium(II), and rhodium(III) on HA from peat and marine sediments is satisfactorily described by the equation of the Langmuir's isotherm. Calculation of isothermal parameters using a non-linear least square method allows to deduce values of conventional constants of affinity of sorption centers of HA with respect to rare metal ions (Table). These constants are a quantitative characteristics of the strength of chemical bonding of metal ions with the functional HA groups.

Table. Conventional constants of affinity of HA sorptioncenters with respect to Au(III) and PGE ions

Metal ion	lg β			
	HA of peat	HA of marine		

		sediments		
Au(III)	4.4	6.0		
Pd(II)	4.7	5.0		
Rh(III)	3.4	3.2		
Ru(IV)	3.5	-		

Calculations of functions of distribution of HA sorption centers by logarithms of the conventional affinity constants with respect to each metal ion using the CAS algorithm showed that the functions were in accordance with the Gauss distribution function. An energetic inhomogeneity of the functional HA groups during the sorption of the above metal ions practically does not appear.

Strength of chemical bonding is the parameter which determines a relation of chemical species of rare metals in carbon-bearing rocks and a possibility of their commercial and analytical extraction.

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# Livshits L.D., Pernik L.M. Permeability of wet sand.

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An air permeability of the unconsolidated porous media containing liquid, which moistens a solid phase, at the small Reinolds numbers is experimentally studied. In addition to well-known ideas, it is shown, that a coefficient of permeability  $K_G$  for wet media is larger then that for dry media for similar porosity.

Gas transportation in a porous media containing a liquid phase plays an important role in the processes, which relate to many branches of science and technology. In nature, it is significant for the processes in solid Earth's spheres (crust and mantle degassing, ore formation, recycling in the subduction zones), their interaction with hydrosphere (for example, in the rift zones), biota (on different levels), and with atmosphere (escape of gases from soils). Because of its complexity, the phenomenon is studied mostly by means of direct experiment. As a rule, numerical models are restricted by geometrically ordered systems and weak fluxes.

A general conclusion, which can be done from the published studies, is that liquid in porous media creates an additional resistance to transport of gas flux, because of narrowing a free space and requirement of gas bubbling through the viscous liquid.

The purpose of the present study is to investigate an influence of partial filling of the porous space in the unconsolidated media by moistening liquid on the gas transportation at small Reinolds numbers (Re).

Quartz sand was used as a model media. Sand grains are rounded, their predominant size is 0.25-0.35 mm. Sand was preliminarily washed and dried at temperature above  $100^{\circ}$ C.

Water was added to the sand charge, and the charge was carefully stirred in order to produce a homogeneous water distribution in volume. A good reproduction of runs shows, that such procedure is satisfactory.

Permeability was measured at uni-dimensional steady gas streaming within the Darcy law operation. The runs were carried out by upward air streaming in cylindrical tubes. The air escape was measured by rotameter. Pressure was measured by water manometer. Flux rate per cylindrical area was about 0.01 m/sec, pressure gradient was about 10 Pa/m, Re < 0.1-1.

Water content varied from 5 to 70 % of dry porous space. An increase of air escape at above 40 % causes an escape of water to upper layers and surface of the sample with an abrupt changes of its effective permeability. Sand saturated in water acquires features of the consolidated porous media, where water moves predominantly along the water-generated fissure net-work, the gaseous phase looses its continuity, and its motion becomes unstable, that is characteristic for two-phase streaming (bubbling, mostly, along separate channels and wall layer, etc.). Water leaves the surface after ceasing air supply.

Water behaves as a residual liquid at its content below 40 %. Suspension and flooding are not observed, air flow is unstable. In this region at similar porosity,  $K_G$  is 1.4-1.5 times higher, than that of the dry system. If water occupies less then 20 % of the porous space,  $K_G$  does not decrease, and even can increase. Discussing the results, which can be regarded as preliminary, we note, that water firstly moistens narrow inactive zones of the porous space, while a decrease of the free space, apparently, is compensated by changes of the mechanisms of gas sliding along wet walls and an increase of hydraulic radius of channels (in the case of hexagonal packing of spheres, it has a maximum of filling at about 20 % of the narrowest area).

# Likhoidov G.G., Plyusnina L.P., and Afanas'eva T.B. Kinetics of gold and platinum solubility in the formation of Mn-compounds

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In connection with the problem of the genesis of Pt (Au)bearing ferromanganese crusts the solubility of metallic Pt and Au in water and aqueous chloride solutions was studied experimentally at 200-400°C and 1 kb total pressure. To define the oxygen fugacity the next starting mixtures were used: MnO- $Mn_{3}O_{4}$  (Mn1),  $Mn_{3}O_{4}$ -Mn<sub>2</sub>O<sub>3</sub> (Mn2), and  $Mn_{2}O_{3}$ -MnO<sub>2</sub> (Mn3). The HM traditional buffer was used for comparison. Experiments were conducted in externally heated autoclaves made of Ti and Ni alloys for temperatures less and more than 400°C, correspondingly. Accuracy of T and P was equal to  $\pm 2.5^{\circ}$ C and  $\pm 50$  bar. walls of welded Pt and Au ampoules were used as a source of Pt and Au . The charges included 3-5 gr of starting solution (water, 1mNaCl, or 0.1mHCl) along with 200-250 mg of buffer mix per run. Optical and X-ray diffraction analyses were used to control the final buffer composition. The Pt and Au contents in quenched solutions were measured by

AAS with an accuracy of  $\pm 20\%$ . Experimental results are shown in Table 1.



**Fig.1,2.** The kinetic curves of platinum (a) and gold (b) dissolution in different media at 300°C, and 1 kb total pressure. Arrow notes metal precipitation upon quenching

X-ray analysis of the final Mn1 phase composition has revealed that, at 200 and 300°C, MnO was oxidized to Mn<sub>3</sub>O<sub>4</sub> with spontaneous formation of a new solid phases:  $\beta$ -MnOOH, Mn(OH)<sub>2</sub>, and Mn<sub>2</sub>(OH<sub>3</sub>)Cl. These intermediate hydroxides are metastable in virtue of their disappearance in the course of prolonged runs, which result in crystallization of Mn<sub>3</sub>O<sub>4</sub> alone. The transformations in Pt or Au bearing systems are accompanied by an increase in both Pt and Au content in coexisting solutions to about 1-2 orders of magnitude in terms of molality. Some of the runs finished with precipitation of Pt metal globules during quenching. Such precipitation of Au was noted only in unit runs, whose final solid mixture contains about 50% of Mn(OH)<sub>2</sub>. Kinetic runs show that maxima of Pt and Au content in coexisting solutions coincide with maximal crystallization of bulk Mn-hydroxides. In the end, their spontaneous transition into Mn<sub>3</sub>O<sub>4</sub> is accompanied by an essential decrease in both Pt and Au content in guenched solutions. So, mentioned kinetic anomaly accompanied nonequilibrium processes in the systems.

The following sequence of Mn-mineral assemblages was fixed at 200°C in the 1mNaCl and 0.1mHCl solutions depending on runs duration: MnO  $\rightarrow \beta$ MnOOH + Mn<sub>3</sub>O<sub>4</sub> (9 days)  $\rightarrow$  Mn(OH)<sub>2</sub> + Mn<sub>3</sub>O<sub>4</sub> +  $\beta$ MnOOH (15 days)  $\rightarrow$  Mn<sub>2</sub>(OH)<sub>3</sub>Cl +  $\beta$ MnOOH + Mn<sub>3</sub>O<sub>4</sub> (30 days)  $\rightarrow$  Mn<sub>3</sub>O<sub>4</sub> (60 days). As to the Au-bearing system, the sequence of phase transformation remains the same, but proceeds within more long period (Fig.1 and 2).

With increasing T, a life expectancy of the metastable Mnhydroxides has declined. At  $300^{\circ}$ C, the MnO converts to Mn<sub>3</sub>O<sub>4</sub> during 15-30 days in aqueous chloride solutions or in water, respectively. At  $25^{\circ}$ C, the oxidation time is about 17 months [1].

Table 1. Platinum and gold content in quenched solutions

Solutio	logm	$\tau$ bro	Buffer	logm	$\tau$ hrs	Buffer
n	Pt	ι, 1115	Duilei	Au	ι, 1115	Duilei
H <sub>2</sub> O	-6.51	720	[Mn1]	-5.76	480	[Mn1]
H <sub>2</sub> O	-5.89	720	Mn3	-4.9	480	Mn3
1mNa Cl	-5.68	720	[Mn1] *	-5.21	480	[Mn1]
1mNa Cl	-5.01	720	Mn3	-4.47	480	Mn3
0.1HCl	-5.05	720	[Mn1] *	-4.84	480	[Mn1]
0.1HCl	-3.81	720	Mn3	-4.66	480	Mn3
			300°C			
H <sub>2</sub> O	-3.86	168	[Mn1] *	-6.18	754	[Mn1]
H <sub>2</sub> O	-5.87	330	Mn2	-5.76	240	Mn2
H <sub>2</sub> O	-5.61	248	Mn3	-4.72	240	Mn3
H <sub>2</sub> O	-6.32	248	HM	-	-	-
1mNa Cl	-5.55	330	[Mn1] *	-4.15	198	[Mn1] *
1mNa Cl	-5.65	264	Mn2	-4.42	240	Mn2
1mNa Cl	-4.15	264	Mn3	-3.3	198	Mn3
0.1mH	-3.85	168	[Mn1] *	-	-	-
0.1mH	-5.48	330	Mn2	-4.3	198	Mn2
			400°C			
HaO	-5.88	188	Mn1	-619	238	Mn1
H <sub>2</sub> O	-5 72	188	Mn2	-5.35	238	Mn2
H <sub>2</sub> O	-4 79	168	Mn3	-4 67	230	Mn3
H <sub>2</sub> O	-5.82	168	HM	-		-
1mNa Cl	-5.7	175	Mn1	-5.6	168	Mn1
1mNa Cl	-4.95	198	Mn2	-4.81	238	Mn2
1mNa Cl	-3.68	175	Mn3	-2.31	168	Mn3
1mNa Cl	-5.73	175	HM	-	-	-
0.1mH Cl	-5.46	175	Mn1	-4.82	144	Mn1
0.1mH Cl	-5.66	175	Mn2	-4.35	238	Mn2
0.1mH Cl	-2.87	166	Mn3	-	-	-
0.1mH Cl	-5.39	166	HM	-	-	-

m - molality;  $\tau$  - run duration in hrs; \* - metal deposition upon quenching;

The square parentheses mark changes of starting buffer compositions

Established catalysis effect of Pt on Mn(II) oxidation may be described by step-by-step reactions:

 $MnO + Pt(OH)_{2}^{o} = \beta MnOOH + Pt_{met} + 0.5H_{2}O + 0.25O_{2},$ 

 $3\beta MnOOH + Pt(OH)_2 = Mn_3O_4 + Pt_{met} + 0.75O_2 + 2.5H_2O.$ 

Liberation of oxygen in the course of the interaction is favorable for Mn(II) oxidation.

At 400°C, MnO is stable and the Mn1 buffer mix preserves initial phase composition forever. On the kinetic curves of the

Pt and Au dissolution, any maxima are absent. Kinetic curves representing runs with the HM and Mn1 buffers, causing the same oxygen fugacity, essentially coincided. Thus, it suggests the same mode of approachment to equilibrium.

The Mn2 and Mn3 buffers are stable at any of studied temperatures. Under the stable existence of Mn-bearing oxygen buffers, the above-mentioned kinetic effect of noble metal solubility was not examined. The metastable crystallization of

Mn-hydroxides is well-known in ocean floor media [2]. Thus, the kinetic effects may be used for modeling the noble metals accumulation in oceanic Mn-bearing nodules and crusts.

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# <sup>#</sup>Akinfiev N.N., Ezhov S.V. Experimental and thermodynamic simulation of the coskarn ore deposition

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The intrusive activity going with gradient thermal aureoles formation around the massifs of magmatic rocks does induce reallocation of metals. The concepts of regular metals leaching from sedimentary or volcanogenic rocks in the intrusive thermal field, transporting of ore components by a convective flow, and their concentrating in the area of contact-metasomatic zones are in the base of convective ore formation model in skarn that is being under the development by now [1]. The

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speciality of the model is the admission of an initial infection of the system in ore components: an impurity of ore metals in skarn is initial, but not introduced by later portions of solutions. Thus metals from the very beginning participate in the processes of mineral formation together with other petrogenic elements. The simulation could not only affirm such a possibility, but also display the main features of these processes.

More than hundred experiments of bimetasomatic mineral formation in the systems initially enriched by ore elements had been carried out in the Lab of Ore Deposits Modelling (IEM) during last years. It was shown, that in the whole skarn formation temperature range (350-600°C) the deposition of ore minerals definitely correlates with bimetasomatic zones, and the most concentrated deposition is observed on boundaries between separate zones [3] (fig. 1). The coskarn deposition of galena, sphalerite, chalcopyrite, pyrite, magnetite, chalcosine, scheelite, powellite, native gold, copper, platinum, etc. is experimentally reproduced. Thermodynamic simulation of coskarn ore deposition process was carried out with the help of code "BALANCE" [4], designed for computing equilibria in multisystems. At the first step the methodology problem of such a simulation was set. Galena, sphalerite, and chalcopyrite were assigned as ore minerals. The computation runs were conducted for temperature 450°C and pressure 1 kbar. The salinity of the fluid was assumed to be 0.3 mol/kg NaCl.



3

2

1

Fig. 1. Experimental skarn column. 1 – Ep+Ksp, 2 – Ep+Cpx; 3 – Wo+Gr; 4 – Cc; white – sulphides



Fig 2. The computational skarn colun



Fig 3. Equilibrium concentrations of ore elements vs column zones

The initial presence of galena, sphalerite and chalcopyrite in the system enables to observe regularities in ore minerals solubility at each of isolated zones. The general regularity is that equilibrium concentration of ore elements definitely falls while moving from granitoid toward carbonate zones (fig. 3). So the concentration of Pb and Zn decreases more than in 20 times, copper – in 100 times. The drop of ore components solubility in pore solutions controls their deposition on the boundaries of skarn mineral zones.

The proposed method also allows to model gradients of deposition of various ore elements. In our case it is brightly exhibited concerning copper. So, if lead and zinc are deposited in the first three zones in about equal amounts (37 and 39, 35 and 33, 28 and 27 mol % from total amount accordingly), the relative amount of copper essentially varies: from 23 mol % in a zone of the slightly invided granitoid, up to 45 % in endoskarn. The 100 % of total ore load lay on copper in the exoskarn part of the column.

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1. Ezhov S.V. Convective model of formation of skarncomplex deposits of Altyn-Topkan region as a basis for the

The process of coskarn column formation was simulated by step-bystep magnification of a carbonaceous material (calcite) amount in the originally granite system. Thereby diffusion of opposite fluxes of components from the uninvaded granitoid and calcite was imitated. Such a flux cause change in the pore solution composition. Thus minerals of an initial silicate rock (quartz, anorthite, biotite, accessory magnetite) become unstable relative to the changing solution, being completely diluted on those or diverse stages of the process. Simultaneously appearance of new minerals typical for skarn paragenesises takes place. Their appearance and disappearance is also step-typed, that displays the key feature of bimetasomatic process (fig. 2). The first one, starting from the uninvaded granitoid, epidote arises. This zone can be correlated with the granitoid which has exposed to a slight changes variation in a halo of skarn stratum. As to the next zone of epidotepypoxene-plagioclase rocks the appearance of hedenbergite and disappearance of quartz is typical. After that epidote-pyroxenegrossularite endoskarn zone is allocated (appearance of grossularite, disappearance of plagioclase). The exoskarn part of a column is presented (especially by pypoxene-garnet garnet-wollastonite andradite) and zones. Such a sequence of zones is identical completely to manv experimental and natural columns of skarn deposits.

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This article is devoted to the features of vein quartz from the gold-silver different scale deposits, localized within East-Asiatic volcanogenic belts.

The samples of vein quartz from the ore bodies and from the quartz veins formed on different removal from intensive geochemical anomalies "ore nature" and without ore mineralization in the different methasomatic facies have been studied. This quartz belongs to single generation - vein overflow quartz. However intensity of gas emission, and, consequently, energy factor of fluide of thisquartz are different. There are three groups of quartz samples differing in this parameter : with high, average and low gas emission (Fig.1).

The average scale deposit Dvoinoi has been choosen for demonstration. This object is situated within Illirnei ore district (area 40x30 km), covering south part of volcanogenic Tytylveem depression and east part of Illirnei granite array. Ore knot Dvoinoi (area 18x12 km) locates on the joint of south part of volcanogenic Tytylveem depression and east part of Illirnei granite array. The cover and subvolcanic facies of andesites which are under multiform and deep hydrothermal influences, are widespread. Ore bodies belong to the goldquartz-sulphide type of gold-silver formation and represents quartz and adular-quartz veins.

Sampling was carried out at diametrical profiles, according to the methods [1].

For the study by EPR and Tl methods samples (fraction 0,2-0,3 mm) were prepared by the methods [2, 3]. For the clarification of radiation dependence the study of amount of electronic centers has been carried out on samples having got a dose of natural irradiation and irradiated in addition by gammaquantums (integral dose 1 Mrad) from the source <sup>60</sup>Co ( dose 50 rad/sec).

The study of the number of O- -Al - and E- centres in monofractions of quartz was carried out using standard techniques [3]. Determination of contentrations of centres was produced by means of the internal standard (Cr in  $Al_2O_3$ ), situated inside the resonator.

Curves of thermoluminescence have been taken on the modified instrument "TERMOLUM" in the interval 20-450°. The measurement of accumulated lightsum was carried out relative to specially prepared sample. In EPR spectra [AlO 4]<sup>4-</sup>,  $Ti^{3+}/M^+$ ,  $Ge^{3+}$ , E- centres were fixed and their relative contents were calculated.



**Fig.1.** Typical decreptograms of quartz samples: a- with high; b- with average; c—with low gas emission **Fig.2. Distribution of E-centers, gross and** structural Al in the quartz samples of ore knot Dvoinoi

The study of spatial distribution of AL-centres in natural samples shows a sharp reduction of their quantity in the orebearing area, as well as good coincidence with particularities of distribution of gross contents of aluminum in quartz (Fig. 2). Relative contents of aluminum centres in irradiated and natural samples (Al<sub>ir.</sub>/Al<sub>nat.</sub>) were calculated. Central part of ore system, containing deposit, is noted by the clear maximum. The behaviour of titanium is similar to the behaviour of aluminum. Presence of germanium centres is connected with its presence in a fluid. The central part of an ore system is characterized by the minimum contents of E-centres. The contents of E-centres and fluid content are in inverse correlation. It is possible to expect, as far as E-centre represents a vacancy of oxygen, under the conditions of high fluid content they are occupied by fluid components (for instance, Cl<sup>-</sup>) and so the amount of E-centres will decrease. It should be noted that although such distribution of E-centres is characteristic of all the objects, whatever the scale, but the degree of contrast for small objects is vastly lower than that of medium and large ones.

The intensity of Tl peaks of all natural quartzs is vastly below that of Tl peaks of samples. For all the objects for samples from potentially ore-bearing veins in natural samples an intensive peak under  $270^{\circ}$  is observed, but in irradiated ones there is much more intensive peak under 220 degrees. Such behaviour of Tl is a result of temperature influence.

Unificated location of Tl peaks is observed after irradiation. It was investigated by the method of consequent heating on the strategy of Soukharjevsky (1984) as a result of the series of three independent experiments that Tl curves represent a position poles of peaks. An analysis of the intensity of separate Tl peaks and intensities of signal of separate electronic centers in EPR- spectra suggested the dependency between the peak under  $186^{\circ}$  and contents of E- centres, between the peak under  $160^{\circ}$  and contents of titanium centres (correlation values are 0,95 and 0,56, accordingly), but significant correlations between the intensity of Tl and contents of aluminum centres was not established.

Thereby, using the methods of EPR and TL allows to safely separate ore veins from barren, but for mapping ore areas by the Tl method it is reasonable to use not total integral intensity ,but the intensity of Tl peak under  $186^{\circ}$ .

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## <sup>#</sup>Alekseyev V.A., Medvedeva L.S., Tatsii Y.G. Distinction between mechanisms and rates of quartz–water direction and reverse reactions

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The influence of solution saturation state on the rate of quartz-water reaction  $SiO_2 + 2H_2O = H_4SiO_4^0$  is expressed by the following equation [1-3]:

$$dm/dt = k_d (1 - m/m_{eq}) S/M,$$
 (1)

where m and  $m_{eq}$  are the actual and equilibrium concentrations of silica in a solution (mol/kg); t is the time (sec);  $k_d$  is the dissolution rate constant (mol m<sup>-2</sup> sec<sup>-1</sup>); S is the surface area of a mineral (m<sup>2</sup>); M is the mass of water (kg). The overall reaction rate expressed by equation (1) is considered as a rate difference of forward and reverse reactions:

$$dm/dt = k_{d}S/M - mk_{p}S/M,$$
(2)

where  $k_p$  is the precipitation rate constant (kg m<sup>-2</sup> sec<sup>-1</sup>). The identity of the equations (1) and (2) is provided using a principle of microscopic reversibility (or detailed balancing) [2]:

$$m_{eq} = k_d / k_p.$$
 (3)

The acceptance of this principle means an assumption that the processes of mineral dissolution and precipitation proceed through a series of common elemental steps one of which controls the rate of the both processes. Due to the principle of microscopic reversibility, the equation (1) is used for the description of not only kinetics of quartz dissolution (m <  $m_{eq}$ ) well investigated experimentally, but also kinetics of its precipitation (m >  $m_{eq}$ ) with few experimental data.

To fill this gap and to test the validity of the abovementioned principle, we have carried out experiments with quartz and water (ratio of masses is 0.5) in platinum ampoules. These experiments have shown that the needed time to reach equilibrium from above is greater than that from below by approximately two orders (fig. 1). Unexpected circumstance that approaching from below, measured silica was concentrations in solution flatten out above an equilibrium concentration and the more pore size of the filter, the higher these concentrations (series B and C). This is indicative of ultra fine quartz particles yielding an additional contribution to the results of solution analyses (inductively coupled plasma spectrometry). As judged from the divergence of curves B and C with time, these particles are not primary, but formed during dissolution. They are likely to separate from the surface of large pieces as a result of preferential dissolution of micro cracks formed during quartz crushing. To diminish the influence of these particles, we have used more rough quartz fraction. This led to lowering silica concentration in solution (series D).

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**Fig.1.** Dependences of aqueous silica concentrations on time in quartz–water system at 150°C. The initial quartz grains were ultrasonically cleaned from ultra fine particles by water. The empty and filled symbols mean approaching the equilibrium from above and from below. The vertical lines with bars designate the scatter limits of the published values of  $\alpha$ -quartz (Qtz) and  $\alpha$ -cristoballite (Crs) solubilities.

However, there was a suspicion that ultra fine particles also distorted the shape of kinetic curves for this fraction. Because of this, we treated the rough quartz fraction in addition with fresh batches of water (5 times each during 3 days) at 250°C. After such treatment, the initial dissolution rate of this fraction has indeed decreased by 30 times (series D' in fig 2 in comparison with series D in fig 1). For series D', seven values of  $k_d$  are calculated using the integrated form of equation (1):

$$k_{d} = -m_{eq}/t/(S/M)ln((1-m/m_{eq})/(1-m_{0}/m_{eq})), \qquad (4)$$

where  $m_0$  is the initial silica concentration in solution (mol/kg). The mean value of  $k_d$  is  $(9.7\pm2.2)\times10^{-11}$  mol m<sup>-2</sup> sec<sup>-1</sup>. It practically coincides with the published dada [3]. The quantity m can be calculated from the equation (4) after its transformation:

$$m = m_0 \exp U + m_{eq} (1 - \exp U), \qquad (5)$$

where  $U = -t(k_d/m_{eq})(S/M)$ . The curve D' (fig. 2) relevant to the equation (5) with  $m_0 = 0$ ,  $S/M = 20 \text{ m}^2 \text{ kg}^{-1}$ ,  $m_{eq} = 0.00214$  mol/kg and the above-mentioned value of  $k_d$ , well describes the experimental data approaching the equilibrium from below.



**Fig. 2**. The same as fig. 1 for series D and E, but initial quartz grains were treated in addition with fresh batches of water (5 times each during 3 days) at 250°C. The curves D' and E'' correspond to the equation (5) with  $m_0 = 0$  and 0.0065 mol/kg

Using the same  $k_d$  value for the description of quartz precipitation kinetics ( $m_0 = 0.0065 \text{ mol/kg}$ ) yields a curve E" that contradicts the experimental data sharply (series E' in fig.2). Thus, it is impossible to describe kinetics of both processes with the help of equation (1). It means that the precipitation of quartz proceeds through other mechanism than its dissolution. It is evident that the ultra fine particles of quartz and unevenness on its larger grains are active sites for precipitation. Previous hydrothermal treatment of crushed quartz grains causes the dissolution (disappearance) of these active sites. As a result the precipitation of silica is sharply retarded. The fact that silica concentrations during approach to equilibrium from above (series E' in fig. 2) stay too long at a level of solubility of  $\alpha$ -cristoballite, suggests that this metastable modification of silica can precipitate instead of quartz.

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# <sup>#</sup>Kravchuk I.F., Slutsky A.B., Senin V.G., Ignat"ev Y.A. The major factors of ore element fractionation in a water-saturated magmatic system.

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The studies of regularities of ore elements distribution between water-fluid and aluminosilicate melt is one of the most important problems in developing the general theory of the genesis of ore deposits.

The experimental modelling of element distribution among the phases in the system fluid-melt at the acidic magmatism parameters has been carried out. The objects under study were natural and model aluminosilicate melts and model water-chloride and water-fluorine solutions. Zn, Cu, Mo, W ( as the most typical of ore magmatic deposits) were selected as ore elements.

The factors of ore elements distribution between phases were obtained. In the model system Ab-Ort-Qz- 1 m NaCl at 800°C and 2 kbar they decrease in the sequence Cu-Zn-W-Mo, remaining in all cases more than unit ( in favor of fluid).

**Zn** forms complexes with chlorine, distribution coefficient  $(K_{Zn})$  decreases with pressure, the value of  $K_{Zn}$  critically depends on the structure of a melt (molar ratio of alkalis to aluminum) and concentration of a fluid.

Cu forms complexes with chlorine , practically does not vary with pressure.  $K_{Cu}$  increases with fluid acidity.

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The literature data on W and Mo distribution between fluid and melt are the most contradictory, therefore, this problem was given proper attention.

The significance of the distribution factor of tungsten between fluid (1 m NaCl) and model melt of granite composition was installed. The value of  $K_W$  is close to unit and increases monotonously with NaCl concentration up to the conditions of "dry" melted salt. At 1200°C and 1 bar  $K_W$  was estimated to be 70.

**Mo** distribution between fluid ( $H_2O$ ,  $H_2O$ -NaCl) and melts of natural and artificial aluminosilicates was investigated at 800°C and 1, 0, 1, 5, 2,0 kbar. The ratio of Na<sub>2</sub>O +K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> in glasses changed from 0,62 to 1,1. The content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>No in melts had no significant influence on Mo distribution between phases. Based on the data obtained and those available in literature, the negative correlation between KMo and CaO content in a melt has been suggested. With increasing NaCl concentration in fluids from 0 up to 100% no trend in distribution of Mo between phases was observed. The values of KMo were lower for the dry system Ab-NaCl than those for the water-containing systems. This fact attests to the water forms of Mo presence in fluids within the whole range of NaCl concentrations. So the water/chlorine ratio is a controlling factor of the extraction of Mo or connected with chlorine ore elements into a fluid. If the water to chlorine ratio is low, chlorine will be accumulated in a melt and in case of the saturation of melt in water the fluid phase will be considerably enriched in chlorine and connected with it ore elements. On the contrary, at high water content in the initial melt an early separation of the chlorine-poor fluid effective for Mo extraction is expected. One of the reasons of different behaviour of ore elements may be the opposite pressure effect: KMo content increases with pressure, but that of KZn, Kcu decreases. This underlines an important role of heterogenization of fluid as a principle factor governing formation of ore-bearing fluid. The distribution coefficients of ore elements between two unmixed fluid phases were determined from the study of fluid inclusions in artificial quartz and analysis of ore content in the inclusions.

An analysis of data on the distribution of ore components at the interaction of aluminosilicate melt with fluorine-water fluid showed the negligible role of fluorine complexes for the whole group of elements (Cu, Zn, Mo, W). Fluorine is not the main component of a magmatic fluid in the majority of water systems, especially at the final stage of crystallization.