Hydrothermal equalibria and ore formation

Dadze T.P., Kashirtseva G.A., Novikov M.P., Plyasunov A.V. Experimental study of solubility of powellite $CaMoO_4$ in weakly acidic solutions at 573 K.

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Abstract: Solubility of powellite $CaMoO_4$ was studied in dilute HCl or $HClO_4$ solutions (from 10^{-4} to ~ 0.03 m) at 573 K and ~ 100 bars. The obtained experimental data for $CaMoO_4$ are satisfactorily reproduced with species $HMoO_4^-$ and H_2MoO_4(aq), which Gibbs energies were calculated earlier (Dadze et. al., 2017) from data on solubility of MoO_3 in acid solution, demonstrating an internal agreement of solubility values for these phases.

Keywords: *powellite $CaMoO_4$, solubility, acidic solutions, modeling*

Solubility of powellite $CaMoO_4$ was studied in dilute HCl or $HClO_4$ solutions (from 10^{-4} to ~ 0.03 m) at 573 K and ~ 100 bars. Crystalline $CaMoO_4$ is obtained by sintering $CaCO_3$ and MoO_3 in equivalent proportions. The Ca:Mo atomic ratio based on 4 microprobe (Tescan VEGA TS 5130MM) analyses in the synthesized phase is equal to (0.981±0.014):1.0. Experiments were performed in titanic autoclaves from VT-8 alloy, passivated by 20% nitric acid at 673 K within a day. Autoclaves were placed into a vertical cylindrical furnace. Temperature was controlled by the regulator Miniterm-300. Fluctuations of temperature during runs were within ±2 K. Pressure in autoclaves was set by a degree of filling based on PVT – data of water. Duration of experiments was 4-7 days. A weighed quantity of $CaMoO_4$ was loaded into a titanic container that was suspended the upper part of the autoclave. The solid phase before and after experiments was controlled by X-ray diffraction, confirming that $CaMoO_4$ was the only phase present. The Mo concentration in solutions was determined by a colorimetric method (Marchenko, 1971) on Specol-11 at λ=453 nm and controlled by the weight loss method. Solubility of powellite increases with concentrations of acids, see Fig. 1.

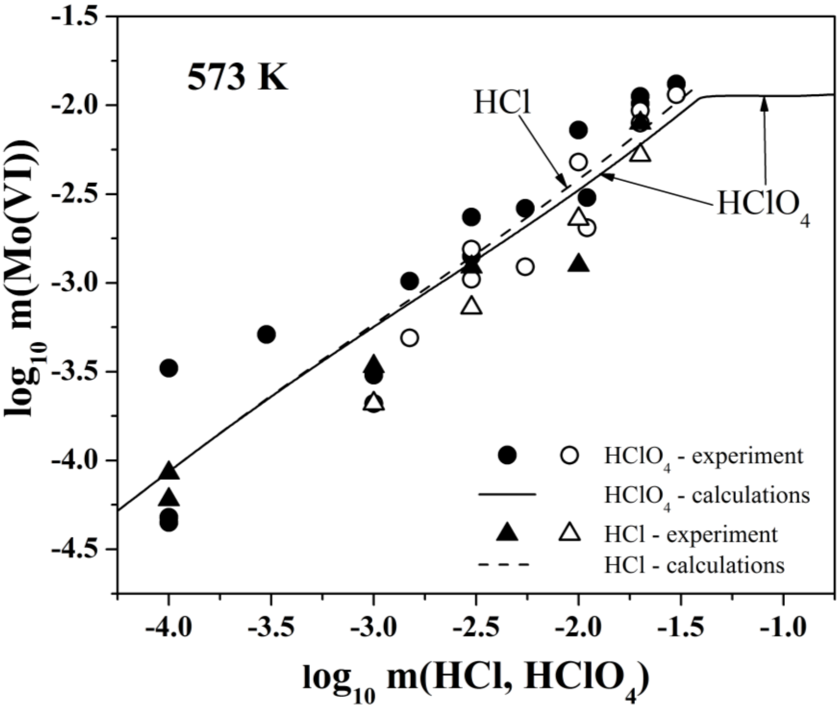

Fig. 1. Experimental (symbols) and calculated (lines) values of solubility of $CaMoO_4$ in solutions of acids. The filled symbols represent data of the chemical analysis, open symbols – the weight loss data.

Modeling of experimental results was carried out with the HCh program (Shvarov, 2008). The Gibbs energies of aqueous species H^+, OH^-, Cl^-, HCl(aq), ClO_4^-, Ca^{2+}, $CaOH^+$ are calculated the HKF model, $CaCl^+$, $CaCl_2$(aq) – taken from (Arcis et al., 2014), $HMoO_4^-$, H_2MoO_4(aq) – taken from (Dadze et al., 2017). Thermodynamic properties of powellite $CaMoO_4$ at 298.15 K are recommended recently (Gamsjäger and Morishita, 2015), the temperature dependence of the heat capacity to 1200 K is calculated based on data of (Zhidikova and Khodakovsky, 1984). According to calculations, powellite is stable up to concentrations of acids ~ 0.04 m, at greater acid concentrations the stable phase is molybdenum trioxide MoO_3. The obtained experimental data for $CaMoO_4$ are satisfactorily reproduced with species $HMoO_4$- and H_2MoO_4(aq), which Gibbs energies were calculated earlier from data on solubility of MoO_3 in acid solutions, demonstrating an internal agreement of solubility values for these phases.

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Korzhinskaya V.S. Effect of the fluid composition (Hf + HCl) on the behavior of metals (Ta, Nb, Mn, Fe) at dissolution of tantalite at T = 550°C, P = 1000 bar (Co-CoO buffer) UDC: 550.8.014

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Abstract. We present new data on the solubility of natural tantalite $(Mn,Fe)(Nb,Ta)_2O_6$ in mixed fluids (HF + HCl), which allowed estimating the equilibrium metal contents (Ta, Nb, Mn, Fe) in solutions at T = 550 °C, P = 1000 bar in the presence of an oxygen buffer Co-CoO. The initial HF concentration varied from 0.01 m to 2 m, and the HCl concentration remained constant and was 0.5 m. It is concluded that in (HF + HCl) solutions, tantalite dissolves incongruently with a predominant release into a solution of Mn and Fe in comparison with Ta and Nb. The comparison is made on content of tantalum in pure solutions of HF, HCl in the concentration range of 0.01 - 2 m and in mixed solutions (HF + 0.5m HCl).

Key words: experiment, tantalite, solubility, mixed fluoride-chloride solutions

To determine a quantitative estimate of the role of postmagmatic processes in the formation of rare-metal deposits of tantale and niobium, we do systematic experimental investigations on mineral solubility of Ta and Nb (columbite, tantalite, pyrochlore) under hydrothermal conditions, since the experimental data available in literature are not quite enough to solve this problem. Earlier we investigated tantalite solubility in fluoride and chloride solutions what is valid for the tantalum deposits connected with lime-alkaline, including lithium-fluoride granites (apogranites) [Zaraisky et al, 2010; Korzhinskaya et al, 2014].This paper describes the investigation of the behavior of Ta, Nb, Mn and Fe at tantalite dissolution in the fluids of the mixed composition (HF + HCl).

We got new data on solubility of tantalite natural mineral $(Mn, Fe)_2(Ta, Nb)_2O_6$ in mixed fluids (HF + HCl) at T = 550°C and P = 1000 bar in the presence of oxygen buffer Co-CoO. For the experiments we chose tantalite mono crystals from quartz-amazonite-mica pegmatites of the Etyka tantalum deposit, having composition according to the data of the microprobe CamScan:Ta_2O_5-17,70%; Nb_2O_5-58,99%; MnO-13,51%; FeO-4,42%; TiO_2-2,59%; SnO_2-1.54%; WO_3-1,24wt.% (the average values from seven analyses). The initial concentration HF varied from 0.01 m to 2m, but HCl concentration remained constant and was 0.5 m. Experiments were carried out on hydrothermal apparatus of high pressure in sealed platinum capsules using the ampoule technique. The quenched aqueous solutions were analyzed using ICP / MS and ICP / AES (mass spectrometry and atomic emission) methods. The composition of the solid product was characterized using X-ray diffraction and electron microprobe analysis.

Figs.1 and 2 show the obtained results on the behavior of metals of Ta, Nb, Mn and Fe at tantalite dissolution.Fig.1 shows concentration dependence of equilibrium content of Ta in (HF + HCl) solutions. Here the data of tantalum content in pure HF and HCL solutions are given for comparison. As seen from the diagram, concentration curve has a weakly marked positive dependence. It is determined that in the region of low initial concentrations in (0.01m HF + 0.5 m HCl) solution tantalum equilibrium concentration is very low, attains the values $1.44*10^{-7}$ mol./ kg H_20 what is an order of magnitude lower than that in pure 0.01m HF [Zaraisky et al, 2010] and coincides with tantalum content in pure HCl. As HF concentration grows, tantalum content in equilibrium solution rises in essentially and attains the values $n*10^{-6}$ in the solution (2m HF + 0.5m HCl). In this case Ta content is 4 orders of magnitude lower than that in 2m HF and only by one order higher than that in HCl [Korzhinskaya et al, 2014].

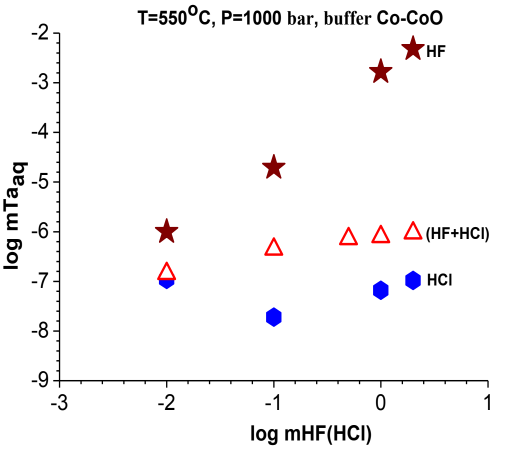

Fig.1 The concentration dependence of tantalum content in the HF, HCl and (HF+HCl) fluids when dissolving natural tantalite at T=550 °C, P=1000 bar (buffer Co-CO).

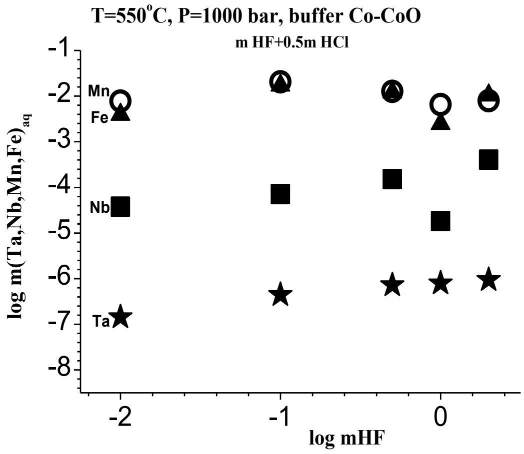

Fig.2 The concentration dependence of metal content (Mn, Fe, Nb, Ta) in the (HF+HCl) fluids when dissolving natural tantalite at T=550 °C, P=1000 bar (buffer Co-CoO).

A comparative analysis of equilibrium contents of metals: Nb, Ta, Mn and Fe at dissolution of natural tantalite in mixed (HF + 0.5m HCl) solutions at 550°C, 1000 bar is made **(Fig.2).** It is determined that the contents of Mn and Fe in mixed (HF + HCl) solutions are considerably higher than those of niobium and tantalum. In (0.01m HF + 0.5m HCl) equilibrium content of Mn is $7.74*10^{-3}$, but that of Fe is 3.94 $*10^{-4}$ mol/ kg H_2O. In (2m HF +0.5m HCl) solution equilibrium concentrations of Mn and Fe are comparable and are $n*10^{-2}$ mol./ kg H_2O, what is by 2.5 orders higher than the content of Nb and 4.5 orders higher than that of Ta. We could see the similar picture in chloride solutions where the content of Mn and Fe for all chloride solutions is markedly higher than that of tantalum and niobium and is almost the same for both metals [Korzhinskaya, 2014]. Thus, for both pure chloride solutions and mixed ones (HF + HCl) natural tantalite and synthetic Mn-tantalite dissolve markedly incongruently with a predominant transition into the Mn and Fe solution as compared with Ta and Nb.

On the basis of the performed experimental studies we got comparative characteristics of metal behavior of Nb, Ta, Mn and Fe at dissolution of tantalite natural mineral from a change of concentration of mixed solutions of the composition (mHF +0.5m HCl) at T = 550°C and P = 1000 bar in the presence of the Co-CoO buffer. The conclusion is made that a hydrothermal transport of Ta and Nb metals in the amounts necessary to form their industrial concentrations is only possible by concentrated fluoride-bearing solutions.

The obtained data prove unambiguously that participation of acidic fluoride solutions, high concentration of fluoride and redox conditions are favorable for solubility and Ta and Nb transfer by aqueous fluids. The sediment of Ta and Nb minerals from solutions with the formation of their deposits can occur as a result of neutralization of acidic fluoride solutions, a decrease of fluorine concentration and increase of oxygen fugacity.

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Kotelnikov A.R.[1], Korzhinskaya V.S.[1], Kotelnikova Z.A.[2], Suk N.I.[1] Pyrochlore solubility in fluoride solutions at 550-850°C, P=1 kbar in presence of silicate material. UDC 550.8.014

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Abstract. The experimental results of natural pyrochlore $(Ca, Na)_2(Nb, Ta)_2O_6(O, OH, F)$ behavior in KF solutions in quartz presence at 550-850°C, 1 kbar are presented. It has been estimated that at T=550°C and P=1 kbar quartz presence decreases Nb content in solution 3 orders of magnitude more. Investigation of fluid inclusions in quartz shows that in experiment condition the reactions of KF high temperature hydrolysis take place and phase of silicate glass (water solution-melt) forms as a result of interaction with quartz. This phase of alkaline glass is concentrator of Nb (Nb_2O_5 up to 16 wt %). Partition coefficient of Nb between glass and fluid is about 500 in favor of the glass. It has been shown that phase of alkaline solution-melt can be effective concentrator of ore component (Nb) at last low temperature stages of rare metal granites crystallization.

Keywords: experiment, pyrochlore, solubility, fluoride solutions, fluid inclusions

To estimate the influence of quartz (the most wide-spread mineral of ore rare-earth metal granitoid complexes) on pyrochlore solubility $(Ca, Na)_2(Nb, Ta)_2O_6$ (O, OH, F) special runs (with quartz and without it) have been done. The runs lasted 7-15 days at 550°, 650° and 850°C and pressure 1 kbar in the solutions LiF (0.08 M), NaF (1M); KF (0.5 and 1M) on hydrothermal devices with the external heating and cold valve and in "gas bombs". The accuracy of temperature regulation was ±5°C; pressure ±50 bar. As initial materials quartz (d. Perekatnoye, Aldan) and natural pyrochlore of the following composition (recalculation by 4 cations taking charge balance into account) have been used:

$(Na_{0.92}Ca_{0.95}Sr_{0.06})_{1.93}(Ti_{0.04}Nb_{2.02})_{2.06}O_6$ $[F_{1.02}(OH)_{0.18}]_{1.20}$. To estimate phase fluid state we used a method of synthetic fluid inclusions in quartz. Quenching solution after the run was analyzed by ICP/MS and ICP/AES (mass-spectral and atomic-emission) method for the elements (Nb, Ta, Na, Ca, Mn, Fe, Ti etc.). Solid charge was analyzed on the electronic microprobe CamScan MV2300 (VGA TS 5130MM) and by the x-ray phase method.

Fluid Phase State

The runs with LiF solution (concentration 0.08 M). At pressure 1 kbar and temperatures 550°, 650°C a fluid was in a heterogeneous state: two-phase gas-liquid (G+L) and three-phase gas-liquid-crystal (G-L-C) inclusions occurred in the samples. Two-phase inclusions are homogenized into liquid. In three-phase inclusions one more liquid phase is formed at heating. It accumulates itself round a gas bubble, what testifies to the fact that its density is lower than that of the remained liquid (Figs.1, 2).

The runs with NaF solution (concentration 1M). In contrast to LiF solutions at pressures 0.5 and 1 kbar and temperature 550°C a fluid was in a homogeneous state: only two-phase G-L inclusions were found. At temperature rise up to 650°C the interaction of the fluid with solid phases resulted in precipitation of a small amount of solid phases. The process of homogenization of two-phase inclusions is closely critical what shows the approximation of the run parameters to the critical point of the system.

The runs with KF solution (concentration 0.5-1M). At 550°C and 1 kbar in case of the initial concentration of the solution 2.9 mass% (0.5M) a fluid is homogeneous: only G+L inclusions occur. If at the same P-T conditions the concentration of the initial solution increases up to 1M (5.8 mass %) then a fluid is heterogenized what testifies to the formation of different-type inclusions (Fig. 3). Multi-phase inclusion (Fig.3) is shown at different temperatures; homogenization at heating up to 500°C is not attained, though all crystals (C) are dissolved and a gas bubble (G) has markedly got smaller. Together with (G+L+L+C) inclusions, inclusions (G+L) also occur what proves fluid inhomogeneity.

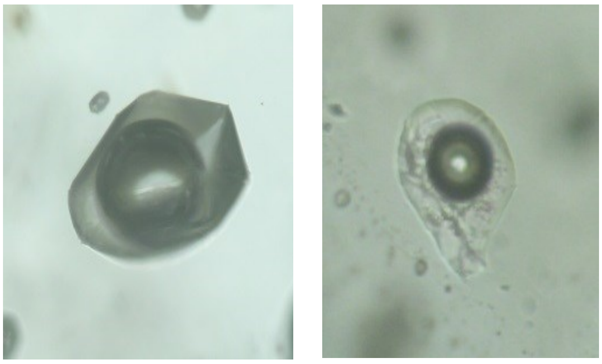

Fig. 1. Two-phase and three-phase inclusions in quartz

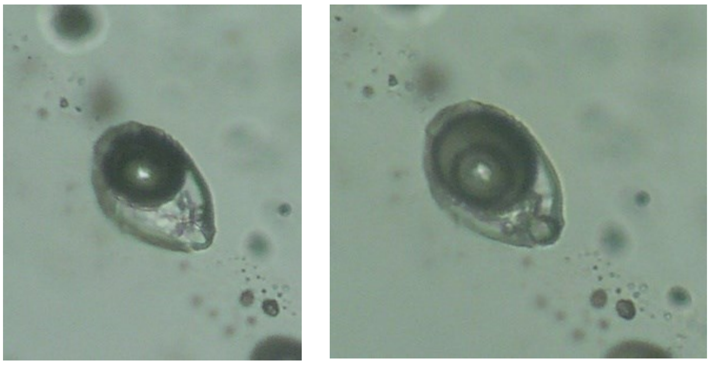

Fig. 2. Layering of liquid into two phases at heating of the inclusion. On the left is room temperature, on the right is 352°C

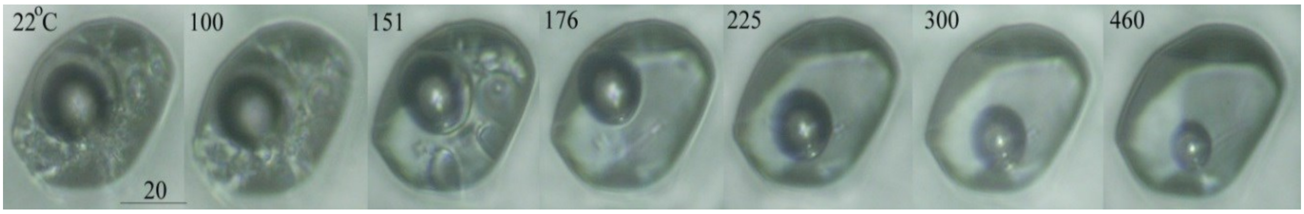

Fig. 3. (G+L+L+C) inclusions synthesized from 1M KF solution at 550°C and P 1kbar.

Pyrochlore solubility

It is experimentally determined that at T = 550°C quartz presence decreases essentially Nb content in KF solutions (more than by 3 orders). For temperatures 650°C and 850°C quartz presence in the system increases the equilibrium content of Nb in the solution by an order of magnitude: at 650°C Nb content in 1mKF without quartz is $2.91*10^{-5}$, but in quartz presence it is $1.59*10^{-4}$ mol/ kg H_2O; at 850°C the number of Nb without quartz is $2.38*10^{-4}$, but with quartz (or with granite melt) is $2.39*10^{-3}$ mol/ kg H_2O. The measurement of pH solutions before and after the runs has shown that for 550°C the initial solution 1m KF gets alkaline after the run, what decreases pyrochlore solubility; for 650°C pH shifts into the acidic region but only by half an order of magnitude (Tabl.1); for 850°C pH after the run shifts into the acidic region markedly: (pH bef/exp. =7.32, but pH aft/exp. = 1.901). It has been suggested that by means of fluid-magmatic interaction at T=850°C HF concentration in fluid essentially increases (fig. 4, 5).

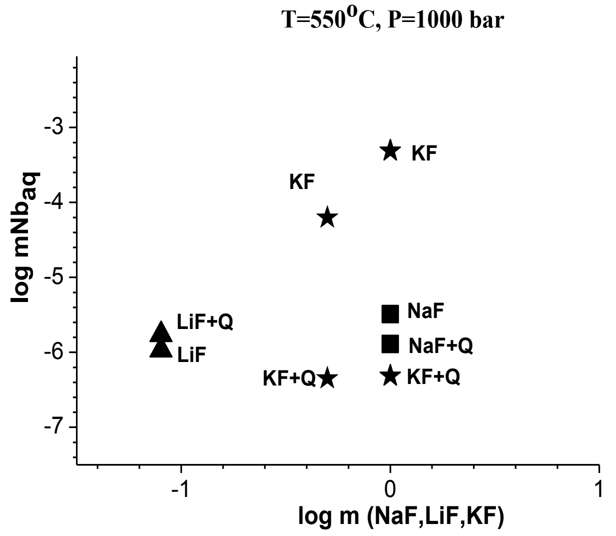

Fig. 4. Pyrochlore solubility in the solutions 0.08M LiF; 1M NaF; 0.5 and 1M KF at 550°C and P = 1 kbar (in the presence of quartz and without it).

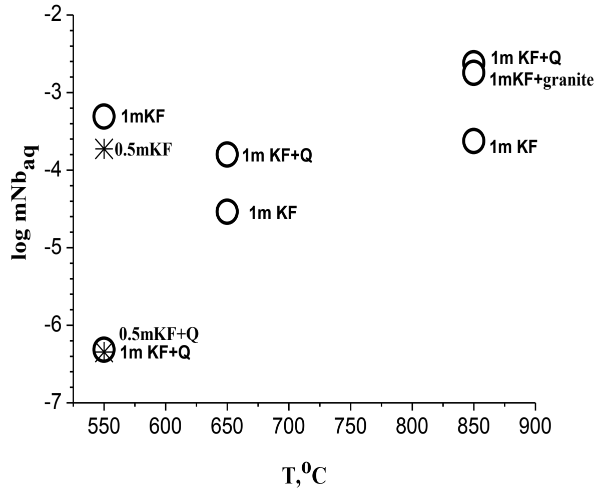

Fig. 5. Pyrochlore solubility in the solutions 0.5 and 1M KF at 550°, 650° and 850°C and P = 1 kbar (in the presence of quartz and without it).

The investigation of fluid inclusions in quartz has shown that under the conditions of the runs the reactions of high-temperature hydrolysis KF take place: $KF + H_2O = KOH\downarrow + HF\uparrow$; here the interaction with quartz takes place: $SiO_2 + 2KOH = K_2SiO_3 + H_2O$, with the formation of silicate glass phase (aqueous solution-melt). A phase composition of the run products on study of pyrochlore solubility in the presence of quartz (granite) is given in Tabl.1.

The phase of silicate glass synthesized in the runs on pyrochlore solubility at 650° and 850°C and pressure 1 kbar (in the solution 1M KF) is shown in Figs. 6 and 7. This phase of alkaline glass is a concentrator of Nb (Nb_2O_5 up to 16 mass %). The distribution coefficient of Nb between glass and fluid is equal to 500 (in favor of glass).A composition of phases is given in Tabl. 2. It is shown that the phase of the alkaline silicate solution-melt can serve as an effective concentrator of the ore component (Nb) at the last low-temperature stages of crystallization of rare-metal granites. On the basis of the obtained results, the following scheme of the process of ore genesis of fluoric granites with Nb-Ta type of mineralization can be outlined (Table 3).

Tabl.1. Phase relationships in the runs on pyrochlore solubility in the presence of quartz (granite) at P = 1 kbar.

T,°C	The initial charge	Solution	pH bef/exp.	pH aft/exp.	The run products
550	Qz(cryst.)+ Pchl1)	1M KF	7.3	8.2	Qz + Pchl + fluid
550	Qz(cryst.)+ Pchl1)	0.5M KF	6.7	7.5	Qz + Pchl + fluid
650	Qz(cryst.)+ Pchl1)	1M KF	7.3	6.9	Qz+Pchl+Sil.glass+fluid
850	Qz(cryst.)+ Pchl1)	1M KF	7.3	1.9	Pchl+Sil.glass+fluid+ph.A
850	Granite + Qz(cryst.)+ Pchl1)	1M KF	7.5	6.1	Sil.glass+Pchl+fluid

1) phases: Pchl – pyrochlore; Qz – quartz; Sil.glass – silikat. glass; ph.A – $KNbSi_2O_7$

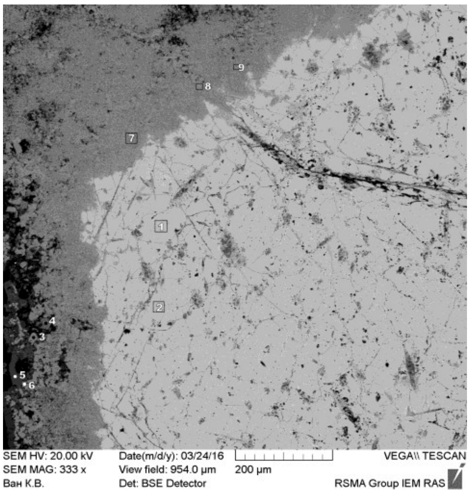

Fig. 6. SEM-photography. Light –pyrochlore, dark-silicate glass (650°C, 1kbar).

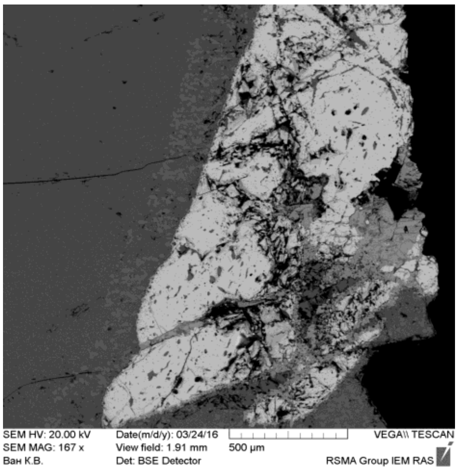

Fig. 7. SEM-photography. Light-pyrochlore, dark-silicate glass (850°C, 1kbar).

Tabl. 2. A composition of phases in the runs on pyrochlore solubility in the presence of the silicate phase

Oxide	850ºC, 1 kbar, 1M KF (Pchl+Qz)			850ºC, 1 kbar, 1M KF (Pchl+Qz+granite)			650ºC, 1 kbar, 1M KF (Pchl+Qz)	
	Pchl	Sil.glass	Ph.A.	Pchl	Sil.glass	Ph.A.	Pchl	Sil.glass
F	5.46	2.16	-	5.41	3.02	-	4.82	0.98
Na_2O	6.90	1.28	-	7.66	2.81	-	7.55	0.36
Al_2O_3	-	-	-	-	10.13	-	-	-
SiO_2	-	57.75	39.05	-	55.18	38.90	-	71.35
K_2O	1.75	14.18	16.04	-	15.53	15.93	1.20	10.69
CaO	14.76	0.21	-	13.84	0.87	-	15.28	-
TiO_2	1.15	0.14	-	1.26	-	-	0.40	0.26
SrO	1.47	1.19	-	-	-	-	-	-
Nb_2O_5	71.74	15.78	44.62	69.94	6.02	45.52	72.11	8.16
Σ	103.23	92.70	99.71	99.21	93.56		101.36	91.80
Σ(2F=O)	100.07	91.45	-	97.13	92.33	-	99.34	91.39

Ph.A – a recalculation for 4 cations with the correction of 7 atoms (O): $K_{1.023}Nb_{1.023}Si_{1.967}O_7$.

Tabl. 3. A possible scheme of ore-genesis process

PT-parameters	**Rock (melt): phase condition in the presence of the redundant fluid (of $KF+H_2O$ type)**	**The behavior of ore elements (Nb, Ta)**
T<650ºC; P<1 kbar	Total crystallization of granite melt (including alkaline silicate phase), crystallization of ore minerals of tantalum-niobates	Ore elements are in the form of minerals of tantalum-niobates
↑		
T~800ºC; P<1 kbar	Subliquidus conditions, beginning of crystallization of feldspars, presence of liquid phase of alkaline silicate (quasi-granite) melt.	Ore elements are concentrated in the phase of alkaline silicate melt.
↑		
T<900ºC; P~1 kbar	Melt (or two melts) under the conditions of fluid separation from the silicate melt (“retrograde boiling”), fluid heterogenization into liquid and vapor phases. Melt and fluid rise upwards. Hydrolysis reactions of a fluid with the formation of the alkaline silicate phase: $KF+H2O \rightarrow HF\uparrow +KOH$; $2KOH + SiO_2 \rightarrow K_2SiO_3 + H_2O$ (“a heavy fluid”).	Redistribution of ore elements in the system silicate melt-alkaline silicate melt in favor of the alkaline melt (“a heavy fluid”).
↑		
T~900ºC; P≤2÷3 kbar	Granite melts (rich in F, Li, K) with the fluid (in a subsaturated state of the melt). Rising of the melt upwards (at a simultaneous decrease of PT –parameters); heterogenization of the melt is possible in this case.	Available in the phase of the silicate (granite) melt.

Conclusions

1. A considerable influence of quartz presence on pyrochlore solubility in aqueous solutions of fluorides of alkaline metals under hydrothermal conditions is shown.
2. A phase composition of a fluid under the run parameters is studied by method of synthetic fluid inclusions in quartz
3. It is shown that at temperature 650°C and higher a phase of silicate melt is formed (due to fluoride potassium hydrolysis).
4. A phase of silicate alkaline melt concentrates niobium (up to 17 mass% Nb_2O_5) and can serve as a phase-concentrator of ore elements under the formation of tantalum-niobates deposits.

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Persikov E.S., Bukhtiyarov P.G. Viscosity of water free and water bearing basaltic, ultramafic and kimberlite magmas during origin, evolution and volcanic eruptions

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Abstract. The viscosity of magmatic melts is a key physical property which significantly governs the dynamics of their origin in the Earth's mantle, ascent and volcanic eruptions. Here we use both new experimental data on viscosity of water free and water bearing ultramafic, kimberlite and basaltic melts in the wide range of temperatures and pressures, and our physical chemical model for prediction the viscosity of magmatic melts to determine the fundamental features of viscosity of such magmas during their origin in the mantle, evolution and volcanic eruptions. Prediction results on the ascent of diamonds carrier kimberlite and ultramafic magmas from mantle to the crust with the appreciable acceleration is an unique in that the viscosity of such magmas will decrease by more than 3 times during this process despite of the decreasing magmas temperature by more than 150 °C. On the contrary, the viscosity of basaltic magmas will increase by more than 2.0 orders of magnitude during their origin, evolution and the ascent from the mantle to the crust.

Keywords: Viscosity, high temperature and pressures, ultramafic, kimberlite and basaltic melts, model, Earth crust, mantle

Viscosity of magmatic melts of different compositions is very important physical property which is drastically affect magma differentiation, transport, ascent and eruptions dynamics. Therefore experimental and theoretical investigations of viscosity of magmatic melts at high temperatures and pressures have been actively done for several decades in many laboratories in the world [for example: Persikov, 1998; Reid et al., 2003; Liebske et al., 2005]. However, the viscosity of kimberlite melts at the T, P – parameters of the Earth's mantle and crust is unknown [Persikov et al., 2015], and experimental date on viscosity of ultramafic and basaltic melts at the T, P – parameters of the Earth's mantle is scarce [Reid et al., 2003; Liebske et al., 2005]. Here we use both a new experimental and correct predicted data on viscosity of water free and water bearing ultramafic, kimberlite and basaltic melts in the wide range of temperatures (1300 – 1900 °C) and pressures (0.1-7.5 ГПа) for analysis of the possible changing of the viscosity of such type magmas during their origin in the mantle, evolution during ascent and volcanic eruptions. Experimental data on temperature dependences of viscosity of water free and water bearing ultramafic, kimberlite and basaltic melts have been obtained for the first time at 100 MPa of CO_2 pressure and at lithostatic pressures up to 7.5 GPa in the temperature range 1300 °C – 1950 °C. Experimental data obtained on temperature dependence of viscosity of these melts at moderate and high pressures is compared with predicted data in the same T, P – range and with the values of uncertainties of experimental and calculating data ± 30 % rel. Dependence of the viscosity of such melts on temperature are consistent to the exponential Arrenian – Frenkel - Eyring equation in the T,P - range of experimental study (Fig. 1a and Fig. 1b). The correct values of activation energies of viscous flow of these melts have been established for the first time [Persikov, 1998; Persikov and Bukhtiyarov, 2009; Persikov et al., 2015].

The pressure dependence of viscosity of water free and water bearing ultramafic, kimberlite and basaltic melts at 100 MPa of CO_2 pressure and at the lithostatic pressures up to 7.5 GPa has been established for the first time too. Experimental data obtained show that viscosity of ultramafic and kimberlite melts increases on about one order of magnitude with increasing pressures from 100 MPa to 7.5 GPa at the isothermal condition (1800 °C). The linear increasing of activation energies of viscous flow of ultramafic melts with pressure have been obtained for the first time too. Here we use both new experimental data on viscosity of ultramafic and kimberlite melts and our physical chemical model to compare the fundamental features of viscosity of these melts with the same features of basaltic melts. Viscosity of ultramafic and kimberlite melts at the moderate pressure (100 MPa) is lover on about one order of magnitude than viscosity of basaltic melts but at the high pressure (7.5 GPa) on the contrary higher on about half order of magnitude at the same values of the temperatures. Moreover, the dependence of viscosity on pressure of basaltic melts at the isothermal conditions (T = 1800 °C) has inverse character with minimum value for the water free melts at the pressure ~ 5.5 GPa and minimum value for the water bearing melts at the pressure ~ 4.5 GPa (Fig. 2 and 3).

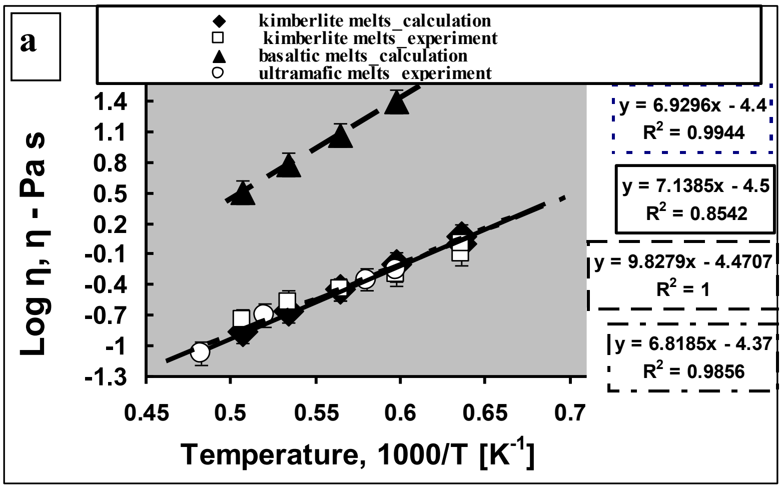
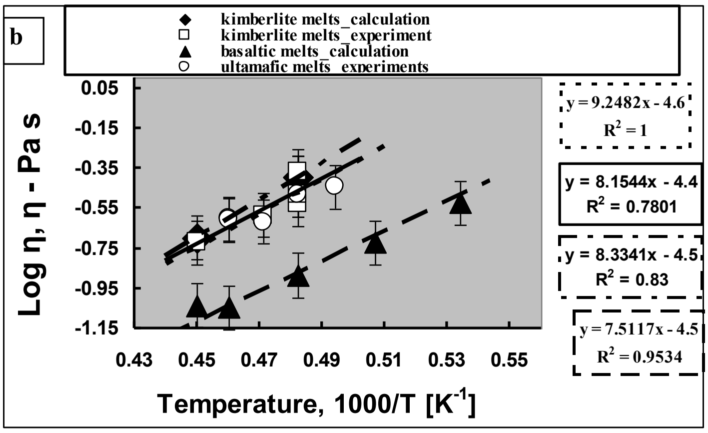


Fig. 1. Temperature dependence of the viscosity of water free ultramafic, kimberlite and basaltic melts (uncertainties of experimental and calculating data are ± 30 % rel.). a - Pressure is 100 MPa, b - Pressure is 5.5 GPa,



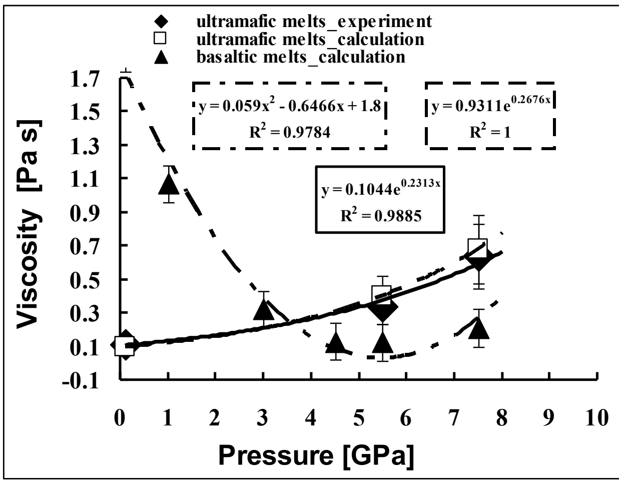


Fig. 2. Isothermal (1800 °C) dependence of the viscosity of ultramafic and basaltic melts on pressure (uncertainties of experimental and calculating data are ± 30 % rel.).

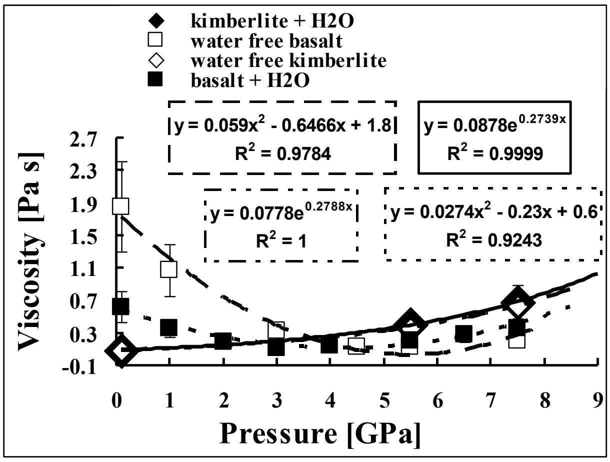


Fig. 3. Isothermal (1800 °C) dependence of the viscosity of water free and water bearing kimberlite and basaltic melts on pressure (uncertainties of experimental and calculating data are ± 30 % rel.).

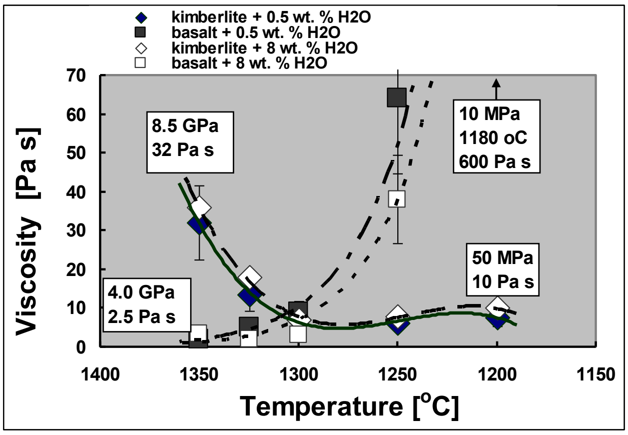


Fig. 4. Changing of the viscosity of water free and water bearing kimberlite and basaltic magmas during their origin, ascent from Earth's mantle to the crust and during volcanic eruptions.

Here we use both new experimental data on viscosity of water free and water bearing ultramafic, kimberlite and basaltic melts in the wide range of temperatures and pressures, and our physical chemical model to predict the viscosity of magmatic melts [Persikov, 1998; Persikov and Bukhtiyarov, 2009; 2015] to determine the fundamental features of viscosity of such magmas during their origin in the mantle, evolution and volcanic eruptions. Prediction results on the ascent of diamonds carrier kimberlite and ultramafic magmas from mantle to the crust with the appreciable acceleration is an unique in that the viscosity of such magmas will decrease by more than 3 times during this process despite of the decreasing magmas temperature by more than 150 ^{0}C. On the contrary, the viscosity of basaltic magmas will increase by more than 2.0 orders of magnitude during their origin, evolution and the ascent from the mantle to the crust.

Dissolution of water in kimberlite and basaltic magmas (up to 8 wt. % of water) has no affect on the dynamics of their viscosity during the ascent (Fig. 4). The mechanism of this new and unexpected phenomenon is conditioned by the much stronger influence of the pressure on viscosity of kimberlite and basaltic magmas compared to water content effect.

The Russian Foundation for Basic Research, (RFBR, Project 15-05-01318) is acknowledged for the financial support.

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REE distribution between ferrous mica, K-feldspar and kalsilite at 500°C and 1 kb in KOH solution UDC 549. (623.5+651.11) : 546.654/.668

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Abstract. The mineral association of Fe-mica, K-feldspar and kalsilite was synthesized in hydrothermal experiment at 500°C and 1 kb pressure in KOH solution in low-carbon steel insert. The phases obtained and REE distribution between them were studied by the methods of X-ray diffraction, EPMA, and LA-ICP-MS. The partition coefficients increase from light to heavy REE up to one order of magnitude (from La to Yb). Fe_2O_3 content in Kfsp amounts 1.4 wt. % on the average. Mica is represented by tetraferri-annite containing ~5.5 wt. % Al_2O_3.

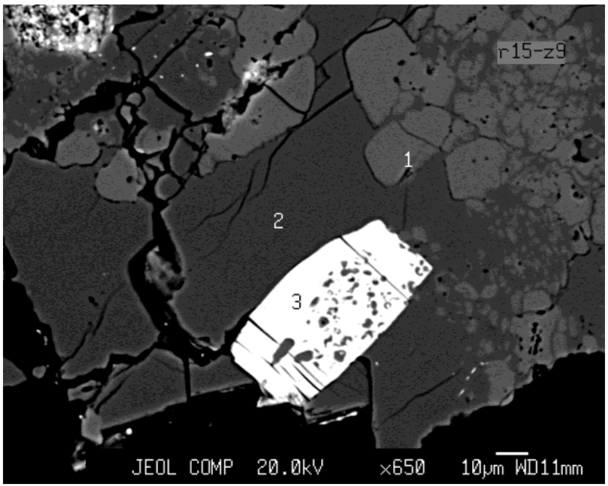
Keywords: ferrous mica, potassium feldspar, kalsilite, REE, partition coefficients, XRD, EPMA, LA-ICP-MS

Introduction. Rare earth elements (REE) are considered in geochemistry as indicators of rocks and minerals genesis (Larsen, 2002; Hulsbosch et al., 2014), redox-sensors of oxidative state of magmatic systems (Smythe, Brenan, 2016), etc. However, coefficients of their distribution between minerals of natural and imitating experimental systems, in particular, haplogranite system, remain unknown. This reduces the indicating capabilities of lanthanoids in the definition of conditions and factors of their accumulation in subsolidus phases, nature of Ce and Eu anomalies, distribution of light and heavy REE, tetrad-effect. We have acquired the first data on the distribution of REE between phases of Fe-mica, K-feldspar and kalsilite in the system SiO_2-K_2O-FeO-Al_2O_3-Ln_2O_3 under hydrothermal conditions.

Methods. The present paper presents the results of the experiments performed in mild steel containers, sealed by argon-arc welding. Synthesis of mica – KFsp - kalsilite association was carried out before (Taroev et al., 2008), but using nickel containers (inserts); this resulted in acquisition of nickel micas, which are exotic enough for natural systems. Experiments were performed in a KOH solution with optimum concentration (15.25%); the substances in the batch were taken in oxide form, with REE additives selected in a way to preclude formation of their own K-silicates and aluminosilicates, which are quite often crystallized under these conditions (Taroev et al., 2015). Experiments were carried at 500 ± 5 °C and at a pressure of 1 kb, set by the container-filling factor. To activate the interaction between components with the help of convective mixing we applied a small temperature drop (10° C on the external wall of the autoclave). The conditions of the experiments correlated with oxygen fugacity of magnetite-iron buffer. Parallel experiments differed only in duration amounting to 40 and 50 days. X-ray diffraction analysis (XRD) and electron probe microanalysis (EPMA) indicated the identity of the products and lack of notable microinclusions of REE phases. Method of mass spectrometry with inductively coupled plasma and laser ablation (LA-ICP-MS) was largely used to study the crystals from a longer experiment, the size of which reached 0.5 mm. Many of them proved to be close agglomerates of the target phases (Fig. 1), each of which usually did not exceed 100 microns in diameter. In the course of LA-ICP-MS analysis of REE, preference was given to such associations (Fig. 2). Chemical composition of crystals was determined by electron-probe microanalyzer Superprobe JXA-8200 (Jeol Ltd., Japan) using spectrometers with wavelength dispersion, 20 kV accelerating voltage, current of the primary electron beam 20 nA, diameter 1 µm. Concentrations were calculated by ZAF method. Natural orthoclase was used as a standard for K, Si, Al and hematite Fe_2O_3 – for Fe. Information on the peculiarities of morphology, homogeneity and phases correlation was received by image analysis in back-scattered electrons (Figures 1 and 2) and characteristic element radiation.

Powder X-ray diffraction data were obtained using a Bruker D8 ADVANCE diffractometer equipped with Göbel mirror and VÅNTEC-1 PSD detector in stepwise mode acquisition within diffraction angles 2θ range from 2 to 70 degrees using CuKα radiation. Experimental conditions were as follows: 40 kV, 40 mA, exposure time-1 s, step size is 0.02° 2θ. Data processing was performed using the DIFFRAC^{plus} software package. Mineral phases in samples were identified using the Database of powder diffractometry PDF-2 (ICCD, 2007) using EVA software (Bruker, 2007).

Analysis by LA-ICP-MS method was performed using a New Wave Research UP–213 Laser Ablation system coupled with an Agilent 7500ce ICP-MS (USA) in the Common Use Center "Ultramicroanalysis" in LIN SB RAS. The following parameters were set: plasma power 1400 W, carrier gas flow rate – 1 l/min, plasma-forming gas flow rate – 15 l/min, cooling gas flow rate – 1 l/min. Laser energy is 0.63 mJ, frequency 20 Hz, laser spot diameter 20 µm. Exposition time for each mass – 0.3 s. Ablation occurs at a point within 32 s. Calculation of concentrations was based on standard sample NIST 612.



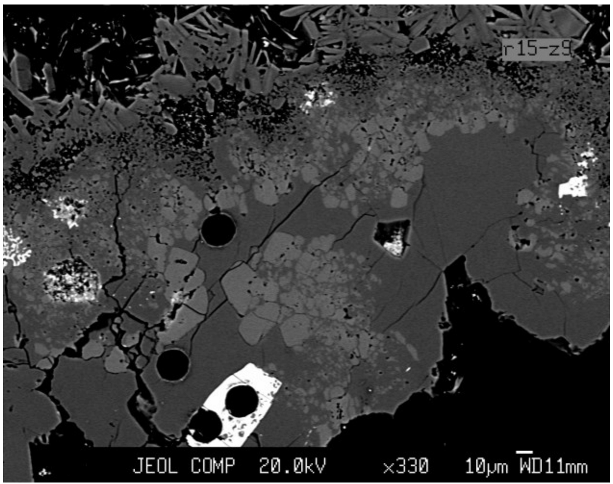


Fig. 1. Association: kalsilite (1) + Kfsp (2) + mica (3). Image in the back-scattered electrons.

Fig. 2. LA-ICP-MS analysis of kalifeldspar and mica (2 points). Image in the back-scattered electrons. Laser spot diameter 20 µm.

Results. XRD method diagnosed mica (tetraferriannite), Kfsp (orthoclase) and kalsilite. EPMA confirmed the presence of these phases and showed the amounts mainly from 99 to 100%, indicating a high homogeneity of crystals. Kfsp contains an average of 1.4% by weight % Fe_2O_3, which is far from exhausting possibilities of its isomorphic incorporation into the orthoclase at a given temperature (Taroev et al., 2008), kalsilite contains 0.6% of Fe_2O_3, mica- on average 5.5% Al_2O_3 (Table 1).

Table 1. Contents of main components (EPMA) and REE (LA-ICP-MS) in co-existing Kfsp, mica and kalsilite at 500° C and 1 kb

Component, element	Potassium feldspar $K(Al,Fe)Si_3O_8$	Kalsilite $K(Al,Fe)SiO_4$	Mica $KFe_3^{2+}[(Fe,Al)^{3+}Si_3O_{10}](OH)_2$
Major components, wt.%*			
SiO_2	$\frac{63.9-64.9}{64.4}$	$\frac{36.9-38.0}{37.5}$	$\frac{32.1-34.9}{33.4}$
K_2O	$\frac{16.5-17.0}{16.8}$	$\frac{29.3-30.1}{29.7}$	$\frac{7.8-9.6}{8.4}$
Al_2O_3	$\frac{15.1-17.9}{17.0}$	$\frac{30.4-31.5}{30.9}$	$\frac{4.0-6.7}{5.5}$
Fe_2O_3	$\frac{0.5-2.8}{1.4}$	$\frac{0.5-1.2}{0.6}$	$\frac{50.6-54.7}{51.9}$
REE, average contents, ppm			
La	11.0	5.0	7.0
Ce	3.4	2.9	5.7
Pr	4.6	5.1	7.3
Nd	5.5	5.0	6.9
Sm	2.6	4.1	5.7
Eu	2.7	3.7	11.0
Gd	2.8	2.7	7.8
Tb	1.5	3.2	7.8
Dy	2.7	4.3	12.2
Er	2.1	5.3	15.1
Tm	1.8	5.6	14.5
Yb	2.6	12.8	24.3

*From-to and average.

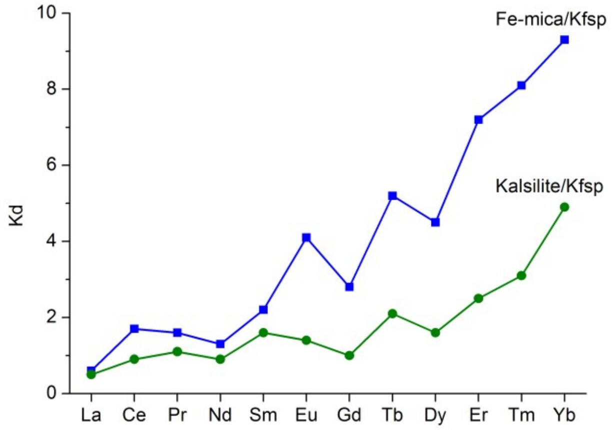


Fig.3. REE distribution coefficients between mica (ferriannite), Kfsp and kalsilite at 500°C and 1 kbar

Distribution coefficients of most lanthanoids (Fig.3) indicate their fractionation into Fe-mica. This tendency shows weakly in medium REE, but is quite salient in the case of heavy REE. It results from the increase in REE in mica with their relatively constant content in kalifeldspar and kalsilite.

Discussion. Information on REE in hydrothermal minerals was classed as quite scarce (Raimbault et al., 1993), although it is acknowledged, on the example of apatite-scheelite, that determining REE in co-existing minerals is an efficient tool for analysis of process equilibrium and sequence of the inflow events of ore-forming fluids. The higher the value of the data on fractionation of lanthanoids in the pair Kfsp-mica, from the viewpoint of information concerning the stage of rock history, at which it was enriched by certain elements of rare earth group.

Fairly unexpected is the increase in heavy REE in mica as compared to light REE, as the latter are considered more mobile in hydrothermal fluids, which accounts for their prevalence over heavy lanthanoids in rocks and minerals. Nevertheless, such data are acquired for chloride systems and connected to higher stability of chlorine-aqua-complexes of light REE^{3+} (Mayanovic et al., 2009). It may be assumed that during the REE ion exchange between framework silicates and micas, advantage in the form of lower exchange energy is acquired by heavy REE interacting with OH^- in interlayer spacing.

We express our gratitude to RFBR for the support through grant № 16-05-00392. In the course of the study, we used the equipment of Common Use Center “Isotope-geochemical studies”, the Institute of Geochemistry, SB RAS.

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Kotova N.P. Experimental study of temperature influence on niobium oxide solubility in NaF and LiF solution.

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Abstract. The dependence of Nb_2O_5 solubility as a function of temperature was investigated in NaF solutions with concentrations 0.01 and 1 m and LiF solutions with concentrations 0.03 and 0.1 m from 300 to 550 °C and 100 MPa under Co-CoO oxidizing conditions. Comparison of the experiments results on Nb_2O_5 solubility in NaF and LiF aqueous solutions showed that the temperature dependence of Nb_2O_5 solubility Is weakly expressed, while dependence of Nb_2O_5 solubility on the fluorides concentration is positive, which agrees with the previous experimental studies of Nb_2O_5 solubility in fluoride solutions.

Key words: experiment, oxide niobium, hydrothermal solubility, temperature, fluloride solutions

The temperature dependence of niobium oxide solubility was investigated in aqueous fluoride solutions consisting of 0.1 and 1.0 m NaF and 0.03 and 0.1 m LiF at 300, 400, 500, and 550 °C and 100 MPa under Co-CoO oxidizing conditions. The run duration was 30 days at 300; 21 days at 400 and 500 °C; and 15 days at 550 °C. Experiments were performed on a hydrothermal line. A sealed-capsule quench technique was employed. The same technique was used to study Ta_2O_5 and Nb_2O_5 solubility in fluoride and chloride solutions. (Kotova, 2016; Korzhinskaya et al., 2014).

The quenched aqueous solutions were then 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,.

To control congruent or incongruent dissolution of Ta oxide and to determine chemical composition of newly-formed phases (in case of their detection) the initial materials and solid run products were studied by X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM).

The experimental data show that in 0, 1 m NaF solution the content of Nb increases from $10^{-3.3}$ mol / kg H_2O to $10^{-2.4}$ mol/кг H_2O with increasing temperature from 300 to 500 °C and remains at the same level as the temperature increases up to 550 °C. In 1 m NaF solution with an increase in temperature from 300 to 550 °C, the equilibrium content of Nb practically does not change, remaining at the level of $10^{-2.4}$ mol / kg H_2O Fig. 1).

Analysis of the experimental results on the solubility of niobium oxide in 0.03 and 0.1 m LiF solutions showed that the trends in the dependence of the solubility of niobium oxide on temperature are comparable (Fig. 2). The temperature dependence of Nb_2O_5 solubility in solutions of NaF and LiF is observed only in the temperature range 300-400 ° C.

When the temperature rises from 300 to 400 ° C, the content of Nb in the solution increases by 1 order of magnitude from 10^{-4} to 10^{-3} mol / kg H_2O, and then practically does not change with increasing temperature to 550 ° C.

The X-ray diffraction analysis of the solid run products showed that in solutions of NaF, niobium oxide dissolves incongruently over all temperatures considered. There were found various newly formed phases. In a 0.1 m NaF solution at T = 300 ° C, $NaNb_6O_{15}F$ is formed as the new phase. At T = 400, 500 and 550oC, niobium oxide is completely replaced by NaNb6O15F, and another new phase is formed, which is a structural analog of the compound Ca0.4H1.2Nb2O6H2O (cubic syngony). In 1 m NaF solution, a structural analogue of Ca0.4H1.2Nb2O6H2O is also formed.

In LiF solutions, niobium oxide dissolves congruently over all temperatures considered

It has been experimentally established that a positive concentration dependence of the niobium content is observed in NaF and LiF solutions, while the temperature dependence of Nb2O5 solubility in the temperature range 300-550 ° C, P = 100 MPa, the Co-CoO buffer is weakly expressed.

The obtained results can serve as an objective basis for assessing the possibility of mass transfer of niobium by hydrothermal solutions under natural conditions, because based on the type of concentration curves obtained, it is possible to judge the maximum possible concentration of Nb in an aqueous fluid at an early postmagmatic stage after its separation from a crystallizing granite melt. The data obtained unambiguously indicate that the solubility and transport of Nb (as well as for Ta) by aqueous fluids is favored by the participation of acidic fluoride solutions. The deposition of Nb minerals from solutions with the formation of their deposits can occur as a result of: neutralization of acidic fluoride solutions; decrease in the concentration of fluorine. The change in temperature and pressure under the selected T-P conditions has little effect on the solubility of minerals.

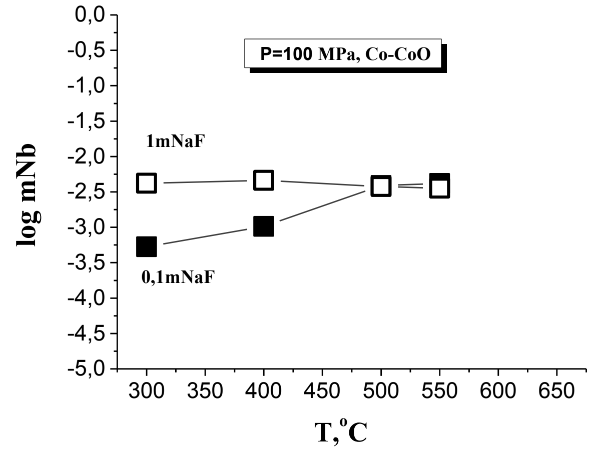

Fig.1. The temperature dependence of Nb_2O_5 solubility in NaF solutions at P = 100 MPa (Co-CoO buffe)r

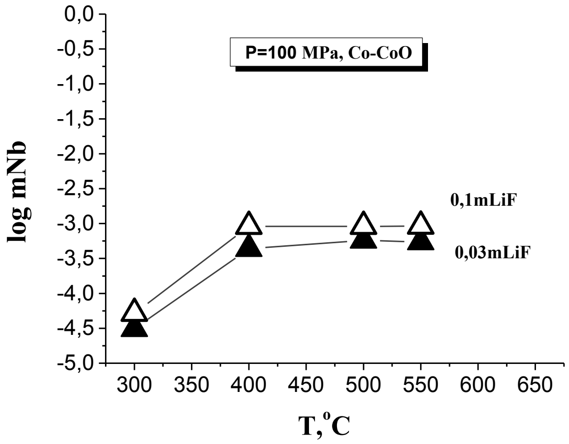

Fig.2. The temperature dependence of Nb_2O_5 solubility in LiF solutions at P = 100 MPa (Co-CoO buffe)r

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Kotova N.P. Experimental study of the influence of fluid compound (Hf + HCl) on tantalum oxide solubility at T = 550°C, P = 100 MPa.

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Abstract. New data on the solubility of tantalum oxide in mixed fluids (HF + HCl) at T = 550 °C and P = 100 MPa in the presence of the oxygen buffer Co-CoO are obtained. The initial HF concentration varied from 0.01m to 2m, and HCl concentration remained constant and was 0.5 m. The limiting contents of tantalum in hydrothermal fluids of different composition are determined and the comparative characteristics of Ta's behavior depending on the concentration and composition of the solution are obtained. It is established that in the region of low initial concentrations of solutions (0.01 m HF + 0.5 m HCl) the equilibrium concentration of Ta is only 10^{-6} mol / kg H_2O, and in the region of high fluid concentrations (2 m HF + 0.5 m HCl) it increases to 10^{-2} mol / kg H_2O,

Key words: experiment, oxide tantalum, hydrothermal solubility, mixed fluids.

New data on the solubility of tantalum oxide in mixed fluids (HF + HCl) at T = 550 °C and P = 100 MPa in the presence of the oxygen buffer Co-CoO are obtained. The initial HF concentration varied from 0.01m to 2m, and HCl concentration remained constant and was 0.5 m.

Experiments were performed on a hydrothermal line. A sealed-capsule quench technique was employed. . The chemical reagent Ta_2O_5 (>99.99% purity) was used as the starting material. Solutions of a given concentration were prepared from the corresponding reagents (>99.99% purity) using bidistilled water. The run duration was 15 days. After the run, the capsules were weighed and opened. The quenched aqueous solutions and the solid products were separated using a centrifuge. As much of the solution, as possible, was then withdrawn using a fixed-volume micropipette. This normally consisted of 0.2 ml. The quenched aqueous solutions were then 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 solid product was rinsed several times with distilled water and then dried at 90 to 100 °C. The composition of the solid product was characterized using optical microscopy, X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM

As a result of the experimental study, the limiting contents (solubility) of tantalum in hydrothermal fluids of different composition were determined and the comparative characteristics of the Ta behavior were obtained depending on the concentration and composition of the solution **(Fig. 1).** It has been established that at low fluoride concentrations of solutions (0.01mHF + 0.5mHCl), the equilibrium concentration of Ta is only 10-6 mol / kg H_2O, and at high fluoride concentrations (2 m HF + 0.5 m HCl) it increases to 10-2 Mol / kg H_2O. Thus, it can be stated that in mixed fluids (HF + HCl), at T = 550 ° C and P = 100 MPa, Ta_2O_5 solubility has a strong positive correlation with fluoride concentration.

In Fig. 1, there are also shown trends of concentration dependence of tantalum oxide solubility in pure fluoride and chloride solutions obtained by us earlier (Zaraisky et al, 2010, Korzhinskaya et al., 2014). As in the case of the solubility of niobium oxide in mixed fluids (HF + HCl), (Korzhinskaya et al, 2016), the trend of the concentration dependence of tantalum oxide solubility in mixed fluoride-chloride solutions occupies an intermediate position between the trends of niobium oxide solubility in pure fluoride and chloride solutions. The addition of Cl ion to fluoride solutions of low concentration reduces the solubility of tantalum oxide by about 1-1.5 orders of magnitude, and at high F-ion contents (1 and 2 m solutions), the trends of tantalum oxide solubility in fluoride and mixed solutions become comparable. The solubility of tantalum oxide reaches 10-2 mol / kg H_2O.

The obtained results can serve as an objective basis for assessing the possibility of mass transfer of niobium by hydrothermal solutions under natural conditions, because based on the type of concentration curves obtained, it is possible to judge the maximum possible concentration of Nb in an aqueous fluid at an early postmagmatic stage after its separation from a crystallizing granite melt.

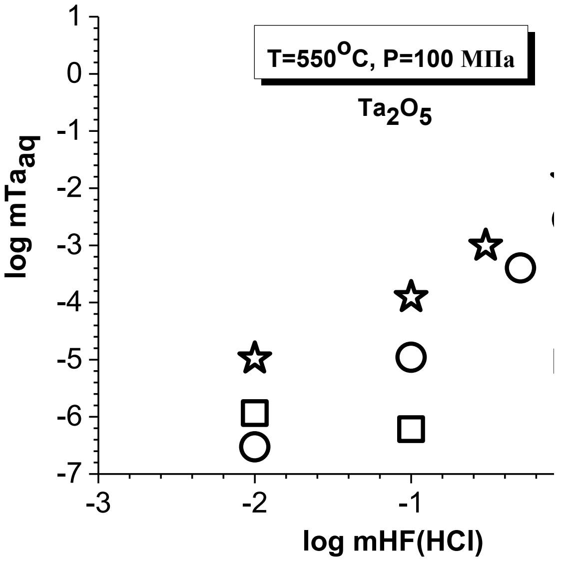

Fig.1. The concentration dependence of Ta2O5 solubility in mixed solutions of (HF + HCl) at T = 550 ° C and P = 100 MPa (Co-CoO buffer)

This work was supported by the Grants of RFBR 15-05-03393-a and Program ONZ RAN N2

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Korzhinskaya V.S., Kotova N.P. Behavior of niobium and tantalum oxides, pyrochlore and tantalite in mixed aqueous solutions (HF + HCl) at T = 550°C and P = 1000 bar.

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Abstract. Experimental solubility of Ta_2O_5 and Nb_2O_5, as well as natural minerals of pyrochlore $(Ca, Na)_2 (Nb, Ta)_2O_6 (O, OH)$ and tantalite $(Mn, Fe) (Ta, Nb)_2O_6$ has been investigated in (HF + HCl) mixed fluids. The initial HF concentration varied from 0.01 m to 2 m, and HCl concentration remained constant and was 0.5 m. The data obtained allowed us to estimate the equilibrium contents of niobium and tantalum in (HF + HCl) solution at T = 550°C, P = 1000 bar under Co-CoO oxidizing conditions. A comparative analysis of Nb and Ta equilibrium contents is carried out.

Key words: experiment, tantalite, pyrochlore, tantalum and niobium oxides, solubility, mixed fluoride-chloride solutions

New data on the solubility of tantalum oxide (Ta_2O_5) and niobium oxide (Nb_2O_5), as well as natural minerals of pyrochlore $(Ca, Na)_2 (Nb, Ta)_2 O_6 (O, OH, F)$ and tantalite $(Mn, Fe)_2 (Ta , Nb)_2 O_6$ in mixed solutions (HF + HCl) at T = 550 ° C, P = 1000 bar (Co-CoO buffer) are obtained. The initial concentration of HF varied from 0.01 m to 2 m, while the HCl concentration remained constant and equal to 0.5 m.

Experiments were carried out on hydrothermal apparatus of high pressure in sealed platinum capsules using the ampoule technique. The quenched aqueous solutions were analyzed using ICP / MS and ICP / AES (mass spectrometry and atomic emission) methods. The composition of the solid product was characterized using X-ray diffraction and electron microprobe analysis.

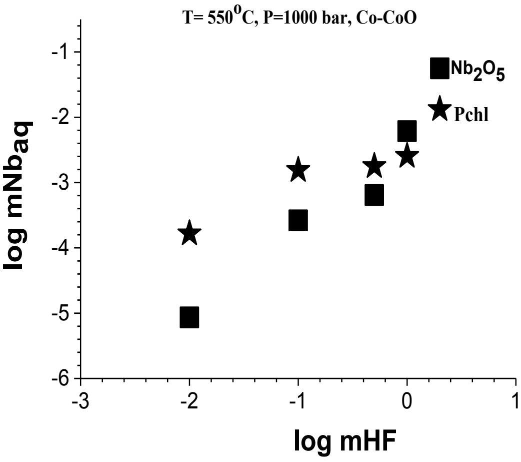

Fig.1. Concentration dependence of niobium content in (HF + HCl) fluids when Nb_2O_5 and natural pyrochlore are dissolved (T = 550 ° C, P = 1000 bar, Co-CoO buffer)

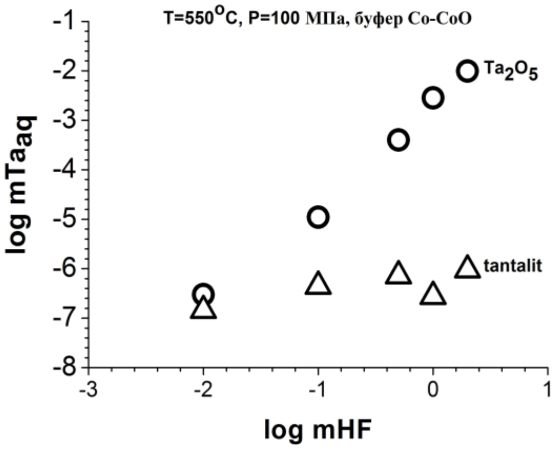

Fig. 2. Concentration dependence of tantalum content in (HF + HCl) fluids when Ta_2O_5 and natural tantalite are dissolved (T = 550 ° C, P = 1000 bar, Co-CoO buffer)

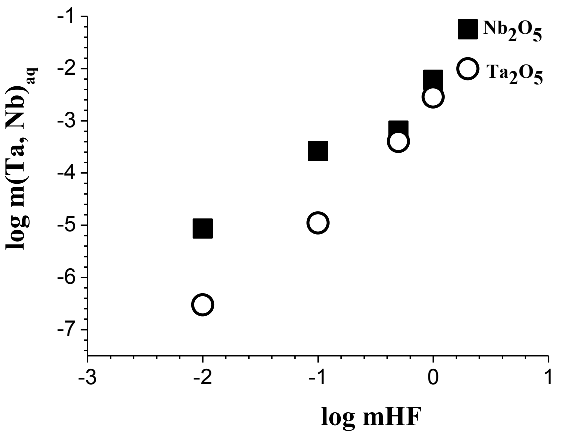

Fig. 3. Concentration dependence of Nb and Ta content in (HF + HCl) fluids when Nb_2O_5 and Ta_2O_5 are dissolved (T = 550 ° C, P = 1000 bar, Co-CoO buffer)

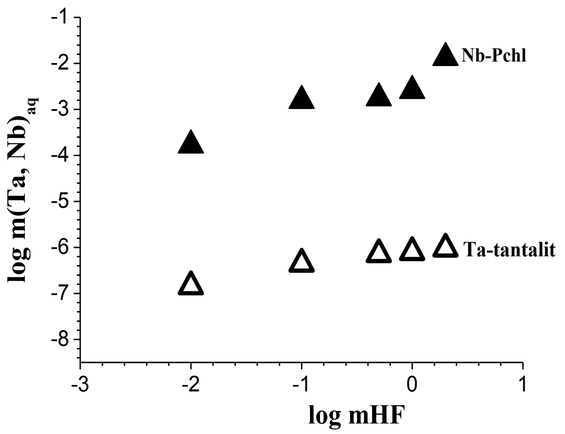

Fig. 4. Concentration dependence of Nb and Ta content in (HF + HCl) fluids when pyrochlore and tantalite are dissolved (T = 550 ° C, P = 1000 bar, Co-CoO buffer)

Experimental results on the solubility of niobium oxide and pyrochlore in (HF + HCl) solutions are presented in Fig. 1. Analysis of the data obtained showed that at low fluoride concentrations (0.01 m HF + 0.5 m HCl) and (0.1 m HF + 0.5 m HCl), the solubility of Nb_2O_5 is approximately an order less than that of pyrochlore. At high fluoride concentrations (1 m HF + 0.5 m HCl), the solubility of niobium oxide becomes greater than the solubility of pyrochlore, and in the solution of (2 m HF + 0.5 m HCl) is n * 10^{-1} mol / kg H_2O (Korzhinskaya, Kotova, 2016). Such concentrations are quite sufficient for the real mass transfer of niobium by hydrothermal solutions

Comparison of experimental results on the solubility of tantalum oxide and natural tantalite in mixed solutions (HF + HCl) (Fig. 2) showed that at low fluoride concentrations (0.01 m HF + 0.5 m HCl) the solubility of tantalum oxide and tantalite is comparable. But with increasing concentration of HF, the Ta_2O_5 solubility increases sharply and reaches a value of 10-2 mol / kg H2O in the solution of (2 m HF + 0.5 m HCl), which is 4 orders of magnitude higher than that of tantalite. This can be explained by the presence of Mn and Fe in tantalite, which dissolving tantalite form highly soluble complexes with Cl-ion.

Analysis of experimental results on the solubility of niobium and tantalum oxides in mixed fluoride-chloride solutions (Fig. 3) showed that at low fluoride concentrations, the solubility of niobium is about 1-1.5 orders of magnitude more than the solubility of tantalum. However, at high F-ion contents (1 and 2 m solutions), the trends of the solubility of Nb and Ta oxides in mixed solutions become comparable, and the solubility of niobium and tantalum oxide reaches 10^{-1} and 10^{-2} mol / kg H_2O, respectively.

It was found that when the pyrochlore is dissolved in (HF + HCl) solutions in the region of low concentrations of HF (0.01 m HF + 0.5 m HCl), the equilibrium concentration of niobium reaches 10^{-4} mol / kg H_2O. In the region of high concentrations of the F-ion, the Nb content increases by two orders of magnitude and is 10^{-2} mol / kg H_2O. When tantalite is dissolved in (HF + HCl) solutions, with increasing HF concentration, the Ta content increases insignificantly and in the solution of (2 m HF + 0.5 m HCl) reaches 10^{-6} mol / kg H_2O, which is 4 orders of magnitude less than the Nb content in mixed fluoride-chloride solution of the same concentration (Fig. 4). Thus, both for pure chloride solutions and for mixed (HF + HCl) solutions natural tantalite and synthetic Mn-tantalite dissolve sharply incongruently with a predominant transition into a solution of Mn and Fe in comparison with Ta.

The experimental results obtained give grounds to state that the experimentally established fact that the hydrothermal transport of these ore metals in quantities necessary for the formation of their industrial concentrations is possible only by concentrated fluorine-containing solutions is fundamentally important for understanding the genesis of tantalum and niobium deposits.

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Redkin A.F., Kotova N.P. Experimental study and thermodynamic modeling of pyrochlore incongruent solubility IN NaF-HF solutions at 800 °C and 200 MPa

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Abstract. The pyrochlore (NaCa) Nb_2O_6F solubility was studied in NaF soluptions with concentration from 0.1 to 16 m and 1.0 m NaF + HF (0.01-0.3 m) solutions at 800 °C and 200 MPa. The formation constants of predominant Nb^{5+} species were calculated using the HCh and Optima-A software. The thermodynamic calculations provided indicate that pyrochlore solubility in NaF solutions is 1-1.5 orders of magnitude more than that of microlite.

Keywords: experiment in NaF-H_2O system, incongruent solubility, pyrochlore, fluorite, microlite, immiscibility region

The forms of transfer of ore components, the mechanisms of their accumulation and separation in host rocks are of great importance for building models of deposits formation. Of particular interest are solutions containing high concentrations of fluorides in which fluid immiscibility is observed, leading to a sharp change in the solubility of ore minerals. For hydrothermal solutions that are in equilibrium with melts of the composition of Li-F granites, the main component is NaF. Fluid immiscibility in the NaF-H_2O system, according to the available experimental data (Kotel'nikova, Kotel'nikov, 2008), occurs at T > 750-780 °C and a pressure of about 200 MPa. This served as the basis for choosing the parameters of the experiments. Pyrochlore, along with columbite, is the most important niobium-containing mineral. In pyrochlore, (NaCa) Nb_2O_6F unlike columbite (FeMn) Nb_2O_6F there are no elements of variable valence (Fe, Mn), which frees us from having to set constant the partial pressure of O_2 (or H_2) in the investigation of mineral ore solubility. Therefore, most of the experiments were carried out in the gas vessel. Since pyrochlore has low solubility in hydrothermal solutions, it could not significantly change the acid-base properties of the hydrothermal solution and influence the immiscibility boundaries in the NaF - H_2O system.

Earlier, by us (Redkin et al., 2016), were defined immiscibility boundaries in the NaF-H_2O system at 800 °C, investigated the features of sodium fluoride hydrolysis, and determined Ta concentrations in solutions that are in equilibrium with microlite and fluorite. In this connection, the study of the solubility of Nb-pyrochlor in NaF solutions is important for comparing the behavior of niobium and tantalum in fluoride solutions.

The materials were pyrochlore (Pcl) obtained by hydrothermal synthesis from an equimolecular mixture of the composition NaF $CaCO_3$ Nb_2O_5 in the runs at 800 °C, P = 200 MPa in 1 m NaF for 7 days and fluorite (Fl) obtained from the CaF_2 reagent by recrystallization in 0.1 m HF at 500 °C, 100MPa for 2 weeks, subsequent drying at 100 °C and annealing in air at 500 °C.

All runs were carried out in Pt capsules with a volume of 0.5-0.7 cm^3. In the Pt capsules were placed 10-15 mg of pyrochlore, 1-5 mg of CaF_2, from 0 to 100 mg NaF and 0.15 ml of H_20. After the runs, the solution was diluted in 25-35 times with water and then analyzed by the methods of ICP-AES, ICP-MS in the certified laboratory of IPTM RAS. The solid phases were studied by the XRD, REM (CamScan, Vega-II) methods in the laboratory of physical research of the IEM RAS.

We investigated the equilibrium between pyrochlore and fluorite or the reaction of incongruent dissolution of pyrochlore with the formation of fluorite, which can be represented in the generalized form by the following reaction:

Pcl + solution$_{init}$ ↔ ***Fl*** + solution$_{fin}$(+species of Nb^{5+}),

where solution$_{init}$ and the solution$_{fin}$ are the components of the initial and final solution (HF, NaF, H_2O), which must be introduced to maintain the balance of the masses of all elements

The studies covered two homogeneous regions (HS-I-homogeneous solution of "low" concentrations of NaF and HS-II-highly concentrated NaF solution), as well as the immiscibility region of fluid phases L_1 (fluid of moderate density) and L_2 (dense fluid) located between HS-I and HS-II. In work (Redkin et al., 2015), the effect of salt concentration on the solubility of the ore component in homogeneous solutions and in the field of fluid immiscibility is considered in detail.

The effect of the concentration of NaF on the content of Nb in solutions that are in equilibrium with Pcl and saturated Fl is shown in Fig. 1 by square symbols. The region of fluid immiscibility in the NaF-H_2O system at 800 °C, P = 200 MPa, is in the following range of mass concentrations of NaF (5.0 <CNaF <25.7} (shown in Fig. 1 by vertical dashed lines). In the region of fluid immiscibility, the concentrations of Nb and NaF correspond to apparent values, i.e. the concentrations of Nb and NaF that will be after mixing the two fluid phases L_1 and L_2.

Using the program OPTIM-A (Shvarov, 2015) and experimental data on the incongruent solubility of Pcl in homogeneous fields of HS-I and HS-II, the inverse thermodynamic problem was solved: the most probable species of Nb^5 were found and their stability constants were calculated. The best convergence of the calculated and experimental data was obtained using the following niobium species: $HNbO_3^0$, NbO_2F^0, $NbOOHF_2^0$ and $Na_6H_2Nb_6O_{19}^0$. These species are selected by analogy with tantalum particles (Redkin et al., 2015, Redkin et al., 2016). To identify $NbOOHF_2^0$ specie, the results of experiments in 1.0 m NaF + HF solutions (0.01-0.3 m) were taken (Fig. 2). Thermodynamic calculations

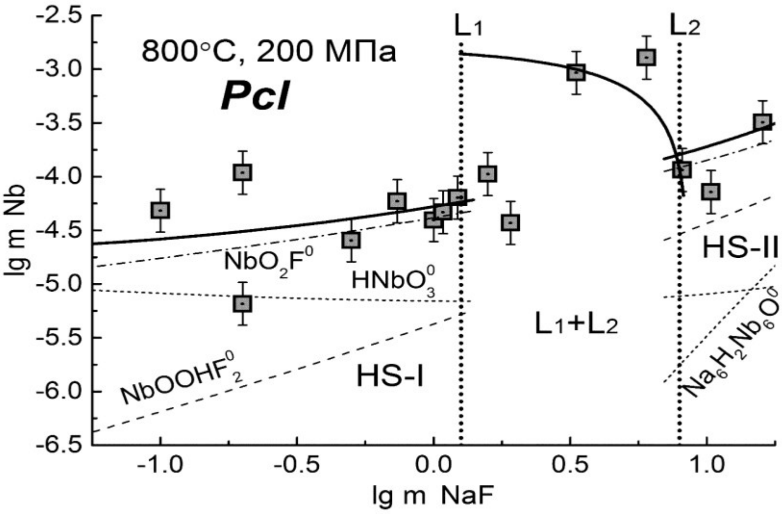

Fig. 1. Effect of m NaF on Nb content in solutions that are in equilibrium with Pcl and Fl at 800 ° C and P = 200 MPa (experimental and calculated data). The lines show the trends of change m Nb on m NaF and the concentration of the predominant species of Nb^{5+}. Symbols: HS-I - homogeneous solution at low concentrations of NaF, HS-II - a homogeneous solution at high concentrations of NaF, $L_1 + L_2$ – field of immiscibility of fluid phases L_1 and L_2 in the NaF-H_2O system.

show that the main contribution to the total Nb concentration in the homogeneous solutions studied is made by the NbO_2F^0 specie. In NaF solutions containing NaF> 10 m, the mole fraction of Nb in the form of species $NbOOHF_2^0$ and $Na_6H_2Nb_6O_{19}^0$ does not exceed 20 mole%.

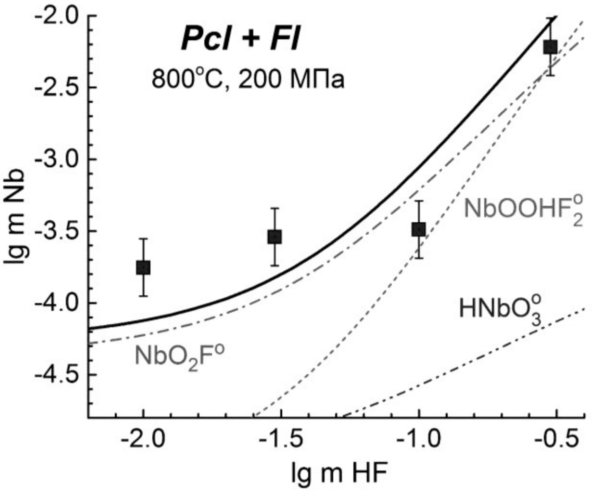

Fig. 2. Effect of m NaF on Nb content in solutions that are in equilibrium with Pcl and Fl at 800 ° C and P = 200 MPa (experimental and calculated data). The lines show the trend change of m Nb on m HF and the concentration of the predominant species of Nb^{5+}.

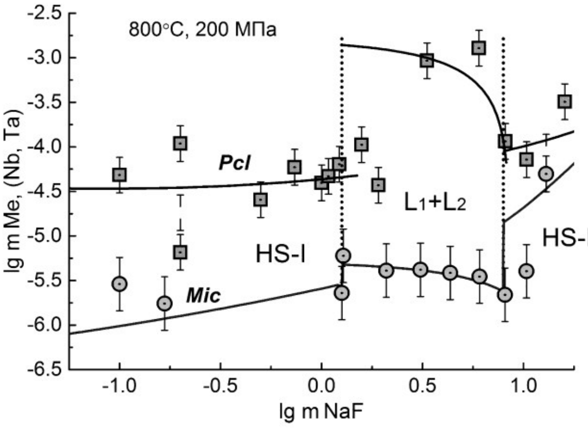

Fig. 3. Effect of m NaF on Nb content and Ta in solutions that are in equilibrium with Pcl and Fl at 800 ° C and P = 200 MPa. The lines show the trends change of m Nb and m Ta on m NaF.

Using literature data on the thermodynamic properties of niobium hydroxy- and hydroxophosphoride species (Akinfieva et al., 2015) and our experimental data, the free energy of pyrochlore formation was calculated at 800 ° C and 200 MPa. The calculations performed with these thermodynamic data show that the predominant niobium specie in a solution in equilibrium with Pcl and Fl is $Nb(OH)_4F^0$ specie (the hydrated specie NbO_2F^0) whose contribution to m Nb exceeds 99%. The important contribution of this specie to the solubility of Nb_2O_5 in fluoride solutions is also indicated by the results of the studies (Timofeev et al., 2015).

Data on the incongruent solubility of pyrochlore and microlite in NaF solutions at 800 ° C and 200 MPa are shown in Fig. 3. From these data it follows that the molar concentration of niobium in equilibrium with pyrochlore is more than 1 order higher than the tantalum concentration in equilibrium with microlite. Critical phenomena in the immiscibility field of L_1-L_2 lead to a sharp increase in the solubility of pyrochlore and microlite (Mic) in the L_1 fluid phase and a decrease in solubility in the L_2 phase.

This work was supported by the Grants of RFBR 15-05-03393-a, 14-05-00145 and Program ONZ RAN N2

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