

Kotel'nikova¹ Z.A. and Kotel'nikov² A.R. Experimental Study of the Na₂CO₃-Bearing Fluids Using Synthetic Fluid Inclusions in Quartz

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Fluid inclusions in quartz were synthesized from Na₂CO₃ solution. It was shown that at the experiments conditions the fluid was heterogeneous and was not inert with respect to quartz and albite. The liquid separation occurred in some inclusions during heating. This indicates on the possibility of multi-stage heterogenization of the fluid.

Key words: synthetic fluid inclusions, heterogenization, liquid separation

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Experimental studies of phase equilibria in fluid systems are necessary for reconstruction of natural mineral formation conditions and further progress in theoretical and experimental research. The heterogeneous fluid equilibria in the second type H₂O–Na₂CO₃ system in the presence of SiO₂ or SiO₂ + NaAlSi₃O₈ are considered in this paper.

The both boundary binary H₂O–Na₂CO₃ and H₂O–SiO₂ systems belong to the second type with metastable liquid immiscibility. In the H₂O–SiO₂ system coordinates of point Q correspond to 1050°C, 9.8 kbar, and 40–50 wt % SiO₂ according to Kennedy [Kennedy *et al.*, 1962]. The location of the upper critical point Q of binary H₂O–Na₂CO₃ system corresponds to 480°C, 1600 bar, and 30–40 wt % Na₂CO₃ according to Ravich [1974] or 500 ± 10°C, 1505 ± 0.01 bar, and 12 ± 2 wt % Na₂CO₃ according to Koster van Groose [Koster van Groose, 1962]. Butuzov and Bryatov [1957] investigated a fragment of the H₂O–Na₂CO₃–SiO₂ system enriched in H₂O at 300–400°C and under a pressure exceeding the pressure of saturated vapor. They noticed that solubility of quartz in the homogeneous region directly depends on salt concentration in water, but when the fluid became heterogeneous with appearance of two liquids differing in density, called heavy and light phases, the loss of quartz in weight increases abruptly. The heavy phase contained 30–50 wt % SiO₂ and concentrated Na₂O.

Method of synthetic fluid inclusions used. The runs were conducted under 1–3 kbar and at 700°C. Special runs with addition of albite were carried out. It is suggested that the effect of aluminosilicate on experimental results can be regarded as indirect evidence for interaction of quartz with fluid.

Run at $P = 1$ kbar. Fluid inclusions studying implies that the inclusions entrapped a heterogeneous fluid: two immiscible vapor- and liquid-like phases contrasting in density coexisted under the run conditions. Heating of synthesized inclusions resulted in appearance of one more immiscible liquid phase in some inclusions at a temperature of ~ 250°C. These data are completely consistent with the results obtained by Ravich [1974], who described equilibrium of two liquids rather than liquid and vapor in the upper two-phase region. The results of freezing experiments on inclusions with liquid immiscibility show that salt is the last phase melted at a positive temperature. The salt concentration of the solution

filling such inclusions is sufficiently high (13.5–13.8 wt %). A light denser liquid that arose between the inclusion's wall and residual liquid phase slightly increased in volume with further rise of the temperature and existed up to 550°C. Two aqueous salt-bearing solutions and vapor coexisted within a temperature range of 250–382°C.

Run at $P = 1$ kbar in the presence of albite. In contrast to the run without albite, liquid immiscibility was not observed in the presence of albite. Low-density inclusions were not detected, so that fluid remained homogeneous under the accepted run conditions. At the same time, a wide dispersion of the measured thermometric characteristics indicates that the run conditions were close to the phase boundary of heterogenization. Comparison of experimental results obtained for the inclusions synthesized in the presence of albite and without this phase shows that albite exerts effect on equilibria in fluid, which shift markedly. Thus, solubility of albite in carbonate-bearing solutions is rather high.

Run at $P = 2$ kbar. The increase in pressure led to the absence of the vapor phase: inclusions homogenized only into liquid at 352–365°C. The salt concentration determined from freezing experiments ranged from 8 to 17 wt %. Sporadic inclusions revealed liquid immiscibility. The run conditions were close to the phase boundary. The low-density phase was likely formed in insignificant amounts and entrapped only together with high-density liquid. As a result, the thermometric characteristics of inclusions are widely scattered. Because quartz interacted with aqueous salt-bearing fluid, the established temperature range of homogenization and melting of salt reflects kinetics of such interaction: inclusions varying in composition and density were captured at different stages of proceeding reaction.

Run at $P = 2$ kbar in the presence of albite. In two- and three-phase inclusions with a glasslike phase (Gl+V+S), when temperature rises up to 250°C, numerous small liquid bubbles arise, gradually increasing in volume and merging. While heating, they accumulate around a gas bubble, which dissolved in liquid at 351–361°C. Thus, the phase entrapped in the inclusions at $T = 700^\circ\text{C}$ and $P = 2$ kbar, being cooled, enables to bind a significant amount of water. If is assumed that fluid is composed of pure water and glass is sodium silicate, the volumetric proportions make it possible to estimate an amount of H₂O dissolved in glasslike phase at room temperature at 9–13 wt %.

Run at $P = 3$ kbar. The occurrence of low- and high-concentrated inclusions and the inclusions containing glasslike phase of heavy fluid implies that three immiscible phases coexisted under the run conditions. This is additional evidence for interaction of quartz with fluid and existence of tricritical point in the ternary H₂O–Na₂CO₃–SiO₂ system. Thus, the interaction of silicate phase with aqueous salt-bearing fluid is supported by all experimental results obtained at various pressures and in the presence of albite.

The experimental results for the H₂O–Na₂CO₃–SiO₂–NaAlSi₃O₈ systems confirm liquid immiscibility in the lower two-phase region. Because of this, heterogeneous fluid equilibria are reached in much wider temperature range than in the first type systems. The immiscible phase of heterogeneous fluid entrapped under experimental conditions in the upper two-phase region, in turn, can separate into two noncrystalline phases when temperature and pressure drop.

Heterogenization in the upper two- or three-phase-region is accompanied by radical redistribution of dissolved components between immiscible phases. According to Ravich (1974), the Na_2CO_3 concentrations in immiscible liquids are distinguished by no less than an order of magnitude. Immiscible liquids are also enriched or depleted in ore components. Thus, fluid immiscibility is an efficient mechanism of partitioning of ore components. If heterogenization proceeds during several stages, partitioning will be even more efficient.

The available experimental data allow us to suggest that fluid immiscibility is widespread in nature within a range of temperature and pressure beginning from the magmatic fluid release and up to the following hydrothermal process; multistage heterogenization of fluid is possible. The hydrolysis resulted in contrasting pH of immiscible phases is noted in many aqueous salt-bearing systems under high temperature heterogeneous conditions. A relatively dense and concentrated heavy fluid acquires alkaline reaction and interacts with quartz and other silicates with formation of intermediate compounds. The apparent solubility of silicates under heterogeneous conditions markedly increases with formation of intermediate compounds. Solubility of other poorly soluble compounds, for example, some ore minerals having the second type phase diagrams, can increase in the same manner. Such a fluid phase is able to transfer components of both gangue and ore minerals. Pressure release can be more important for the discharge of that fluid than a drop in temperature.

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Kotova N.P. Experimental study of concentration dependence of niobium oxide solubility in fluoride solutions at $T=550^\circ\text{C}$, $P=500$ bar and low oxygen fugacity (Co–CoO buffer)

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The dependence of Nb_2O_5 solubility as a function of fluoride concentration was investigated in HF, KF solutions with concentrations from 0.01 to 2 m at 550°C and 1000 bar under Co–CoO oxidizing conditions. It is found that at low concentrations of fluoride (less than 10^{-2} m) the niobium concentration is at 10^{-4} – $10^{-3.5}$ m. Nb_2O_5 solubility strongly increases with increasing fluoride concentration and achieves significant values on the order of 10^{-2} to $10^{-1.5}$ m in aqueous solutions with high fluoride concentrations

of 1 m and greater. Under such conditions hydrothermal mass transfer of Nb is really possible.

Key words: experiment, oxide tantalum, oxide niobium, hydrothermal solubility, fluoride solutions, concentration dependence

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The peculiarity of the ore-bearing granites and associated greisenized and albitized deposits of rare metals is that their formation along with magmatic, it is necessary to consider the role of hydrothermal-metasomatic factors. However, the published data on the behavior of tantalum and niobium minerals in hydrothermal solutions of different compositions in a wide range of concentrations, temperatures, pressures and oxygen fugacity are insufficient to understand the role of hydrothermal-metasomatic processes in the genesis of rare metal deposits of tantalum and niobium and estimate the reliability of the genetic hypothesis. Therefore, we carry out a systematic experimental study on the solubility of natural columbite and pyrochlore [Korzhinskaya, Kotova., 2011; Kotova., 2011]. The use of columbite and pyrochlore experiments has its advantages, consisting in the possibility of direct application of experimental data to estimate the natural conditions of ore formation in connection with the identity in both cases, the main carrier minerals of tantalum and niobium. The disadvantage of the choice of columbite and pyrochlore to study the behavior of Ta and Nb in hydrothermal solutions is the relative complexity of their composition. This makes the thermodynamic interpretation of the experimental data more difficult. Therefore, to increase the reliability of experiments in parallel with the solubility of natural minerals was investigated under the same conditions the solubility of the tantalum and niobium oxides, which have been used as a pure chemical reagents. The solubility of simple Ta and Nb oxides, restricts the upper concentration limit of these elements under hydrothermal conditions. Stable under natural conditions, the mineral phase of tantalum-niobates of a more complex structure (columbite, pyrochlore, etc.) are less soluble than the oxides.

The study is aimed at solving a specific problem: the experimental determination of the solubility of niobium oxide in aqueous fluoride solutions at high temperatures and pressures for a quantitative estimation of the possibility of hydrothermal transport and precipitation of niobium at formation of commercially viable ore deposits.

The dependence of Nb_2O_5 solubility as a function of fluoride concentration was investigated in HF, KF solutions with concentrations from 0.01 to 2 m at 550°C and 1000 bar under Co–CoO oxidizing conditions. Earlier, it has been shown that the solubility of columbite-tantalite is 1.5 to 2 orders of magnitude higher under more reducing conditions (buffer Co–CoO) than under more oxidizing conditions (buffer Ni–NiO). Consequently, the experiments were carried out at low oxygen fugacity (buffer Co–CoO). Experiments were performed on a hydrothermal line. The chemical reagent Nb_2O_5 (>99.99% purity) was used as the starting material. Fifty mg of Nb_2O_5 and 1 ml of the fluoride solution were sealed into Pt capsules (80 mm long, 8 mm diameter, 0.2 mm wall thickness) using arc welding. The run duration was 15–20 days. Before and after the experiments all capsules were

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weighed on electronic balances with an accuracy of ± 0.01 mg to check for leaks during the run.

After the run, the quenched aqueous solutions were analyzed using ICP/MS (Inductively Coupled Plasma Mass Spectrometry) and ICP/AES (Atomic Emission Spectroscopy) for Nb, Ta, Mn, and Fe and admixture elements Ti, W, and Sn. The composition of the solid product was characterized using optical microscopy, X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM)).

The experimental results are shown in (Fig. 1). The data show similarities in Nb_2O_5 solubility in fluoride solutions. The dependence of Nb_2O_5 solubility on fluoride concentrations follows linear trends in HF and KF solutions. The experiments indicate that at low concentrations of fluoride (less than 10^{-2} m) the niobium concentration is at 10^{-4} – $10^{-3.5}$ m. However, Nb_2O_5 solubility strongly increases with increasing fluoride concentration and achieves significant values on the order of $10^{-1.5}$ to $10^{-0.5}$ m in aqueous solutions with high fluoride concentrations of 1 m and greater. Under such conditions significant hydrothermal mass transfer of Nb is really possible. At high fluoride concentrations (1 and 2 m) the highest Nb_2O_5 concentrations ($10^{-0.5}$ m) were detected in HF solutions. Nb_2O_5 is less soluble in KF solutions than in HF solutions (up to $10^{-1.5}$ m in 2 m KF).

The results of X-ray diffraction of solid products of the experiments show that in HF solutions of low concentrations niobium oxide dissolves congruently, without changing the composition. In highly concentrated HF solutions niobium oxide has an incongruent solubility. In 1 and 2 m HF solutions the crystals of niobium oxide (Nb_3O_7), referring to orthorhombic crystal system, are formed as a solid phase.

For all KF concentrations considered, niobium oxide dissolves incongruently. In 0.01 and 0.1 m KF solutions fluorides are formed with the formula $\text{KNb}_6\text{O}_{15}\text{F}$, referring to monoclinic system. In 0.3 m, 1 m and 2 m KF solutions the crystals of K-niobate- $\text{K}_2\text{Nb}_4\text{O}_{11}$, referring to tetragonal system, are formed.

The data shown in Fig. 1 show, in general, and the same kind of dependence of the Nb_2O_5 solubility on F-ion concentration in all studied fluoride solutions – HF and KF. All curves can be well approximated by straight lines having a slope. All available data correlate well. The discrepancy in the values of Nb_2O_5 solubility in HF and KF solutions does not exceed one order of magnitude.

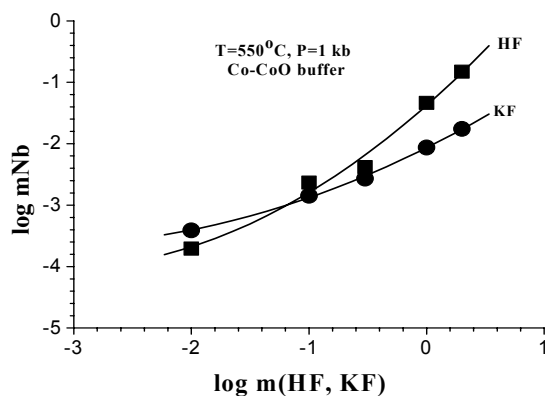


Fig. 1 The solubility of Nb_2O_5 as a function of HF and KF concentration at $T=550^\circ\text{C}$ and $P=1$ kbar (Co–CoO buffer)

In comparison with niobium at low concentrations of fluoride the solubility of tantalum is very small and is located at 10^{-5} – 10^{-6} (Fig. 2). This indicates a low probability of hydrothermal transport of tantalum in such solutions. However, with increasing concentration of fluoride the Ta_2O_5 solubility greatly increases and at fluoride concentration 1.0 m and higher reaches 10^{-3} – 10^{-2} . At such concentrations, the real mass transfer tantalum by hydrothermal solutions is possible. By analogy with niobium at low concentrations of F-ions (0.01, 0.1 m) the concentration dependence of Ta_2O_5 solubility in all fluoride solutions (HF, KF, NaF, LiF) has similar values. It was found that the Ta_2O_5 solubility isotherms have a positive trend in all studied fluoride solutions. At high fluoride concentrations (1 and 2 m) the highest Ta_2O_5 concentrations (10^{-1} m) were detected in HF solutions. The dependence of Ta_2O_5 solubility on the HF concentration in a logarithmic scale has a distinct linear. The solubility of Ta_2O_5 in 2 m KF solution is 10^{-1} m, which is the order of magnitude lower than the solubility of Ta_2O_5 in 2 m HF solution. Experiments have shown that the solubility of tantalum in fluoride solutions is approximately 1–1.5 orders of magnitude lower than the solubility of niobium.

The experimental data show that the solubility of Nb_2O_5 and Ta_2O_5 strongly depends on the fluoride concentration. Fluoride solutions with high concentrations of 1 m are the most probable for hydrothermal mass transfer and precipitation of Nb and Ta in the temperature range 400 to 550°C . At saturation the concentration of Nb achieves values on the order of $10^{-1.5}$ to $10^{-0.5}$ m and of Ta of 10^{-4} to 10^{-2} m. It also demonstrates the importance of complexing agents, such as F, in the transport of Ta and Nb. Experimental studies have allowed for the first time establish that Ta and Nb can be transported by hydrothermal acidic fluoride solutions and deposited in the form of its own minerals in quantities sufficient for the formation of commercial deposits, as evidenced by high concentrations of Ta and Nb in 1.0 m HF and KF solutions. Results of the study are important for the development of science-based prediction methods and the search for rare metal deposits of tantalum and niobium associated with granites.

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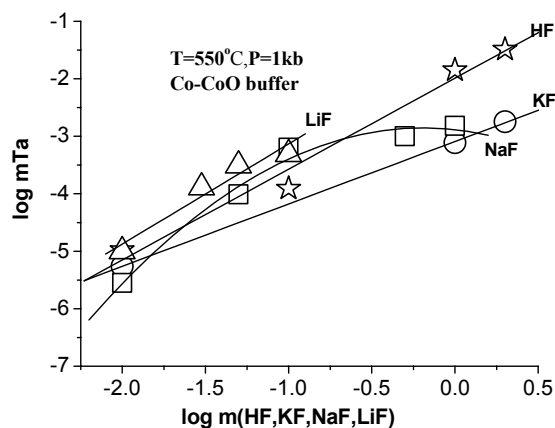


Fig. 2 The solubility of Ta_2O_5 as a function of HF, KF, NaF and LiF concentration at $T=550^\circ\text{C}$ and $P=1$ kbar (Co–CoO buffer)

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Martynov¹ K.V., Asavin² A. M., Konstantinova¹ L. I., Shirokova¹ I. B., Zakharova¹ E. V.
Sorption of actinides on natural Fe-Mn oceanic crusts from seawater

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Under normal conditions we carry out static experiments on the sorption of U-233, Np-237, Pu-238, Am-241 from aqueous solution corresponding to seawater model on crushed samples of ferromanganese ore crusts taken from the Magellan seamounts guyots. The kinetics of sorption was studied on the example of uranium, which was already adsorbed on 96.0% in the first hour, and after the first day it was reached the level closed to the ultimate extraction 99.0%. The equilibrium sorption degree of studied radionuclides for the "young" crust was slightly higher than for the "old" one and increased for both samples among Np<U<Pu<Am from 96.7% to 99.6%.

Keyword: actinides, radioactive waste, sorption, ferromanganese crusts

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Search of new effective natural sorbents for toxic waste, in particular radioactive, is very important task. Besides that in geochemistry of oceanic processes there is unexplored a behavior of radionuclides at long-living sediment processes and geochemical cycles elements. All these questions have forced us to spend studying sorption

characteristics oceanic Fe-Mn ores. There are some publications specifying on high effective properties of Fe-Mn crusts concerning elements having artificial long-living isotopes [Scott, et al., 2005; Duff, et al., 2002, Koschinsky, & Hein, 2003]. However, direct experimental researches on sorption characteristics of radionuclides aren't known for Fe-Mn crusts. Definition of radionuclides (U-233, Np-237, Pu-238, Am-241) sorption parameters was a problem of the present research in conditions close to natural oceanic ones.

We used close to neutral (pH=8.0) a solution haven salt structure as seawater (Table 1) under normal conditions. Radionuclides were entered in the form of nitrates, their abundance in working solutions were: Am – $3.27 \cdot 10^{-9}$, Np – $5 \cdot 10^{-6}$, Pu – $5 \cdot 10^{-10}$, U – $2 \cdot 10^{-7}$ M.

Table 1. Salt composition of the solution (bulk salinity 35 ‰)

Na	468 mM
Mg	53 mM
S	28 mM
Cl	546 mM
K	10.2 mM
Ca	10.3 mM
N(NO ₃ ⁻)	45 µM
N(N ₂)	610 µM
Sr	90 µM

As a sorbent we used average combine samples Fe-Mn crusts taken from the Magellan seamounts guyots. We have created average bulk probe of the top "young" type of ores (III layer) - sample T2 and average bulk probe from the bottom "ancient" layers I-1, I-2 – sample RT. In experiments we used fractions of 0.2–0.04 mm. Composition of samples are given in Table 2.

To determine the phase composition the powder samples were examined by X-ray diffractometer D/MAX-2500 (Rigaku). XRPD patterns of the samples have been removed in CuKα-radiation at a rate of 10°/min and with step 0.02°2θ. Predominant phases in both samples were vernadite and asbolan-buserite (Fig. 1). In addition to them in the ancient layer, it was better crystallized, there were carbonates, hematite, barite, analcime, goethite, and in the young - a large number of probably terrigenous quartz.

Table 2. The chemical composition of the used sorbents

Sample/ element	RT (ancient) wt. %	T2 (young)	Sample/ element	RT (ancient) ppm	T2 (young)
SiO ₂	4.64	9.06	V	577	2
TiO ₂	1.39	1.54	Co	2880	4350
Al ₂ O ₃	1.38	2.02	Ni	2476	3396
CaO	11.71	3.24	Cu	1220	1080
Fe ₂ O ₃	19.48	21.31	Zn	591	511
K ₂ O	0.45	0.60	Sr	1557	1136
MgO	1.14	1.35	Zr	637	550
MnO	20.45	22.15	Mo	546	361
Na ₂ O	1.91	1.86	Nb	58	49
P ₂ O ₅	4.72	1.15	La	212	173
S	0.27	0.17	Ce	1228	766
Total	67.55	64.45			
ppp	31.09	34.2			
Sum	98.64	98.65			

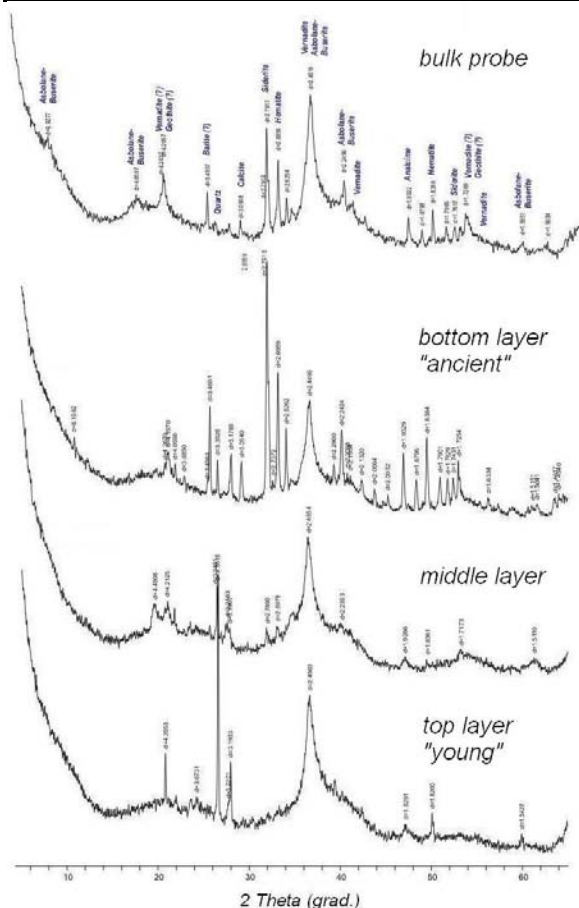


Fig. 1. XRPD patterns and mineral composition of the Fe-Mn crusts, CuK α radiation

Experiments on the leaching and sorption were carried out under static conditions in polypropylene tubes with periodic stirring. Ratio of solid and liquid phases was 1:20 (0.5 g : 10 ml). Aliquots for analysis were collected after centrifugation. The contents of Fe and Mn were determined by atomic absorption spectrometer AAnalyst-400 (Perkin Elmer). Activities of radionuclides were determined by liquid scintillation alpha-, beta-spectrometer SKS-07P-B11 with the detection unit UDBT-003 (Green Star Instruments). As liquid scintillator was used Optiphase HiSafe III (Perkin Elmer).

To estimate the resistance of the crust material in environment conditions with various pH we have studied the leaching of Fe and Mn from the sample T2 in HNO₃ solutions with pH = 2, 3, 4, 6 and NaOH solution with pH = 8. The contact time was 1 day. It is established that the investigated elements behave the opposite way (Fig. 2). Leaching of Mn is lower than Fe, and has, in contrast to the latter as a tendency to increase with increasing and with decreasing pH.

The speed of the process has been studied on the example of uranium sorption on the sample T2. A plot of the extraction of uranium from the solution against the time of contact with the sample is shown in Fig. 3. As can be seen from the plot, uranium was rapidly adsorbed by crust material: already in the first hour it was absorbed 96.0% of substance from the solution, and after the first day it was reached the level closed to the ultimate extraction 99.0%.

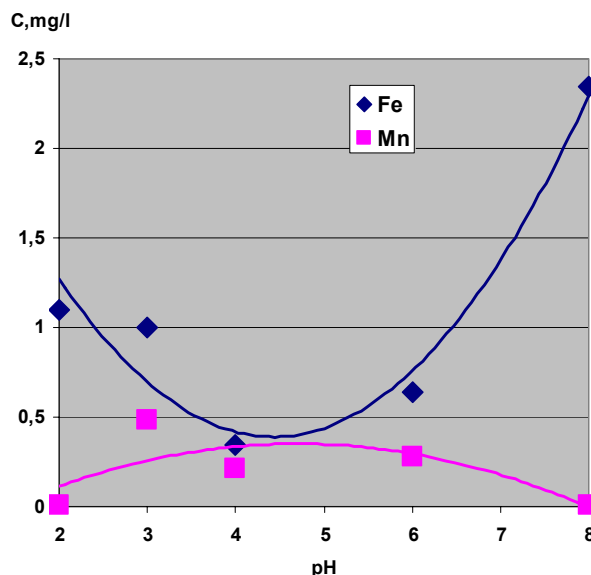


Fig. 2. The dependence of Fe and Mn concentrations in solution vs. pH on leaching of the sample T2 for 1 day

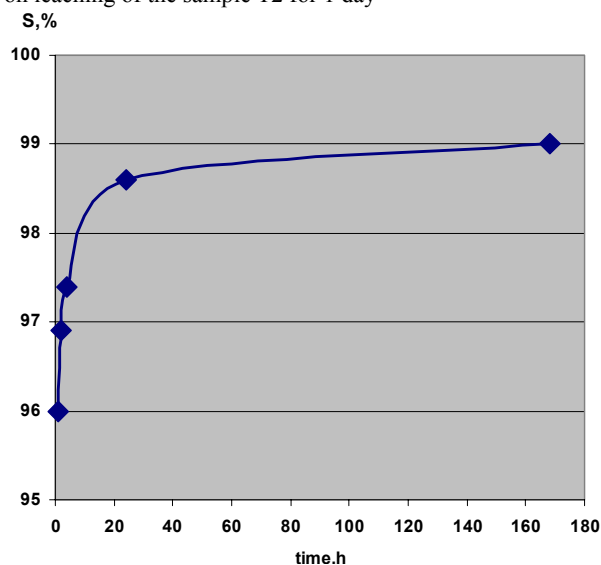


Fig. 3. The kinetic curve of uranium sorption on the sample T2

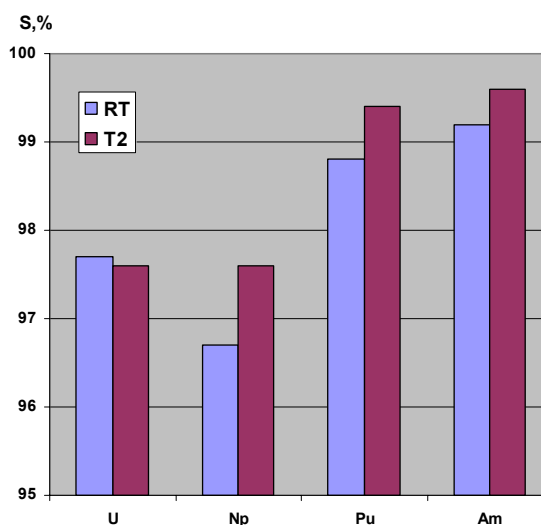


Fig. 4. The degree of radionuclides extraction from the working solution by samples RT and T2 in 10 days of contact

Experiments to determine the sorption of all four radionuclides on both samples have spent at time duration 10 days, certainly more than it was necessary for the establishment of sorption equilibrium (Fig. 4). Degree of sorption reaction for "young" crust was a little above than for "ancient" one also increased for both samples among $\text{Np} < \text{U} < \text{Pu} < \text{Am}$ from 96.7 % to 99.6 %.

Thus, the received experimental results have shown perspectives to use natural material of Fe–Mn ore crusts as effective sorbent for extraction of radionuclides from liquid radioactive salt solutions with pH close to the neutral. Besides, thanks to activity of sorption interaction, it is necessary to recognize possibility of self-cleaning of oceanic waters at pollution of ocean by radionuclides. In the presence of powerful geological processes of Fe–Mn ore mineralization radioactive deposits intruding into oceanic water are concentrated on the surfaces of seamounts and an oceanic bottom and deduced quickly from a geochemical cycle.

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Plyusnina L. P., Kuz'mina T. V. and Likhoidov G.G. Bitumen – graphite transformation (after experimental data)

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The impact of temperature in hydrothermal media on model carbonaceous matter (CM) behavior was studied. The evolution of two types of CM in course of graphitization was described. The process results are favorable for metal concentration during deposits formation.

Key words: carbonaceous matter, experiment, graphite, bitumen, gold

Reference: Plyusnina, L. P., T. V. Kuz'mina, G. G. Likhoidov (2012), Bitumen – graphite transformation (after experimental data). *Vestnik ONZ RAS*, 4, (doi:)

Purpose of the paper was investigation of metamorphism influence of on the carbonaceous matter (CM) composition and structure. Asphaltene (As) and asphaltenic acids (AA) fractionated from the brown coals of the Pavlovskoye deposit (Primor'ye) have been chosen as the model matter. Chemical compositions of the initial As and AA are similar. The former differs only by the lower oxygen content (wt %): As: C – 75.13, O – 18.10, H – 6.54, AA: – C – 72.58, O – 19.98, H – 6.87. Hydrothermal experiments were conducted by the ampoule–autoclave method at 200, 300, 400, and 500°C, $P_{\text{H}_2\text{O}} = 1$ kb. One of a number runs at room temperature and saturated water vapor pressure. Twice-distilled water, CM specimen (~50 mg) were put into the golden ampoule (10×100×0.2 mm) serving as a source of gold dissolution

during run time. The last varied from 30 days at 200°C to 7 days at 500°C. Run products were fractionated onto the water fraction, soluble in alcohol–benzene mix at 50°C one and undissolved residue [Plyusnina et al., 2004].

The fraction soluble in alcohol–benzene (SF) is represented by a yellow oily liquid with a specific smell of oil. The gold concentration in it accounts for $n \times 10^{-5}$ mol/kg at 200, 300°C, and $n \times 10^{-4}$ at 400 and 500°C. Undissolved residue (UR), usually called kerogen, is represented by finely dispersed sootlike matter. The gold content in the kerogen is significantly higher than in the SF: for $n \times 10^{-3}$ mol/kg at 200 and 300°C and $n \times 10^{-2}$ mol/kg at 400 and 500°C.

IR-spectra of the kerogen synthesized at 400°C demonstrate that C–O bonds of carbonyl and carboxylic acids (1340 and 1460 cm^{-1}) become less intensive, and the intensity of well-resolved aromatic group bands (750, 800, 850, and 1630 cm^{-1}) reaches its maximum. The absence of absorption bands of the groups C–H, CH= and CH₂ is an indication of the CM carbonization reactions. The absorption band near 1574 cm^{-1} indicates on the graphitization of amorphous CM.

Kerogen formed at 500°C presents by black lustrous graphite-like flakes. Its X-ray photograph contains one peak of the main graphite lattice ($d/n = 3.36 \text{ \AA}$). Thus, crystallization of weakly structured unordered graphite occurs at 500°C. Electron micrograph of graphite presents the globular microstructure (globules 200 to 500 μm). Our principal concern will be with the presence in the globules of rounded micropores with varying midship from 1 to 25 μm (Fig. 1).

At the microscope numerous pores and channels in the cleavage interplane sites of graphite are observed to form a finemesh framework that may play the role of a molecular sieve analogous to those existing in zeolites. Apparently, it is a peculiar feature of graphite formed by thermolysis of bitumens. The presence of graphite micropore texture reflects devolatilization during the As thermolysis that is proved by great mass losses of the CM at experiments (Fig. 2). A rise in temperature is accompanied by a decrease of the primary mass by 10–90% in the 200–500°C interval.

The relation of the UR and SF masses depends also on the temperature and experiments duration (Fig. 3). As a rule, the expense of the UR amount results in diminishing the SF mass. We have conventionally adopted the relation $m_{\text{UR}}/m_{\text{SF}}$ as an aromatization coefficient (K_a). According to the IR-spectra, the complete aromatization of the CM – aliphatic skeleton occurs at 500°C. Nevertheless, weak absorption bands of aromatic groups CO and COOH still remain. Such a significant release of volatile components during the CM thermolysis (CO, CH₄, CO₂, O₂, H₂ etc.) defines the redox-potential of the media [Plyusnina et al., 2009].

It ought to be noted that hydrothermal thermolysis of bitumens – graphite was obtained at 500°C. Earlier the complete graphitization during the CM dry pyrolyses occurred at 1500°C [Fischbach, 1971]. Our results on the start of the graphitization in the presence of aqueous fluid at $P_{\text{tot}} = 1$ kb are closer to the nature and reflect the influence of pressure. It ought to be noted that graphitization is an irreversible process. Graphite is well preserved also at the superposition of retrograde metamorphism in nature.

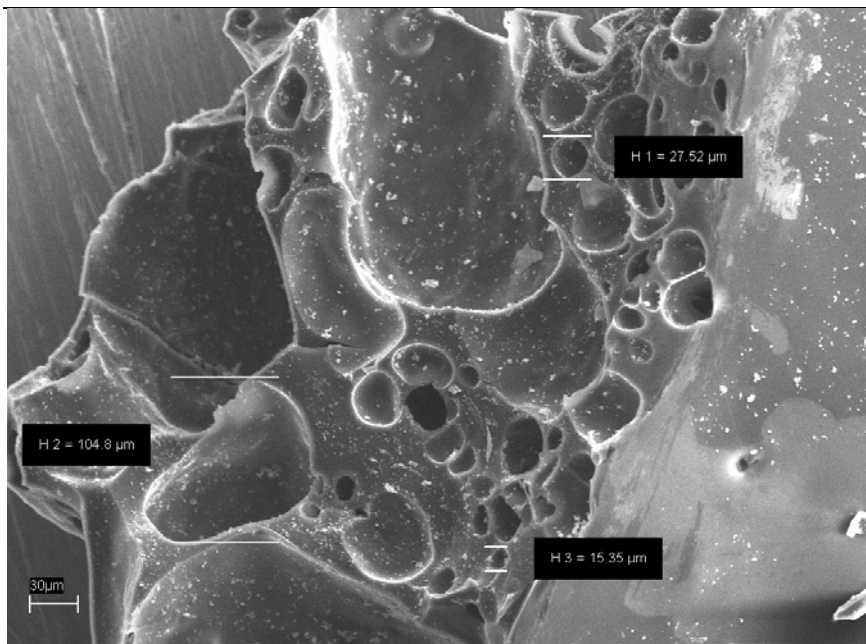


Fig. 1. Globular micropore structure of the apoasphaltene (scanning electron microscope)

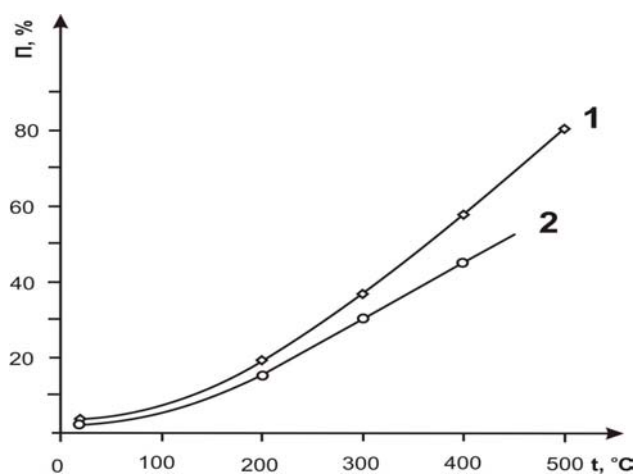


Fig. 2. Bitumens mass losses (Π) as a function of temperature 1 – As, 2 – AA; $\Pi = (m_{\text{ini}} - m_{\text{fin}}/m_{\text{ini}}) \times 100$; m – mass: ini – initial, fin – final

Thus, two mechanisms of metal concentration by the graphite are possible: chemisorption and filling of pores and channels of interlaminar space. The velocities of these processes are incomparable. The chemisorption occurs with relatively high rate: in 7 days at 500°C, the gold concentration becomes measurable in both CM fractions. Filling of pores and channels of kerogen has not been established in the runs. Possibly, it needs a longer term experiment, and may be the flow-type reactor model. In the natural conditions ore-bearing hydrothermal infiltration occurs during prolonged geological time. The discovered micropore texture of the apoasphaltene graphite is of a great interest. It reflects the influence of metamorphism on the volatilization reaction flow and formation of an unstable system at deconsolidation conditions favorable to the influx of hydrothermal ore-bearing solutions and metasomatic processes development.

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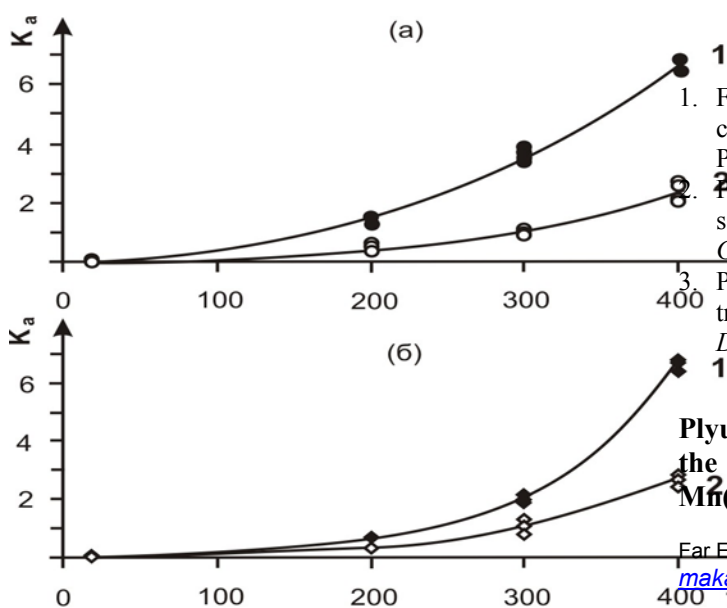


Fig. 3. Coefficient of bitumen aromatization (K_a) as a function of temperature (a) – As, (b) – AA; run time in hrs: 1 – more than 400; 2 – less than 240. $K_a = m_{UR}/m_{SF}$

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Plyusnina L.P. and Likhoidov G.G. Synthesis of the nanocrystalline platinum during Mn(II)–Mn(III) oxidation at 200–300°C and $P = 1$ kb

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Synthesis of metallic platinum in the hydrothermal media was described. The process is connecting with the Pt solubility against a background of manganese oxides evolution and evidence of synergy character.

Key words: synthesis, platinum, manganese oxides, experiment

Reference: Plyusnina, L. P. and G. G. Likhoidov (2012), Synthesis of the nanocrystalline platinum during Mn(II)–Mn(III) oxidation at 200–300°C and P = 1 kb. *Vestnik ONZ RAS*, 4, (doi:)

In preceding studies of metallic platinum dissolution in chloride aqueous solutions (200, 300°C; $P_{\text{tot}} = 1$ kb) [Plyusnina, 2002], new formed platinum microcrystals were deposited on hausmannite crystals. At present we describe the Mn(II)–Mn(III) oxidation kinetics and conditions needed for nanodisperse platinum crystallization.

Platinum solubility under elevated PT -parameters depends considerably from a redox potential [Gammons, 1995]. In this connection, for correct results, we are support the redox potential by means of solid phase mix assemblage compositions. Oxides of manganese variable valency have been used to reach the widest variation range of the redox potential in studied system. In runs carried out at 200–500°C, the following mixtures were used: MnO–Mn₃O₄, Mn₃O₄–Mn₂O₃, and Mn₂O₃–MnO₂ [Plyusnina et al., 2011]. Noteworthy, metallic platinum was crystallized in run products at 200–300°C only, when solid mixture contained MnO - unstable under 400°C [Hem, Lind, 1983].

The study was performed by ampoule method in the Ni-Ti alloy autoclaves. During dissolution the inner surface of sealed platinum ampoules (9 x 80 x 0.2 mm) served as the Pt source. Bidistilled water and 1m NaCl and 0.1m HCl solutions were placed into ampoules (according to P-V-T ratios for water at T of interest, and $P_{\text{tot}} = 1$ kb). At 200 and 300°C f_{O_2} was supported by the MnO–Mn₃O₄ mixture (200 mg).

The solid phase of run products was diagnosed by powder X-ray diffraction and its chemical compositions were determined by EVO-50 XVP scanning electron microscope analysis equipped with INCA 350 system of energy dispersive X-ray spectrometer. Pt concentration in quenched solutions was analyzed by a Shimadzu AA-6800 atomic spectrometer with 0.002 ppm sensitivity.

The runs products (200 and 300°C), which contained up to 5 wt % Pt_{met} , were studied by an electron microscope. Micrographs of disperse metallic platinum fix its crystallization in aggregates (3–5 μm cross sections) of complex geometric shapes. The aggregates were found on facets of idiomorphic hausmannite crystals and consisted of discrete isometric Pt_{met} grains (60–500 nm) with a complex “verrucous” surface (Fig. 1a). The energy dispersive spectrum of platinum microaggregates comprises peaks of C, O, Pt, and Mn (Fig. 1b). The carbon peak is due to a conductive carbon film sputtered to release charges in recording insulators. The oxygen and manganese peaks are associated with characteristic X-rays excited by the matrix manganese oxides.

As a result of Mn²⁺ instability, the oxidation of initial MnO to Mn₃O₄ was observed at 200 and 300°C, and takes place via spontaneous crystallization of metastable intermediates (Mn hydroxides) according to the Ostwald's steps rule. The intermediate phase was feitknechtite (β -MnOOH). And its formation can be described by the protonation reaction: $2\text{Mn}^{2+} + 0.5\text{O}_2 + 3\text{H}_2\text{O} = 2\text{MnOOH} + 4\text{H}^+$ [Murray et al., 1995]. Feitknechtite was identified

by the reflections (d/n): 4.63, 2.66, 2.37, and 1.99 Å (ASTM 18-804). In the 1 m NaCl and 0.1 m HCl solutions, kempite Mn₂(OH)₃Cl, pyrochroite Mn(OH)₂ along with MnOOH crystallized as intermediates identified by d/n : 5.75, 5.40, 4.31, 2.98, 2.91, 2.83, 2.39, 2.33, 2.17, 1.92, 1.78 Å (ASTM 25-1158) and 4.61, 2.48, 2.39, 1.82 Å (ASTM 18-787), the first and second respectively. These phases formation in aqueous chloride solutions may be described by: $3\text{MnOOH} + 0.5\text{H}_2\text{O} + \text{HCl} = \text{Mn(OH)}_2 + \text{Mn}_2(\text{OH})_3\text{Cl} + 0.75\text{O}_2$. This reaction is accompanied by oxygen discharge; as a result, Mn(OH)₂ oxidizes to MnOOH via: $\text{Mn(OH)}_2 + 0.25\text{O}_2 = \text{MnOOH} + 0.5\text{H}_2\text{O}$. Depending on the run duration, β -MnOOH appeared in products periodically, together with Mn₂(OH)₃Cl and Mn(OH)₂. Such periodicity of intermediate metastable phase's crystallization is synchronized with oscillations of the redox potential, water activity, pH values and ultimately leads to an increase in platinum solubility. In result the metallic platinum crystals ($d/n = 2.265, 1.96, 1.387, 1.183, 1.133$ Å) precipitate from solutions.

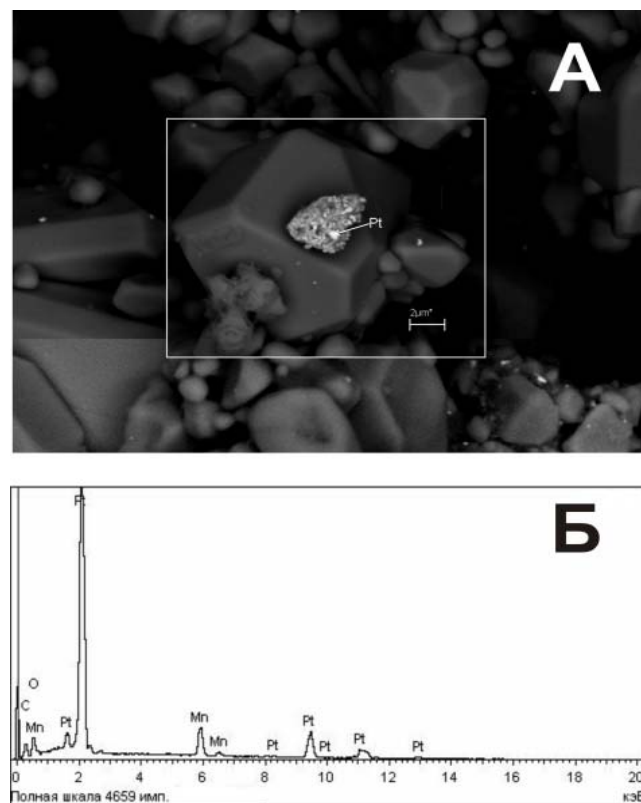


Fig. 1. Aggregates of ultrafine Pt_{met} grains on the hausmannite crystals (A), and energy-dispersive spectrum of one grain (B)

A direct correlation between the Pt solubility, intermediates behavior and metallic platinum crystallization is found. In the aqueous solution Pt_{aq} content varies ($-72 < \log mPt < -03$) depending on run duration (Figs. 2, 3).

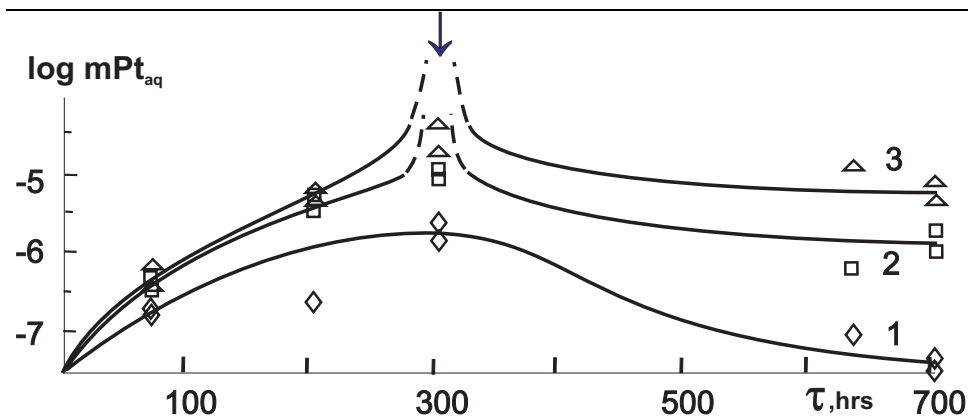


Fig. 2. Pt dissolution rate curves at 200°C (MnO–Mn₃O₄). 1 – in water, 2 – 1m NaCl, 3 – 1m HCl.

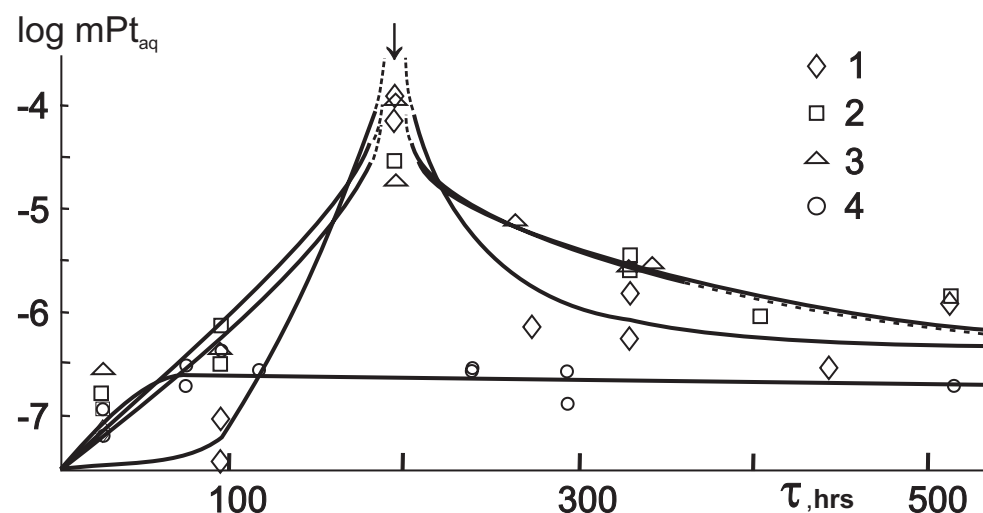


Fig. 3. Pt dissolution rate curves at 300°C (MnO–Mn₃O₄). 1 – in water, 2 – 1m NaCl, 3 – 1m HCl (), and 4 water buffered by Fe₂O₃–Fe₃O₄.

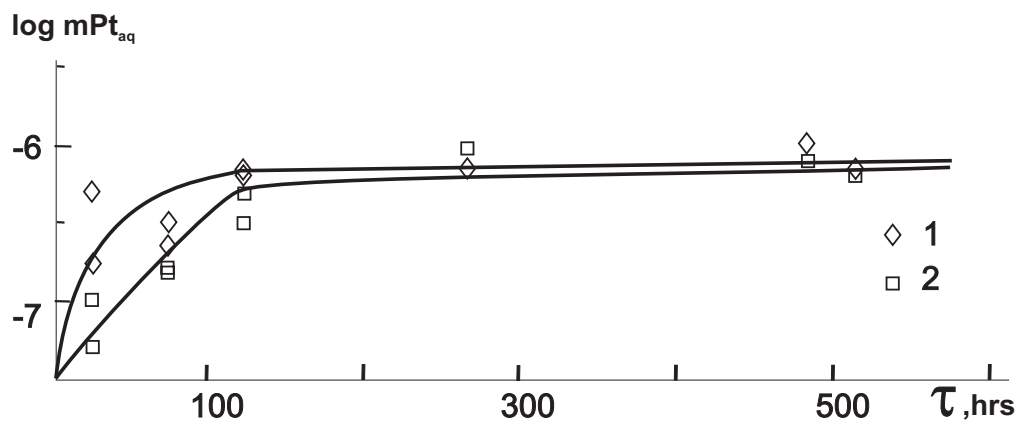


Fig. 4. Pt dissolution rate curves at 400°C, in the presence MnO–Mn₃O₄ (1), and Fe₂O₃–Fe₃O₄ (2)

Along with the maximal Pt_{met} content the greatest MnOOH yield (up to 10% of solids) was observed and maximal intensity of the X-ray diffraction reflections of crystalline platinum. In the 0.1 mHCl solution log mPt_{aq} varies from -5.54 to -3.81. In the case, Mn₂(OH)₃Cl dominates, while MnOOH amounts are under 5%. The most quantity of metallic platinum is observed in the chloride medium (log mPt_{aq} = -3.81) along with increased content of kempite in the solid. Auto-oscillation wave processes are particularly intrinsic to chemical systems far from chemical equilibrium and are accompanied by periodic precipitation of reaction products [Bystray, Pivovarov, 1989]. The absence of manganese hydroxides in the long-term run products proves its intermediate

character and nonequilibrium formation. In comparing platinum dissolution rate curves (Fig. 2, 3), we find that peak Pt concentrations in solutions coincides with period of intermediate phases crystallization. As the intermediates convert to stable hausmannite, the Pt content of solutions drops. At 400°C, MnO is stabilized and the MnO–Mn₃O₄ buffer mix is stable in the course of runs. In

the case, there are no extremes on the Pt dissolution kinetic curves and the equilibrium Pt_{aq} content was established in the first four days (Fig. 4).

The relationship between crystallization of metastable Mn hydroxides and the Pt_{aq} concentration in solutions coexisting with these hydroxides is confirmed by run results at 300°C with Fe₃O₄–Fe₂O₃ buffer. Since these Fe oxides are stable at the temperature, new solid phases in products are lacking and an extreme is absent on the Pt dissolution kinetic curves (Fig. 3). X-ray for the products obtained at the 200°C in the presence of the MnO–Mn₃O₄ mixture reflects next order of changing mineral assemblages in dependence of run duration (days): MnO + Mn₃O₄ (start) → MnOOH + Mn₃O₄ + Pt (9th) → Mn(OH)₂

+Mn₃O₄+ Pt (15th) → Mn₂(OH)₃Cl + MnOOH + Mn₃O₄ + Pt (30th) → Mn₃O₄ (60th). At 300°C the change in mineral assemblages finished in platinum ampoules in 15 days.

The catalytic effect of Pt on Mn oxidation may be described by reactions involving dissolved Pt(OH)₂ and releasing free oxygen, which enhances Mn²⁺ oxidation: MnO + Pt(OH)₂ = MnOOH + Pt_s + 0.5H₂O + 0.25O₂; 3MnOOH + Pt(OH)₂ = Mn₃O₄ + Pt_s + 1.75O₂ + 2.5H₂O. The activation of oxidation processes, in turn, gives rise to anomalies in Pt solubility kinetics.

Noteworthy, a similar process of Pt adsorption onto Mn oxides occurs in natural settings, too. In Pacific substrates, for examples, ferromanganese nodules and crusts with elevated Pt concentration are widely spread. The described relationship between solid phase compositions and the Pt solubility in the Mn–H₂O–Cl system is confirmed by an elevated Pt/Mn ratio in sea water, which exceeds the respective value in the oceanic crust more than 300 times [Jacinto, Berg, 1989].

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Polotnyanko¹ N. A., Khodakovsky^{1,2} I. L. About the solubility of palladium oxide and hydroxide at 25 °C

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The critical review of literary data on thermodynamic properties of substances and aqueous species existing in heterogeneous system PdO–H₂O is performed. The constants of palladium oxide and hydroxide dissolution reactions in water are recommended.

The value of Δ_rG^o_{298.15} obtained in the present study for Pd²⁺ (aq) essentially (at least by 6 kJ/mol) differs from the values specified in fundamental thermodynamic databases and based on experimental data for palladium electrode potential determined at 25 °C.

Key words: thermodynamics, PdO, solubility, Pd²⁺

Reference: Polotnyanko, N. A., I. L. Khodakovsky (2012), About the solubility of palladium oxide and hydroxide at 25 °C, *VESTNIK ONZ RAN*, 4,

Polotnyanko¹ N.A., Khodakovsky^{1,2} I.L. Thermodynamic properties of palladium chloride complexes in aqueous solutions

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On the basis of expert estimates of literature data for thermodynamic properties of substances in the system Cl–Pd (aq) the values of stepwise and total stability constants for [PdCl_n]^{2–n} complexes are recommended. The standard electrode potential of PdCl₄^{2–}/Pd(κ) half-cell (E^o_{298.15} = 0.646±0.007 V) is calculated. This value yields Δ_rG^o_{298.15} = -400.4±1.4 kJ/mol for PdCl₄^{2–}(aq). On the basis of calorimetric studies published in the literature the following thermodynamic quantities are calculated: Δ_rH^o_{298.15} (PdCl₄^{2–}(aq)) = -524.6 ± 1.6 kJ/mol, and Δ_rH^o_{298.15} Pd²⁺(aq) = 189.7 ± 2.6 kJ/mol. Using the accepted values for the total stability constant of PdCl₄^{2–} and the standard electrode potential of PdCl₄^{2–}/Pd(κ) half-cell, the value of Δ_rG^o_{298.15} Pd²⁺(aq) = 190.1±1.4 kJ/mol is defined.

Key words: thermodynamics, electrochemistry, chloride complexes of palladium, palladium ion

Reference: Polotnyanko, N. A., I. L. Khodakovsky (2012), Thermodynamic properties of palladium chloride complexes in aqueous solutions, *Вестник ОНЗ РАН*, 4,

Popova¹ E.S., Plyasunov² A.V. On the linear dependence on the water density at high temperatures of the cation-anion binary interaction parameters for the simple model (SIT) of the activity coefficients

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The analysis of the theoretical model for the activity coefficients predicts that the parameter of the binary cation-anion interaction is constant at isochoric conditions and decreases with the decrease of the density of water. The regression of experimental values of the activity coefficients of a number of 1-1 electrolytes indicates that the agreement between experiment and theory is observed at T>370 K or at the density of water less than 950 kg m⁻³.

Keywords: activity coefficients; correlation

Reference: Popova, E. S., A. V. Plyasunov (2012), On the linear dependence on the water density at high temperatures of the cation-anion binary interaction parameters for the simple model (SIT) of the activity coefficients. *Vestnik ONZ RAS*, 4, (doi:)

1. The theoretical analysis

In thermodynamic modeling of geochemical processes it is necessary to know the activity coefficients of the ions, γ. It is known that at low electrolyte concentrations the forces of electrostatic attraction dominate, causing a decrease in the activity coefficients, whereas at high concentrations the repulsive forces appear and γ increase with increasing concentrations of the electrolyte.

The most accurate method to describe the activity coefficients is the Pitzer method [Pitzer, 1973], which includes both the electrostatic contribution and the repulsive contributions, given as a virial series in the concentration of particles. The Pitzer method uses a large number of parameters, which depend on T and P and have to be determined by regression of experimental data.

For modeling of geochemical systems it would be useful to have a less accurate method, if it can be used to predict the magnitude of the activity coefficients at high T and P. The SIT model [Grenthe et al., 1997] may be regarded as such a model. The SIT model can be viewed as a simplified Pitzer model, since SIT considers, in addition to electrostatic contributions, only binary cation-anion interactions. The following statement is accepted in the SIT model for γ_i , the activity coefficient of an ion i :

$$\ln \gamma_i = DH + \sum_j b_{\gamma}(i, j)m_j \quad (1),$$

where DH designates an electrostatic term (which is based on the Debye-Hückel theory), b_{γ} is the cation-anion binary interaction parameter, j is the counter-ion for i (i.e. if i is a cation, then j is an anion, and vice versa). For mean ionic activity coefficients of an 1-1 electrolyte, $\gamma_{\pm}$, SIT gives the following expression:

$$\ln \gamma_{\pm} = DH + b_{\gamma}m \quad (2),$$

where m is the molality of the electrolyte. Is it possible to predict values of the binary parameter b_{γ} at high T and P?

Pitzer [Pitzer, 1973, 1977] showed that for the combination of the "primitive model" for the interionic mean force potential and the simplest approximation for the cation-anion radial distribution function, the theory gives the following expression for the activity coefficients of 1-1 electrolyte in the molar concentration scale (C):

$$\ln \gamma_{\pm} = DH + 2 \cdot \frac{2\pi a^3}{3} C \quad (3),$$

where a stands for the hard-core diameter of ions.

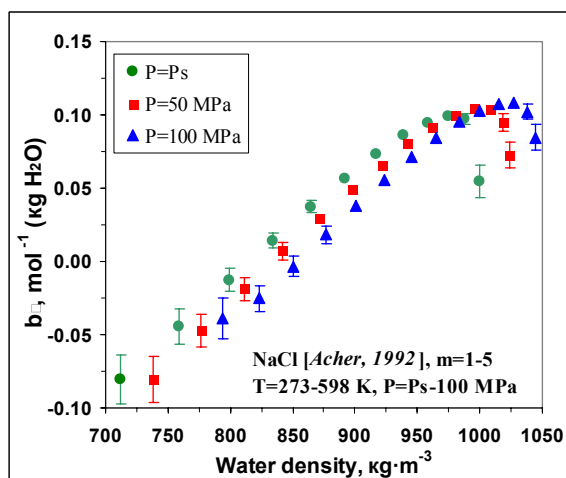


Fig. 1. Values of b_{γ} for NaCl

Equation (3) is valid for the molar scale of concentrations, while equation (2) is written for the molal concentration scale. The ratio of the molar and molal concentrations depends on the molecular weight M of an electrolyte and the density ρ of the solution ρ , and in the limit of low concentrations this ratio is close to the density of pure water ρ_1^* :

$$\frac{C}{m} = \frac{1000\rho}{1000 + mM} \approx \rho_1^* \quad (4).$$

By comparing the constant of equation (3) with the parameter b_{γ} of equation (2) one obtains:

$$b_{\gamma} \approx \frac{4\pi a^3}{3} \cdot \frac{C}{m} = \text{const} \cdot \frac{C}{m} \approx \rho_1^* \cdot \text{const} \quad (5).$$

This analysis suggests that in isochoric conditions (at the constant density of water) b_{γ} is constant. If the water density changes, b_{γ} changes proportionally to ρ_1^* , i.e. it decreases with the decreasing density of water.

2. The analysis of experimental data

In order to verify the relation (5), we determined from the experimental values of activity coefficients of a number of 1:1 electrolytes (HCl, LiCl, NaCl, NaBr) the values of b_{γ} over a wide range of T and P (up to 598 K and 150 MPa). The data are presented graphically in Figures 1-4.

The analysis of results showed that at temperatures below 370 K (or the water density above 950 kg m⁻³) the parameter b_{γ} changes in a complicated way and in the general case does not follow the equation (5).

However, at $T > 370$ K (or the water density less than 950 kg m⁻³) for all studied systems b_{γ} is roughly constant at isochoric conditions and decreases linearly with the decrease of the density of water.

We expect that equation (5) is useful for estimating the binary cation-anion interaction parameter at temperatures of 370 K and above.

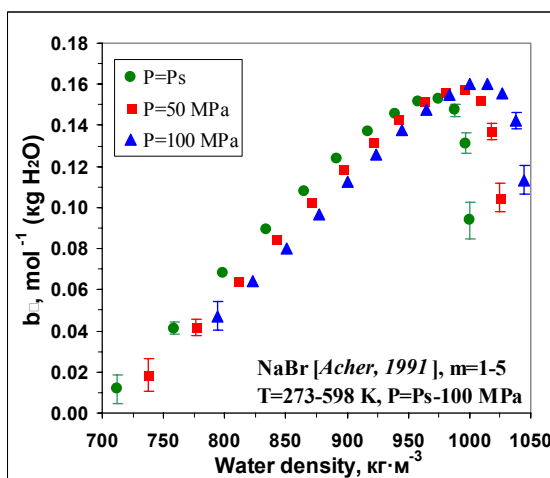


Fig. 2. Values of b_{γ} for NaBr

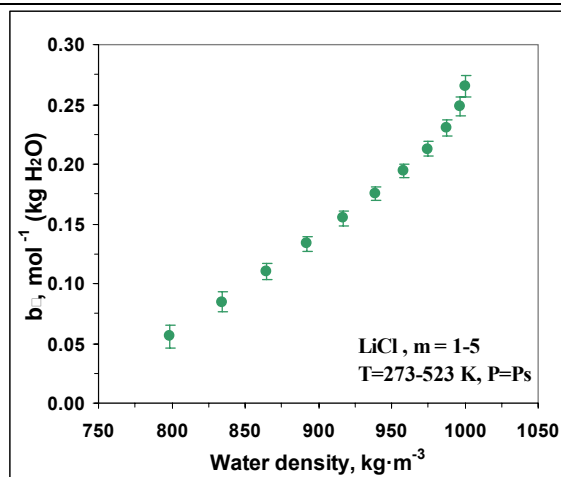


Fig. 3. Values of b_γ for LiCl. Experimental data for $\gamma_\pm$ are taken from Holmes and Mesmer, [1983].

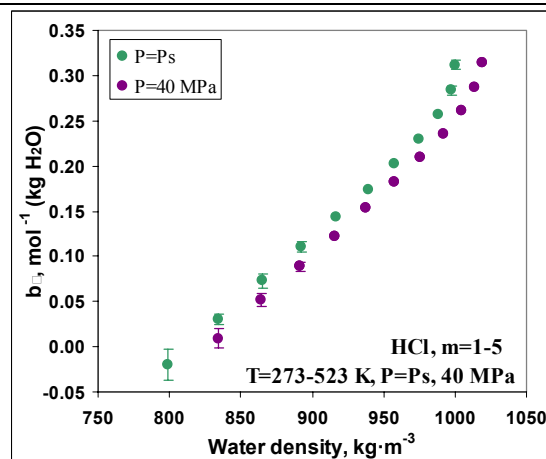


Fig. 4. Values of b_γ for HCl. Experimental data for $\gamma_\pm$ are taken from Holmes et al. [1987].

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Razvorotneva L.I., Markovich, T.I. Physico-chemical peculiarities of uranyl ion accumulation by rutile

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Hydrated rutile exhibits a high adsorption activity with respect to water-soluble forms of uranium – the uranyl ion (UO₂²⁺). Sorption isotherms obtained at pH 3.5 and 5.5 and 8–9 are described using the Langmuir equation. The calculated value of the limiting amount of sorption was 170 mkg/m² at pH up to 5.5, with increasing pH to 8 it was 1.2 mg/m². The sorption behavior of uranium on the mineral sorbent – rutile is determined by: on the one hand, the values of pH, concentration of uranium (U(VI)), and on the other hand, the different surface groups on the surface of rutile, the quality of the pore space and the presence of different types of structural defects.

Key words: radionuclides, sorption, geochemical barriers, rutile

Reference: Razvorotneva, L. I., T. I. Markovich (2012), Physico-chemical peculiarities of uranyl ion accumulation by rutile, *Vestnik ONZ RAN*, 4, ()

To determine the factors influencing the migration behavior of uranium in the environment, it is necessary to

investigate the interaction of soluble forms of the radionuclide with the surface of the host rock and the colloidal particles in the liquid phase. In the landscape migration of chemical elements, including water-soluble forms of uranium, the geochemical barriers where migration decreases and concentration takes place are important. In studying the mobility of radioactive elements in surface conditions, a lot of attention paid to the sorption properties of the barriers on the basis of various natural minerals. One of the natural sorbents is rutile, which along with the clay minerals is often part of the soil absorbing complex. Hydrated rutile exhibits a high adsorption activity with respect to water-soluble forms of uranium – the uranyl ion (UO₂²⁺). The purpose of this work is to evaluate the sorption parameters of rutile as an adsorbent for uranium.

The object of the study is a suspension of rutile, consisting of 75% of natural rutile (solid phase 20 mesh) and of 25% of water.

The samples of natural rutile was ground to a size of 20–30 μm. According to X-ray data, the sample under study corresponded to the rutile phase. Crystal-chemical formula calculated on the two oxygen atoms was the following: (Ti_{0.973} V_{0.016} Fe_{0.007} Cu_{0.008} Si_{0.006} Al_{0.004} Ca_{0.002})_{1.014} O₂.

Experiments on the sorption were conducted of a wide range of pH (from 1.5 to 10) at 20 ± 1 °C. Uranium solutions were prepared from uranyl nitrate (UO₂(NO₃)₂ · 6H₂O). Experiments on the sorption were conducted with the active magnetic stirring. Separation of the liquid phase from the solid was carried out in a centrifuge at 13–15 thousand rev/min. Uranium concentration was determined by a laser spectrometer "Angara". Thermal analysis of samples was performed on derivatograph «Paulik-J», phase composition was controlled by X-ray diffraction method on diffractometer DRON-3. EPR studies performed on radiospectrometer «Kadiopan» SE/X254. Measurements of surface area and pore size were performed on ASAP-2400 ("Micromeritics", USA) on the adsorption of nitrogen at 77°K. Before measuring the samples were heated up to 300°C in dynamic vacuum (2·10⁻³ Torr) during 12 hours. The adsorption isotherms were analyzed by BET.

Previously it was found that the efficiency of immobilization of uranium in rutile is caused by the peculiarities of its surface-active functional groups which

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depend on the pH of the solution, as well as by the presence of various types of irregularities in the structure. The study of sorption in the pH range from 1.5 to 9 showed a significant dependence on the acidity of the process. For example, at pH < 3.5 0.5–1 % of uranyl sorbed. With increasing pH values from 3.5 to 5.5, the rates of sorption increase dramatically (up to 45–57 %) (table. 1). The increase in pH to 8–9 leads to a further increase in the amount of uranium sorbed by the surface of rutile.

The study of sorption kinetics showed that the mobile equilibrium of dilute solutions of uranium (10^{-4} – 10^{-5} M), that is with a low degree of saturation of the surface of rutile, is reached within 20 minutes of the experiment. Increasing the concentration of uranium in solution leads to an increase in time required to reach equilibrium, which indicates a high degree of saturation of chemically active surface groups by uranyl ions, as well as increasing participation in the process of sorption of the surface of the pore space. This is indicated by the change in volume of micropores from 0.08 sm^3/g to 0.11–0.23 sm^3/g , and the diameter of micropores varies from 76 to 115–165 Å. Sorption isotherms obtained at pH 3.5 and 5.5 and 8–9 are described using the Langmuir equation. The calculated value of the limiting amount of sorption was 170 mkg/m^2 at pH up to 5.5, with increasing pH to 8 it was 1.2 mg/m^2 .

Table 1. Dependence uranyl ion sorption on pH of the solution and the rutile specific surface

pH	Sorption uranyl ion, %	Specific surface, m^2/g
4.0	3	40.8
4.3	8	45.2
4.5	21	46.0
5.0	40	46.4
5.3	60	47.0
5.5	85	49.3
6.0	92	54.2
7.0	99	58.0
8.0	100	60.1

X-ray structure analysis of rutile in the crystallographic directions (110) and (001) showed that the ions of U (VI) associated with atoms in the direction of the rutile (110). The oxygen atoms related to the surface of rutile in an acidic environment often remain protonated after the sorption of uranium and do not participate actively in the further process. And the rutile surface areas that are not protonated, on the contrary, absorb uranium by the reaction of: $\geq\text{TiOH} + \text{UO}_2^{+2} + \text{A}^- = \geq\text{TiO}(\text{UO}_2) + \text{A}^- + \text{H}^+$

At low pH uranium in solution present in the form of UO_2^{+2} , and on the surface of rutile $\geq\text{TiOH}_2^+$ groups of atoms dominate. At values of pH > 5.5 the solution contains $\text{UO}_2(\text{OH})^+$ or $(\text{UO}_2)(\text{OH})_5^+$ complexes, and on the surface of rutile surface groups occur, where TiO-form is dominated. After contact with rutile the complexes are fixed: TiOUO_2OH and $\text{TiO}(\text{UO}_2)_3(\text{OH})_5$, it is evidenced by the shift of the absorption bands in the optical adsorption spectra (232, 443 and 610 nm^{-1}) compared with the initial sample of rutile (232, 447 and 613 nm^{-1}).

Another important contribution to understanding the mechanism of uranium immobilization by rutile, is the study of the role of surface defects in the structure. This is

particularly important in the study of landscape uranium migration, where, under the influence of various environmental factors not only a refinement of rutile with a significant increase of specific surface area (from 0.8 to $36 \text{ m}^2/\text{g}$) occurs, but also the appearance of deep structural defects. By the method of thermal analysis on DTA curves during heating of samples of natural rutile at the 400–7000K, exothermic effects appeared that are absent in standard samples of rutile. Evaluation of peak areas showed the thermal effect equal to 26 kJ/mol. However, during the interaction with the uranyl ion, the effect is reduced due to the redox interaction. Thus, by the EPR method the appearance of trivalent titanium in the reaction was reported: $\text{e}^- + \text{Ti}^{4+} = \text{Ti}^{3+}$. In such a way the local destruction of the oxygen cage, the appearance of titanium atoms in the crystal lattice intersite space leads to an increase in the number of paramagnetic chemically active states. It is resulted in an increase of sorption capacity of rutile with respect to uranium.

Thus, the sorption behavior of uranium in the mineral sorbent – rutile is determined by: on the one hand, the values of pH, concentration of uranium (U(VI)), and on the other hand, the different surface groups on the surface of rutile, the quality of the pore space and the presence of different types of structural defects.

Redkin A.F. Experimental study of joint solubility of pyrochlore and uraninite in fluoride solutions at 800°C, 2300 bars, and Co–CoO buffer

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The solubility of a synthetic U-Pyrochlore (approximate composition $(\text{Na}_{1.0}\text{Ca}_{0.7}\text{U}_{0.3})(\text{Nb}_{1.0}\text{Ta}_{1.0})\text{O}_6\text{F}_{0.7}$) and uraninite ($\text{UO}_{2.03}$) has been studied in the solutions of P-Q type containing from 5 to 35 wt. % of fluorides and up to 2 mol/kg H_2O of silica at $T=800^\circ\text{C}$ and $P=2300$ bars. The composition of the fluids were taken from experimental data analyses in the system Li-F-granite – fluoride-chloride fluid at specified T - P conditions. The compositions correspond to 3 phase fluid systems ($\text{L}_1+\text{L}_2+\text{Si}$ -solution-melt). The init solutions also contained 0.667 mol/kg H_2O of chlorides (Na, K, Li) and 0.01 mHCl . The acidity of the solutions in equilibrium with Li-F-granite melt was in range of 0.01–0.1 mHCl . The data obtained indicate that total U and Nb solubility in the fluids was substantial (from 0.001 to 0.01 mol/kg H_2O) and it has a positive trend from total fluoride concentration in the solutions.

Key words: experiment, pyrochlore, uraninite, solubility, fluoride solutions, fluid immiscibility

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The oxide compositions of niobium (V), uranium (IV), and tantalum (V) have low solubility in diluted solutions of electrolytes. The most stable complexes of the concerned elements in aqueous solutions are fluorides. Essential values ($>0.001 \text{ mol}/\text{kg H}_2\text{O}$) of these complexes may appeared only in high-salt solutions. At the same time, the compositions and properties of solutions depend from magma (fulfils a role of basic-acid buffer) composition, ore compounds content in it, temperature, pressure, red ox potential in the system melt – solution – volatile, and total salts concentrations in the solution.

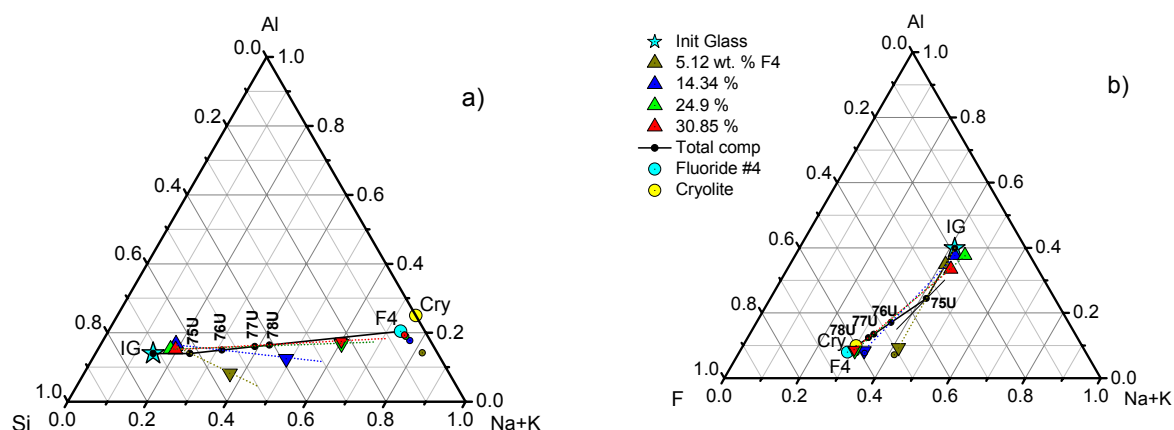


Fig. 1-a, -b. System model granite melt (Δ) – fluoride fluid (▽) at 800°C, 2300 bars, Co-CoO buffer. Symbols: star (IG) – init composition of granite melt, triangles – glasses after runs in solutions of 5.12 wt. % of fluorides (dirty green), 14.34 % (blue), 24.9 (light green), 30.85 % (red); F4 (blue circle) – fluoride glass; Cry (yellow circle) – cryolite; small colored circles – init solutions; small black circles numbered 75U-78U – the total composition in the runs; reverse colored triangles – calculated compositions of the solutions in equilibrium at different fluoride fluid compositions from 5.12 to 30.85 wt. %.

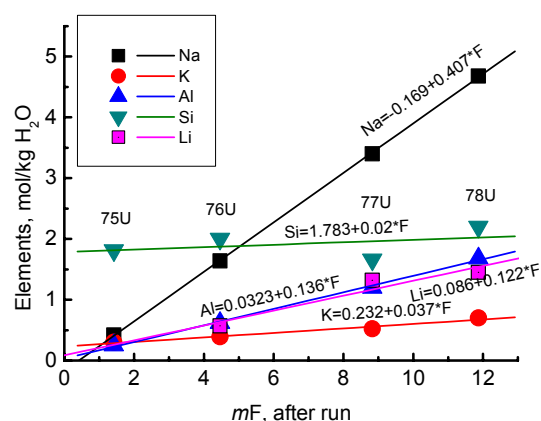


Fig. 2. Dependence of the fluoride solutions compositions in equilibrium with granite melts from the total fluoride in the solutions in the runs # 75U-78U (calculated data)

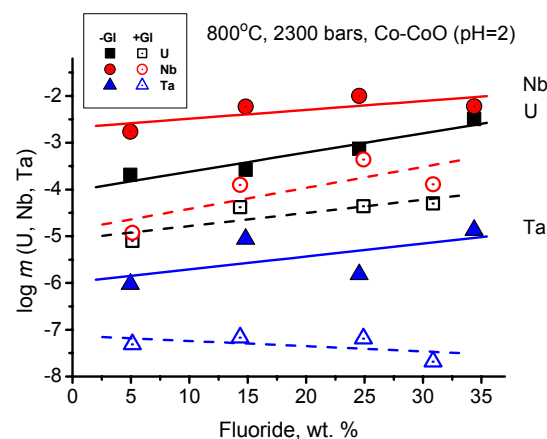


Fig. 3. Apparent solubility of uraninite and U-pyrochlore in 3-phase fluid system based on fluoride glass F4 (experiments with granite melt) and F5 (only solution) (pH=2)

As a possible magmatic source of the ores can be performed a water-saturated granitic magma situated in region (T - P -salt concentration) of fluid immiscibility, i.e. at T - P parameters higher than point Q and the salts concentration lies between L_1 and L_2 fluid phases. The solutions of P-Q type in T - P region of immiscibility are of interest as ore compounds solvent because they give rise to pair of fluid phases L_1 and L_2 of different salts content and the solubility of ores in them. The total salts concentration of P-Q type effects on the ratio L_1 and L_2 phases but do not affect on accumulation of anion compound in co-existent Al-Si-melt. The main compound of solution equilibrated with model Li-F-granite melts is NaF [Redkin *et al.*, 2011]. The system NaF-H₂O is the system of second P-Q type with the critical point Q lies at about $T=760^\circ\text{C}$ and $P=2000$ bars [Kotel'nikova, Kotelnikov, 2010]. Thus, the conditions of the experiments $T=800^\circ\text{C}$, $P=2300$ bars were chosen wittingly from the region of immiscibility of the system NaF-H₂O. Red ox conditions set up with Co-CoO buffer to stabilize uraninite UO_2 as a stable uranium-oxide phase.

The aim of the studies are to find the conditions for mobilize uranium by magmatic origin hydrothermal solutions in concentrations sufficient to form gigantic

hydrothermal ore deposits. This work demonstrate influence of total fluorides concentration on uraninite and pyrochlore solubility in the solutions of P-Q type which have the compositions close to the solutions in equilibrium with Li-F-granite melts at T - P parameters higher than point Q.

Experiments performed in the system granite melt – F-Cl-solution – ores (columbite and uraninite) at 800-950°C, 2300 bars indicated that the composition of granite glass changes during interaction with solution. Smallest changes were determined in the solutions where fluorides compounds ratio was as



As a solvent, we used a next chloride solution (Cl-1): $0.373\text{mNaCl}+0.107\text{mKCl}+0.117\text{mLiCl}+0.0187\text{mAlCl}_3+0.0067\text{mCaCl}_2+0.01\text{mHCl}$.

The results of microprobe analyses of granite glasses after runs (75U-78U) and the compositions of the solutions in equilibrium with them at the condition of the runs are presented on the triangle diagrams in Figs. 1-a, 1-b. The solution compositions in the run were calculated by mass balance method based on the average composition of the

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glasses, the total system taking in account that the melts (glasses) capture 8 wt. % of H_2O . In Fig. 2, the dependences of main rock-bearing compounds in the solutions in equilibrium with granite melts are plotted against the total F⁻ in solutions. In spite of presence of high Si (as K_2SiF_6) in initial solution, a removal of silica from granite melt occurs (Fig. 1-a). The quartz solubility in water at 800°C, 2300 bars according different sources consists from 0.27 [Shibue, 1996] to 0.32 [Manning, 1994]. The total Si (mainly as silica) in heterogeneous solution is about 2 mol/kg H_2O (Fig. 2) and it does not depend from the total fluorides concentration. It is obvious that fluid system is presented at least by three phases: L_1 , L_2 , and Si-solution-melt. The L_1 and L_2 phases is found in granite melt in view of ball inclusions of different density. Silicate fluid-melt phase is not observed in electron microscope visual inspection, but it can participate as a surface-active substance between granite melt, L_1 and L_2 fluoride fluid phases. In spite of high fluoride contents in the fluid-magmatic system, the granite-melt phase did not accumulate fluorine. To the contrary, according electron microprobe analyses it has been found fluorine withdraw from the model granite melt (Fig. 1-b). The solutions compositions after runs including ore elements (Fig. 3) had substantial difference from the total init compositions owing to capture of major part of L_1 , L_2 , and Si-phases as fluid inclusions in the granite melts. Thus, the granite melt was removed in these experiments and as the models (initial) were used the solutions shown in Fig. 2. As in most early carried out experiments, the solution of 0.667 m of chloride, Cl-1 was used as the solvent and fluorides were added in the form of powder (milled fluoride glass F5) in amount from 5 to 35 wt. %, plus calculated amount of amorphous SiO_2 , so that the total SiO_2 contents in the solutions were 2 mol/kg H_2O . The powder F5 was composed from

0.374 NaF, 0.13 AlF_3 , 0.019 K_2SiF_6 , and 0.121 LiF.

The synthetic uraninite ($\text{UO}_{2.03}$) and maximum saturated pyrochlore of pyrochlore-microlyte series (of composition $(\text{Na}_{1.0}\text{Ca}_{0.7}\text{U}_{0.3})(\text{Nb}_{1.0}\text{Ta}_{1.0})\text{O}_6\text{F}_{0.7})$) were used as the ore minerals. The experiments were carried out in Pt capsules on hydrothermal equipment at 800°C, 2300 bars, Co-CoO buffer. Runs lasted 8 days. The run products were washed out from the capsules by 50-fold volume of 0.01M HCl and then were analyzed by ICP methods. The filled symbols and their linear approximation (solid lines) in Fig. 3 represent the results of the analyses. For comparison, the results ICP analyses of the experiments carried out in similar solutions but in the presence of model Li-F-granite melt (hollow symbols and dotted lines) are shown in the Fig. 3. As might be expected, the concentrations uranium, niobium, and tantalum in the system ore minerals – solution were 1-2 order greater than in the system ore minerals – granite melt – solution. Data obtained indicate that 90-99 % U, Nb and Ta remain in fluid inclusions in granite glass after quenching. The saturated concentrations of Nb and U in high-concentrated fluoride solutions interacting only uraninite and U-pyrochlore are substantial (>0.001 mol/kg H_2O) and these solutions may be as a media to produce large uranium ore deposits. As the predominant species of uranium at that conditions could be sodium-fluoride or fluoride uranium complexes which were mainly in L_2 and silica fluid-melted

phase and precipitated from them during quenching in form of low-soluble fluorides of sodium and uranium, $\text{Na}_{1+x}\text{UF}_{6\pm y}$ of pale blue colour. The average composition of sodium-uranium fluoride phase was NaUF_6 , what remain on presence of oxidized forms of uranium (mainly U(V)) in the system despite the reduction conditions (Co-CoO buffer) of the runs.

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